WATER QUALITY GUIDELINE SERIES

pH Water Quality Guidelines (Reformatted Guideline from 1991)

Ministry of Environment and Climate Change Strategy
Water Protection & Sustainability Branch

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BRITISH COLUMBIA

The Water Quality Guideline Series is a collection of British Columbia (B.C.) Ministry of Environment and Climate Change Strategy water quality guidelines. Water quality guidelines are developed to protect a variety of water values and uses: aquatic life, drinking water sources, recreation, livestock watering, irrigation, and wildlife. The Water Quality Guideline Series focuses on publishing water quality guideline technical reports and guideline summaries using the best available science to aid in the management of B.C.'s water resources. For additional information on B.C.'s approved water quality parameter specific guidelines, visit:

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Notes on Reformatted Version:

Sections of this report on industrial water use, drinking water and recreation have been removed. B.C. adopts Health Canada drinking water and recreation guidelines and no longer develops or supports guidelines for industrial water use.

Cover Photograph:

Location: Thetis Lake, B.C.

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1. INTRODUCTION

The purpose of this report is to develop pH water quality criteria for the Province of British Columbia to protect aquatic life, wildlife, and livestock, as well as domestic, irrigation, and industrial water uses.

There are several ways the pH or hydrogen ion activity can be toxic to freshwater organisms. They include:

1) alteration of chemical species (e.g., metals, ammonia-nitrogen, etc.) to toxic forms,
2) destruction of gill tissue (Section 4.7.2.3),
3) acidosis or alkalosis (Section 4.7.4),
4) loss of electrolytes (Section 4.7.3),
5) inhibition of the ammonia excretion mechanism (Section 4.7.10).

The alteration of chemical species to toxic forms is not discussed in this report. The. ambient water quality criteria or objectives issued by the Water Quality Branch for the specific metals of concern will incorporate the necessary considerations to protect aquatic life under varying pH conditions.

2. CHEMISTRY OF pH AND RELATED VARIABLES

The pH of water is a measure of the hydrogen ion activity (aH^+) of a solution. It is defined by the equation:

$$pH = -\log_{10} aH^+$$

The pH of water can be accomplished using colour indicator solutions (both paper and liquid), but is measured more conveniently with a combination pH electrode. Refer to McKean and Huggins (1989) for a detailed summary of the operation, care, calibration, and restoration procedures for pH and reference electrodes.

Airborne compounds of sulphur and nitrogen in the presence of sunlight and water may become oxidized to form the principal components of acid precipitation, namely sulphuric and nitric acid. The global atmospheric sulphur budget is approximately 50% from natural sources and 50% from anthropogenic sources (Dovland and Semb, 1980). Sulphur dioxide is emitted by the incineration of sulphur containing coal and fuels, the smelting of sulphidic metal ores, or from other industries (e.g., pulp mills).

The budget for nitrogen oxides is less clear. Emissions of nitrogen oxides arise from nitrogen gas during combustion, or from the nitrogen content of the combustible material. The. main sources of nitrogen oxides are internal combustion engines and power plants, and the amount of nitrogen oxides produced depend strongly on the design of the burner, combustion chamber, and the operating conditions (Dovland and Semb, 1980). The absolute amounts of nitrogen oxides emitted to the atmosphere are difficult to assess and are generally more uncertain than sulphur oxides.

The Ministry of Environment has monitored extensively the soils and surface waters of the Province to determine the areas that are sensitive to acid precipitation (Figure 2). The areas of highest sensitivity are located on the west coast of the Province adjacent to the ocean. The high degree of sensitivity is primarily caused by the high rates of rainfall (see Section 3.0).

In addition to acid precipitation, acid discharges from industry and acid mine drainage can be a serious problem. There are approximately sixteen metal mines in operation, of which six generate acid mine drainage. In addition, at least six abandoned mines are known to produce acid mine drainage (Ferguson and Mehling, 1986). Acid mine drainage is a particularly serious problem in that the input of hydrogen ions and metals into the receiving environment can potentially continue for hundreds or even thousands of years after the mine is closed.

3. OCCURRENCE

3.1 Freshwater Environment

The range of pH in the surface waters of British Columbia is determined primarily by two factors: the amount of precipitation, and the rate of alkalinity production (weathering) in the bedrock and soils. Because the geology ·of British Columbia is diverse, and the Province is so large, the patterns of pH in surface waters are highly variable. This section attempts to describe the regional variability of pH as it relates to the 6 major geologic or tectonic formations that are found in British Columbia. A more detailed description of the limnological regions of British Columbia has been completed by Northcote and Larkin (1966).

The bedrock geology of British Columbia can be grouped into 6 distinct groups. Moving east to west the first tectonic region is the Alberta Plateau, then the Rocky Mountains Belt, Omineca Belt, Interior System, the Cascade Mountains, and lastly *the* Insular Belt which includes Vancouver and the Queen Charlotte Islands (Figure 3).

Weathering is the process by which primary and secondary minerals in the bedrock and soils are oxidized (broken down into their individual components) in the presence of an acid (see Equations 1 and 2).

$$Al_2Si_2O_5(OH)_4 + 6H^+ \longleftrightarrow 2Al^{3+} + 2H_4SiO_4 + H_2O \quad (1)$$

or

$$CaMg(CO_3) + 4H^+ \longleftrightarrow Ca^{2+} + Mg^{2+} + CO_2(g) + 2H_2O \quad (2)$$

If the weathering process consumes hydrogen ions from carbonic acid associated with water, alkalinity in *the* form of bicarbonate and carbonate ions will be produced (see Equation 3).

$$CO_2(g) \longleftrightarrow H_2CO_3 \longleftrightarrow HCO_{3^-} + H^+ \longleftrightarrow CO_3^{2-} + H^+ \quad (3)$$

The formation of carbonate ions results in the production of alkalinity and the elevation of the water's pH. The rate of weathering is a function of the climate and the chemical composition of the primary and secondary minerals. For example, soft sedimentary rocks will be weathered much faster than hard volcanic rocks composed of silica oxides.

Precipitation is important because in areas of high runoff, the carbonates produced by the weathering process are rapidly leached from the watershed resulting in surface waters with low carbonate and pH levels. In arid areas, runoff is low and carbonates accumulate in the soils, resulting in surface water with high pH that is saturated in carbonates.

The pH of water is the result of the balance between the weathering and leaching process within the watershed. The following sections attempt to outline these processes in general terms to describe the regional differences in pH (Table 1). The section is limited to discussing watersheds that are located entirely within one zone or subregion. Larger rivers that traverse more than one tectonic zone or subregion will have the mixture of the water quality characteristics reflecting the different tectonic regions within its watershed.

Geology and mean annual precipitation records used were obtained from Farley(1979). pH data from lakes were used to reduce the effects of season and stream flow on pH. Lake data were obtained from McKean (unpublished) and are summarized in Table 1.

Table 1. Average pH Values for Different Regions in British Columbia

REGION **Subregion**	**Average pH**	**STD. DEV.**	**Range**	**Sample Size**
INSULAR BELT				
Vancouver Island Mountains	7.2	0.3	6.6-7.8	36
Nanaimo Lowland	7.6	0.8	6.6-9.8	39
Queen Charlotte Mountains	6.9	0.3	6.4-7.3	9
Queen Charlotte Lowland	5.0			1
CASCADE MOUNTAINS				
Cascade Mountains*	6.7	0.5	5.4-7.6	21
Fraser Lowland	7.5	0.4	5.8-8.3	254
INTERIOR SYSTEM				
Southern Plateau	8.4	0.3	7.7-9.2	43
Central Plateau	7.7	0.3	7.1-8.3	28
Northern Plateau	7.8	0.3	7.1-8.3	18
OMINECA BELT				
Southern Region	7.3	0.7	7.0-9.7	24
Northern Region	7.6	0.5	6.7-8.4	20
ROCKY MOUNTAINS				
Southern Ranges	8.1	0.3	7.5-8.8	20
Northern Ranges	8.3	0.1	8.1-8.4	8
ALBERTA PLATEAU	7.9	0.4	7.0-8.5	21

* does not include data from the Chilcotin Range

Insular Belt: The geology of this region is a complex mixture of sedimentary rock (sandstones, shales, marbles, etc.), and volcanic rock (gneiss, granitic intrusions, etc.). The Vancouver Island and Queen Charlotte Mountains are two subregions that have high precipitation (150->350 cm/yr) resulting in very dilute waters with acidic to circumneutral pH.

Lakes in the Vancouver Island Mountains have a range of pH from 6.6 to 7.8 (average =7.2; n =36). Lakes in the Queen Charlotte Mountains have a lower pH range (6.4-7.3; average =6.9; n =9), presumably because of the higher rates of precipitation.

The Nanaimo and Queen Charlotte Lowlands are the two remaining subregions in the Insular Belt. The Nanaimo Lowland is located on the east coast of Vancouver Island, from Sayward to Victoria. It is characterized by deep soil and till deposits, extensive agriculture and urban development, and much lower precipitation (50-150 cm/yr) than the mountain areas. Lakes have a broad range of pH from 6.6 for Keta Lake near Sayward, to 9.8 in Quennell Lake near Nanaimo. The average pH for the Nanaimo Lowland is 7.6 (n =39). The high pH observed in the Nanaimo Lowland lakes is primarily caused by the lower rates of precipitation, and the high rates of primary productivity in the lake caused by the process of anthropogenic eutrophication.

In contrast, the Queen Charlotte Lowland is very boggy, and the water has a high organic colour (McKean, pers. obs.). Only one pH value has been recorded by the Ministry of Environment for this area. Mayer Lake had a surface pH of 5 due to the organic acids produced by the surrounding Sphagnum bogs. The processes of alkalinity generation through weathering and leaching are not evident is this subregion because of the domination of the acid generated by Sphagnum.

Cascade Mountains: This region is located on the west coast of the British Columbia mainland. It is characterized as a high rainfall area (150->350 cm/yr) that has fairly uniform granitic geology with thin soils. The combination of slow weathering of the granitic rock and the high runoff rates produces very dilute levels of carbonate in surface waters. The pH of lakes in this zone range from a low of 5.4 at Kenyon Lake, to 7.6 at Fire Lake (average =6.7; n =21).

The Chilcotin Range is one of the two subregions in the Cascade Mountains. The area is located in the rain shadow on the eastern side of the mountains. The arid conditions have caused elevated pH values (e.g. Choelquoit Lake, pH 8.6) typical of the Southern Plateau of the Interior System, not the coastal Cascade Mountains.

The Fraser Lowland is the second distinct subregion. The area is characterized with deep soils, moderate rainfall, and extensive agriculture and cultural eutrophication. The pH of the surface waters is similar to the Nanaimo Lowland.

Interior System: The Interior System is the most complex of the regions in British Columbia. It includes the Southern Plateau (Okanagan, Thompson Plateau, and Fraser Plateau subregions) in the south, the Central Plateau (Nechako Plateau), and the Northern Plateau (Skeena Mountains, and the Stikine-Yukon Plateaus).

The Interior Plateau is in the rain shadow of the Cascade Mountains and is typically very arid in the valleys (30-50 cm/yr) with moderate increases in precipitation in the Thompson Plateau (50-75 cm/yr). Lakes in this area are typically alkaline, with pH ranging between 7.7-9.2 (average =8.4; n =43).

The Central Plateau to the north includes the Nechako Plateau and the northern portion of the Fraser Basin. The area has more rainfall and lower pH than the Southern Plateau. Lake pH values range from a low of 7.1 in Acorn Lake, to 8.3 in Little Bobtail Lake (average = 7.7; n =28).

The Northern Plateau includes the Skeena Mountains and the Stikine and Yukon Plateaus. This area has a very different climate and geology than the other Interior regions. Precipitation is higher (50-75 cm/yr), the winters are much colder, and the summers (growing season) are cooler and shorter. The geology differs from the volcanic geology to the south, as sedimentary (not necessarily calcareous) rock is the dominant form. Despite the differences in climate, the lakes in the northern region have a similar average pH (7.8; n =18), reflecting the increased weathering potential of the sedimentary rocks.

Omineca Belt: The Omineca Belt is a mountainous area composed of the Columbia Mountains to the south and the Omineca and Cassiar Mountains to the north. The area has a complex geology ranging from granitic intrusions in the south (Castlegar) to metamorphic schists and gneisses (Blue River) and a complex mixture of sedimentary and volcanic rock to the north.

Precipitation is highly variable for the region. The Columbia Mountains to the south have high precipitation in the mountains (150-250 cm/yr) and low precipitation in the valleys (e.g., Cranbrook 30-40 cm/yr). Lakes in this region have an average pH of 7.3, ranging from 7 (Crooked Lake) to 8.4 (Jewel Lake) in the mountains, to as high as 9.7 (Hahas Lake) in the arid valleys. Marl and meromictic lakes are common in the arid zones.

The Omineca and Cassiar Mountains to the north have a much more uniform rainfall ranging from 40-75 cm/yr. The average pH is 7.6, which is similar to the lakes of the Northern Plateau of the Interior System.

Rocky Mountains: The Rocky Mountains have similar precipitation (75-250 cm/yr) and climate as the Omineca Belt. The geology of the Rockies is a fairly uniform calcareous sedimentary rock.

The pH of lakes has a fairly narrow range between pH 7.5 and 8.8 and does not vary greatly between the southern and northern ranges. The presence of the calcareous rock quickly neutralizes any acids present in the precipitation, resulting in alkaline surface water throughout the region. The pH of lakes in the southern Rocky Mountains ranges from 7.5 to 8.8 (average =8.1; n =20). The presence of marl lakes (e.g., Tie Lake) is quite common in the valleys due to the arid nature of the climate. The northern Rocky Mountains have a similar average pH (8.3), but a narrower range (8.1-8.4; n =8). The small sample size may be the reason for the narrow pH range.

Alberta Plateau: The last tectonic region is the Alberta Plateau which is the western extension of the Great Interior Plains. The area is characterized as flat, having deep soils that overlie calcareous sedimentary rock. Precipitation is moderate (40 -75 cm/yr) and quite uniform. The lakes of the region have an average pH of 7.9, and a range between 7.0-8.5 (n =21).

3.2 Marine Environment

The pH of the marine environment is less variable due to the buffering ability of the dissolved salts. The marine data within the Ministry of Environment SEAM data base had an average pH of 7.8 (standard deviation =0.2, n =434). The minimum and maximum pH were 7.1 and 8.6.

4. AQUATIC LIFE

4.1 Bacteria

Heterotrophic bacteria are recognized as an important food source for invertebrates (detritivores and filter feeders), and for the recycling of minerals and nutrients via the decomposition of organic matter. Whole lake acidification projects have also demonstrated the importance of anaerobic heterotrophic bacteria within the lake sediments to neutralize strong acids and ameliorating the effects of acid precipitation (Kelly et al., 1982; Schindler, 1988).

4.1.1 *Decomposition*

Grahn et al. (1974) observed the accumulation of leaf matter and the proliferation of fungi above the sediment-water interface in acidic lakes located in Scandinavia. They hypothesized that the acidification of the water column had depressed heterotrophic bacterial decomposition, resulting in the oligotrophication of the lake (see Section 4.2.3). Although this was a popular theory, the lack of evidence for the process of oligotrophication, and the misidentification of algal filaments *(Mougeotia* sp.) as fungi, has refuted Grahn's initial observations.

Andersson et al. (1978) and Gahnstrom et al. (1980) could not measure differences in the oxygen uptake or carbon dioxide production in acidified sediment cores in comparison to non acidified cores collected from southern Sweden. Andersson acidified the sediments artificially with HCl, while Gahnstrom collected cores from acidified and non-acidified lakes. After 75 h of incubation, elevated hydrogen ion concentrations could not be detected 6 cm below the sediment water interface, indicating that the sediments had a large hydrogen ion buffering capacity (Andersson al, 1978).

Traaen (1980) and Francis et al. (1984) did not detect any difference in planktonic bacterial concentrations from clear water acidic and non-acidic lakes. However, humic or dystrophic lakes in both studies had planktonic bacterial concentrations three to four times higher than the clear water lakes. Higher concentrations of dissolved organic carbon (DOC) in the dystrophic systems was the principal reason for the higher bacterial concentrations.

Francis et al., (1984) also studied sediment bacteria concentrations in three Adirondack lakes. Differences in sediments type (sand, silt, etc.), organic matter content, and other environmental factors prevented the clear differentiation of bacterial communities between lakes. Interestingly, the pH of the sediments showed little variation (pH 6.3 - 6.5), providing further evidence that lake sediments have a buffering capacity to acidification.

The acidification of Lake 223's (Experimental Lakes Area (ELA) in Ontario) water column with sulphuric acid did not result in any difference in heterotrophic decomposition rates. The principal reason was that the interstitial water remained unchanged from pre-acidification conditions (Schindler et al., 1985). Kelly et al. (1984) reported that the microbiological processes within the sediments produced alkalinity through the anaerobic reduction of sulphur compounds. The alkalinity production maintained the pH above 6.0 a few millimetres below the sediment-water interface even though the rate of acidification of Lake 223's water column was approximately six times faster than lakes impacted by acid precipitation.

Laboratory studies with sediments from Lake 223 showed that decomposition rates of residual carbon were unaffected at pH 4.0. However, decomposition rates of newly sedimented material decreased below pH 5.3 (Kelly et al., 1984).

The addition of lime to sediments from an acidified lake caused a substantial increase in oxygen consumption (Gahnstrom et al., 1980). The elevated consumption rates persisted for one year after treatment, indicating that the increased decomposition was the result of the addition of an inorganic carbon source, rather than being pH-induced. Rapid decomposition of organic litter following the addition of lime has been reported in other studies (Francis et al., 1984).

4.1.2 *Bacterial Regulation Of Lake Acidification*

Hydrogen ions in a water basin can be neutralized by the weathering of primary and secondary minerals in the soil and rock formations within the watershed (see Section 3.0). The rate of hydrogen ion neutralization by the weathering process is very slow in areas dominated by non-calcareous rocks and soils.

Within the terrestrial and aquatic environments, acid neutralization also occurs through the reduction of nitrate or sulphate ions. Within lakes, nitrate and sulphate are reduced by primary producers (photosynthesis) or bacteria (denitrification or sulphate reduction). Denitrification and sulphate reduction are strictly anaerobic processes that occur primarily below the sediment-water interface or in an anoxic hypolimnion (Kelly et al., 1982; Rudd et al., 1986).

In lakes receiving significant quantities of nitric and sulphuric acid, short-term H+ neutralization through denitrification was 1.5 to 2 times faster than H+ neutralization through sulphate reduction. Because of the potential oxidation of the reduced sulphur compounds, the long-term H+ neutralization by denitrification was estimated by Rudd et al. (1986) to be 4 to 5 times larger that sulphate reduction. Further addition of sulphuric or nitric acid to the aquatic ecosystems caused elevated denitrification and sulphate reduction, provided that an adequate carbon source was available.

The neutralization of H^+ ions in anoxic sediments is the principal reason why lake sediments from acidic lakes are not affected by acidification (Rudd et al. 1986).

4.1.3 *Decomposition of Allochthonous Plant Litter*

Grahn et al. (1974) observed a large accumulation of allochthonous (terrestrial) plant litter above the sediment-water interface in acidified Swedish lakes. The decomposition of leaf and woody material is slower than autochthonous (formed in the lake) algal detritus because the supportive lignin tissue is less biodegradable. In general, leaf litter in lakes and streams undergoes a brief period of leaching, followed by the colonization of microbial bacteria, and (or) consumption by invertebrates (Francis et al., 1984). The rate of leaf litter decomposition depends on the plant species. but is usually complete within one year (Traaen. 1980).

Experiments by Traaen (1980) showed that the rate of decomposition of allochthonous material (e.g., birch-leaf litter, aspen sticks, etc.) showed a small yet statistically significant decrease with decreasing pH. After 1 year, a weight loss of 52 percent was observed in the shredded birch leaves at neutral pH, while 45 percent weight loss occurred at pH 4. After 2 years the trend of reduced decomposition rates of birch leaves with decreasing pH was still apparent (Traaen, 1980). The main reason for the decreased rate of decomposition at lower pH was attributed to lower concentrations of zoobenthos, not heterotrophic bacteria or fungi.

Researchers at ELA have concluded that the levels of pH required to effect organic decomposition rates in lakes would be well below the pH that would severely affect the growth and reproduction of higher life forms (Schindler et al., 1985).

4.2 Phytoplankton/Periphyton

4.2.1 *Background*

There is a common perception that acidification transforms a lake into a very clear, unproductive, 'dead' system. The terms 'clear' and 'dead' imply that the algal productivity, biomass, and diversity of the lake have been reduced or eliminated. In contrast, the reduction of the carbon dioxide content of freshwater through the elevation of pH has been linked with the shift of the phytoplankton community to cyanobacteria (blue-green algae) which are potentially toxic, cause taste and odours in drinking water supplies, or form aesthetically unpleasant surface scum. The following sections discuss the effects of low and high pH on diversity, biomass, and primary production of the phytoplankton and periphyton communities.

4.2.2 *Community Structure and Diversity*

4.2.2.1 *Effects of Acidification:*

The literature outlining the effects of acidification on the phytoplanktonic community is limited to three major regional pH-phytoplankton surveys, a few long-term studies, three whole lake acidification projects, and studies of lake history using the sediment fossil record. The data and conclusions of these studies form the basis for the conclusions in this section.

Regional Surveys:

Three major regional surveys of acidified phytoplankton communities were completed in Sweden (Almer et al., 1974), Norway (Hendrey and Wright, 1976), and Canada (Kelso et al., 1986). A single surface pH and phytoplankton sample was collected from each lake. The periodicity of the phytoplankton community was assumed to be unimportant by the authors as samples were collected in a relatively short period of time. In the majority of cases, the surveys sampled high altitude head-water lakes because of their susceptibility to acidification. The effects of lake morphology and water chemistry on the phytoplankton community were not considered or discussed by Almer et al. (1974) or Hendrey and Wright (1976).

The focus of the three surveys was on the effects of pH on four algal groups: the chlorophytes, chrysophytes, diatoms, and dinoflagellates. The euglenophytes and cyanophytes (blue-green algae) were typically uncommon in the oligotrophic head-water lakes.

In Sweden, dinoflagellates were the dominant algal group (averaging 3.5 species) in lakes with a pH 4 (Almer filL, 1974). *Peridinium inconspicuum* and some species of *Gymnodinium* were the most common. Chrysophytes were the next most common algal group averaging three species per lake. *Dinobryon crenulatum* and *D. setularia* were the most common chrysophytes. Chlorophytes were also present averaging two species per lake. Diatoms were noticeably absent from these lakes.

Chrysophytes and chlorophytes increased from 3 and 2 species, respectively, in lakes with pH 4, to 7 species each at pH 5. Dinoflagellates increased at a slower rate from 3.5 to 5 species over the same pH range. Very few lakes with pH less than 5 had any pelagic diatom species.

Between pH 5.5 and 6, the number of chlorophyte, chrysophyte, and dinoflagellate species increased in the Swedish survey. Chlorophytes continued to dominate, averaging 15 species per lake. Above pH 6, Almer et al. (1974) reported that the algal biomass was equally distributed between the chlorophytes, chrysophytes, cyanophytes, diatoms and dinoflagellates. Above pH 7, the number of chrysophyte species declined because their physiological adaptation and natural competitiveness in acidic oligotrophic lakes was lost (Hutchinson, 1967).

The general conclusion from the Swedish survey was that lakes with a pH < 5 had a homogeneous and low phytoplankton diversity consisting of about 10 species in total. For lakes with a pH between 5 and 5.5 the chlorophytes and chrysophytes dominated the algal community. The filiform alga *Mougeotia scalaris* was also frequently observed free-floating in the pelagic zone.

The phytoplankton surveys conducted in Norway (Hendrey and Wright, 1976) and Canada (Kelso al., 1986) showed similar trends with some minor exceptions. These surveys found that chlorophytes were the dominant algal group above pH 4.5, however, fewer dinoflagellate species were recorded in both studies and, in eastern Canada, chrysophytes were co-dominant with chlorophytes. The observed differences in algal dominance were not considered important, because differences in lake morphology, trophic status, and planktonic periodicity could explain the observed regional differences.

Kelso et al. (1986) used discriminant analysis to explain variation in the phytoplanktonic community in eastern Canada. A large portion of the variation in the phytoplanktonic community structure was explained by the lake’s elevation, location, chloride, sulphate, colour, alkalinity and magnesium concentrations. No single variable dominated the discriminant functions, and interestingly, the pH of the water was determined not to influence the phytoplankton community in a geographic area. The results of Kelso et al. (1986) suggest that the results of the Swedish and Norwegian surveys are inconclusive because they did not consider other limnological variables. Despite these limitations, their results have been used in the literature to suggest that acidification of lakes reduces algal biomass and diversity.

Long-Term Studies:

To overcome the flaws in the sampling design of regional surveys, researchers have conducted long-term studies in a small number of lakes of different acidities (Conway and Hendrey, 1981; Kwiatkowski and Roff, 1976; Yan, 1979; Yan and Stokes, 1976; Yan and Stokes, 1978; and Crisman et al., 1980). The data collected from lakes near Sudbury, Ontario, published by Yan, were not included in this analysis because the effects of pH on the phytoplankton community could not be differentiated from the effects of high concentrations of heavy metals (Pb, Ni, Zn, Cu) deposited in the lakes from the smelters around Sudbury.

The results of Conway and Hendrey (1981) on three Adirondac lakes of differing pH (pH 7, 6, and 5), had many similarities with the survey results of Almer et al. (1974), Hendrey and Wright (1976), and Kelso et al. (1986). However, differences in lake morphology, trophic status, and water chemistry between the three lakes could not be eliminated from the sample design. Despite these limitations of the Adirondac study (Conway and Hendrey, 1981), their results are summarized below:

1) cyanophyte diversity and biomass decreased with decreasing pH;
2) diatom diversity did not change with pH (pH 7 to 5), however, biomass decreased with decreasing pH;
3) chlorophytes and chrysophytes dominated the community below pH 7;
4) dinoflagellate diversity and biomass were not affected by pH;
5) chlorophyte and chrysophyte diversity was reduced below pH 6, however, chrysophytes were affected to a lesser degree; and
6) at pH 5, the dinoflagellate indicator of acidification, *Peridinium inconspicuum,* made up a significant proportion of the algal biomass during the ice-free season.

Long-term phytoplankton surveys of 13 acidified and 6 non-acidified Florida lakes noted a significant reduction in the number of species with decreasing pH, with the greatest change occurring between pH 5.5 and 6.0 (Crisman et al., 1980). Cyanophytes dominated the non-acidified lakes while chlorophytes dominated the acidic lakes.

The long-term phytoplankton studies did not solve the problems of the influence of morphology and water chemistry on inter-lake phytoplankton surveys. To overcome these problems, whole-lake acidification projects were initiated at the ELA (Ontario, Canada) in 1974, and Little Rock Lake (Wisconsin, USA) in 1984.

Whole-Lake Acidification Studies:

Whole lake acidification experiments provide the most definitive work on the effects of acidification on phytoplankton communities. The results of the acidification of ELA Lakes 223 and 302 are summarized below. Unfortunately, the results from Little Rock Lake have not been published.

Lake 223 was slowly acidified with sulphuric acid from pH 6.7 to 5.1 from 1976 to 1983 (Findlay and Kasian, 1986). Two years (1974 and 1975) prior to the start of the acid addition served as controls. From 1974 to 1976, the pH ranged between 6.6 and 6.7 and chrysophytes and diatoms were the dominant algal groups. In 1976, the pH was lowered to pH 6.1 and the chlorophytes increased. The chlorophyte *Chlorella mucosa,* which was not common to the area, became abundant.

When the pH was lowered to 5.9 in 1978, chrysophytes continued to dominate, and different species of chlorophytes and cyanophytes were observed. The reduction of pH to 5.6 in 1979 and 1980 produced a significant change in the species composition as well as a reduction in species diversity. The filamentous chlorophyte *Mougeotia* formed highly visible, thick mats in the littoral zone and persisted throughout the remainder of the experiment. The chlorophyte *Chlorella mucosa* dominated the algal community in May and June, while the chrysophytes *Dinobryon sertularia, Malomonas, Stichogloea,* and *Uroglena* dominated for the rest of the summer. The acidophilic diatom *Asterionella ralfsii,* which was previously rare, appeared in large numbers.

The most dramatic change in the phytoplankton community occurred when the pH of Lake 223 was lowered to 5 in 1981, and maintained at pH 5.1 for 1982 and 1983. The chrysophyte *Chrysosphaerella longispina* dominated for a short period in May, and the dinoflagellates *Gymnodinium* sp. and *Peridinium inconspicuum* dominated the algal standing crop for the first time. The cyanophyte *Chroococcus minutus* dominated in the fall.

The phytoplankton diversity of Lake 223 for the entire acidification period is shown in Figure 4. The spring and fall diversity did not change when compared to the pre-acidification levels; however, lower diversity was observed during the summer months (Findlay and Kasian, 1986).

The findings at Lake 223 agree with the general conclusions of Almer et al. (1974), Hendrey and Wright (1976), Kelso et al. (1986), and Conway and Hendrey (1981). Below pH 5.6, there was a shift in the phytoplankton community structure, a reduction in species diversity, and the filiform chlorophyte *Mougeotia* became prominent. Although the phytoplankton community structure at Lake 223 was different than the other studies discussed, the pH at which changes occurred was similar. The acidophilic algae *Peridinium inconspicuum, Gymnodinium* sp., *Asterionella raljsii,* and *Dinobryon sertularia* were dominant at Lake 223 and in the survey studies of Sweden, Norway, and eastern Canada. *Chroococcus minutus* and *Chlorella mucosa* have not been reported in other studies, but were important acidophiles in Lake 223.

Acidification of Lake 302 at the Experimental Lakes Area was undertaken to test the reproducibility of the results at Lake 223 and the relative importance of sulphuric and nitric acids on the phytoplanktonic community. Lake 302 is a double basin lake and was divided with a reinforced vinyl barrier. Since 1982, sulphuric acid was added during the summer to the south basin, while the equivalent hydrogen ion activity of nitric acid was added to the north basin. The target pH for the south basin was 6.6 (1982), 5.9 (1983), 5.6 (1984) (Shearer and DeBruyn, 1986); however, the data on the effects of pH on phytoplankton community structure have not been published to date (Shearer, pers. comm.).

Fossil Record Studies:

Changes in the phytoplankton and periphyton community as the result of acidification have also been documented through the fossil record in lakes in eastern North America (Smol et al., 1984; and 1986). Some plankton groups with siliceous exoskeletons (e.g., chrysophytes, and diatoms) have very specific pH ranges. Analysis of these fossil assemblages preserved in lake sediments has allowed the reconstruction of past pH records to an accuracy of 0.2 pH units (Smol, 1986).

Conclusions:

Based on the results of regional surveys, whole-lake acidification experiments, and the fossil record, significant changes in the phytoplankton community structure can be expected when there is a drop in pH. The reduction of pH below 5.6 resulted in large mats of *Mougeotia* sp., a dramatic shift in the species composition, and a decreased phytoplankton diversity during the summer months. Because phytoplankton are the most important primary producers in north temperate lakes with important cold water fisheries resources, stability within the phytoplankton portion of the food web is considered important for the integrity of the zooplankton and fish populations.

4.2.2.2 *Effects of High pH*

Dominance of the phytoplankton community by cyanobacteria (blue-green algae) results from the complex interaction of physical environment (light, water movement, etc.), nutrients, and high pH (Lund, 1965; King, 1970; Hutchinson, 1967; Brock, 1973). At high concentrations, cyanobacteria are a concern as they can cause taste and odour problems in drinking water supplies (Palmer, 1962; Lin, 1977), they can be toxic (although rare), they can form surface scums that are aesthetically displeasing, and they are the principal cause of the muddy flavour in fish during the summer months (Lovell and Sackey, 1973).

Cyanobacteria typically dominate the phytoplankton community during the late summer months in oligotrophic and mesotrophic lakes, and throughout the year in eutrophic lakes. Cyanobacteria out-compete green and diatom algae when nitrogen to phosphorus ratios become low (<29:1; Smith 1983), and dissolved carbon dioxide concentrations drop below 7.5 µmol/L (King, 1970; King and Novak, 1974).

The low nutrient ratios and carbon dioxide concentrations typically occur during the summer months in mesotrophic and eutrophic lakes.

Low nitrogen to phosphorus ratios occur following the spring diatom bloom as a result of the precipitation of dead or dying algae through the summer thermocline. The low ratio provides a competitive advantage to cyanobacteria over other algal species, because certain cyanobacteria can utilize nitrogen gas as a source of inorganic nitrogen.

Algae use carbon dioxide as their inorganic carbon source during photosynthesis (King, 1970). The concentration of carbon dioxide in freshwater is determined by the alkalinity and pH of the water (Appendix 2). Increases in alkalinity without a change in pH result in a linear increase in

carbon dioxide concentrations; however, an increase in pH without a change in alkalinity results in an exponential decrease in carbon dioxide concentrations (King, 1970).

As with most inorganic micronutrients, carbon dioxide is more easily extracted from water by certain algal groups than by others. King (1970) noted that green algae are not efficient at extracting carbon dioxide below a concentration of 10 µmol CO_2/L (0.44 mg/L). At carbon dioxide concentrations below 7.5 µmol CO_2/L (0.33 mg/L), the cyanobacteria have a clear advantage and will dominate the phytoplankton community (King, 1970; King and Novak, 1974.).

Shapiro (1973) tested King's hypothesis by injecting carbon dioxide, acid, and nutrients in small enclosures (mesocosms) that had a mixed phytoplankton community. The addition of nutrients without carbon dioxide or acid resulted in higher concentrations of cyanobacteria. In contrast, the addition of carbon dioxide and nutrients resulted in a shift from cyanobacteria to green algae within 10 days. The reduction of pH with acid was similar to the addition of carbon dioxide, but less dramatic. Shapiro (1973) concluded that the addition of carbon dioxide or the lowering of the pH stimulated a shift from cyanobacteria to green algae, especially when nutrients were supplied simultaneously.

Streams typically have very low cyanobacteria populations (Bothwell, pers. comm.). Bothwell speculated that cyanobacteria do not dominate the periphyton community, except in some Rocky Mountain Streams that have high phosphorus and low nitrogen water concentrations. Consequently, the application of King's hypothesis in streams is not appropriate.

The implication of King's hypothesis and Shapiro's experiments are that the elevation of pH in lakes will favour the dominance of cyanobacteria in the phytoplankton community, which may result in taste and odour problems, toxicity, etc. The relationship between carbon dioxide, pH, and alkalinity for British Columbia lakes is summarized in Figure 5. Data points above the straight line have a carbon dioxide concentration above 7.5 µmol/L. The general trend is for the carbon dioxide concentration to decrease as the alkalinity and pH increase. The implication is that cyanobacteria would become more prevalent as the alkalinity and pH increase.

Conclusion:

The phytoplankton community structure in lakes is influenced by the concentration of carbon dioxide, in association with other nutrient and physical parameters. The epilimnetic carbon dioxide concentration of a lake is determined by the ambient alkalinity and pH (see Appendix 2). dioxide concentration of a lake is determined by the ambient alkalinity and pH (see Appendix 2). Cyanobacteria, which can cause water quality problems, appear to dominate systems with carbon dioxide concentrations below 10 µmoles CO_2/L. Because carbon dioxide concentrations decrease with increasing pH, lakes with high pH are typically dominated by cyanophyte communities.

4.2.3 *Biomass and Primary Productivity*

The phytoplankton surveys of lakes in Sweden and Norway concluded that low pH conditions caused a reduction in phytoplankton biomass and primary productivity. Disruption of the food supply was thought to be an important component of fish extinction, and the term 'dead lake' was frequently used to describe an acidified lake that was crystal clear and devoid of fish. Grahn et al., (1974) hypothesized that the lower algal biomass (measured as chlorophyll-*a*) measured in acidic lakes was the consequence of oligotrophication. The term oligotrophication was used to describe the acid-induced reduction in nutrient availability in lakes. There have been several theories proposed to explain the oligotrophication hypothesis:

1) A build-up of undecomposed organic debris (especially *Sphagnum* moss) was observed over the mineralized sediments of acidic lakes. The organic layers would prevent the exchange of nutrients and other ions across the sediment/water interface (Grahn et al., 1974).
2) Dense mats of *Mougeotia* were observed over undecomposed organic debris at the bottom of the lake. The algae would also prevent ion exchange across the sediment/water interface and fungal decomposition and mineralization of organic matter would be slower than the growth of heterotrophic bacteria (Grahn et al., 1974).
3) Terrestrial decomposition rates were slowed by acid precipitation, reducing phosphorus mineralization and input to lakes via streams and groundwater (Hendrey, 1982).
4) Soil and lake acidification caused high concentrations of hydrolysed aluminum, iron. and manganese which can bind phosphorus in soil or lake sediments. The result is reduced phosphorus release from the lake sediments and lower phosphorus concentrations (Hendrey, 1982).
5) Dense layers of *Mougeotia* in the littoral zone can intercept phosphorus from the littoral sediments or groundwater (Leivestad et al., 1976).
6) Acidification decreased the solubility of dissolved organic carbon. Primary production may be limited by low inorganic carbon levels (Conway and Hendrey, 1981).

Although the process of oligotrophication was used to explain the correlation between low pH and low phytoplankton biomass and productivity, the regional surveys in Sweden and Norway did not consider the fact that small, high altitude lakes would be less productive than larger circumneutral lowland lakes. Schindler (1980) considered the evidence for oligotrophication to be largely circumstantial for this reason.

The research completed at the Experimental Lakes Area provides the best explanation of the effects of acidification on phytoplankton biomass and production. The acidification of Lake 223 and Lake 302 resulted in increased phytoplankton biomass and productivity (Shearer and DeBruyn, 1986; Findlay and Kasian, 1986; and Shearer et al., 1985). For example, the primary production in Lake 223 increased steadily during the first 6 years of acidification, resulting in a 250% increase over pre-acidification levels (Figure 4). Edible phytoplankton biomass (defined as phytoplankton size < 20 µm) also increased when the pH was reduced from 6.8 to 5.6, but declined to slightly below pre-acidification levels at pH 5 (Findlay and Kasian, 1986).

Acidification of the south basin of Lake 302 (sulphuric acid addition) corroborated the findings at Lake 223 (Findlay and Kasian, 1986). Throughout both whole-lake acidification experiments, phosphorus levels did not change relative to the unacidified reference lakes, and decomposition rates did not change (Section 4.1.1). However, water clarity increased in the epilimnion of both lakes during acidification (Schindler et al., 1985).

The increased phytoplankton biomass and productivity in Lakes 223 and the south basin of Lake 302 were the result of the deepening of the euphotic zone due to increased light penetration (Shearer et al., 1987). The mechanism for increased light penetration in Lake 223 was not obvious as there was no reduction in dissolved organic carbon concentrations following acidification. Schindler (1980) hypothesized that the increased water transparency in Lake 223 was due to an acid-induced change in the colour of the dissolved organic matter.

The increased water transparency observed in the south basin of Lake 302 following several years of sulphuric acid addition, however, was attributed to a decrease in the dissolved organic carbon concentrations (Shearer and DeBruyn, 1986). The water transparency of the north basin of Lake 302 did not change following several years of nitric acid additions, suggesting that the interaction of sulphuric acid with the dissolved organic fraction caused the water transparency to increase.

A third whole-lake acidification experiment was conducted at Little Rock Lake (Wisconsin, U.S.A.). Little Rock Lake, which had an original pH of 6, was divided with a vinyl barrier and artificially acidified with sulphuric acid to pH 5.5 in 1985, pH 5 in 1986, and pH 4.5 in 1987. Primary productivity, chlorophyll-a, and phosphorus concentrations between pH 6 (the control year) and 5.5 (1985) were not significantly different (Wachtler, 1987). The effects of further reduction of pH on the phytoplankton community have not been published.

Conclusion:

The limited results from Little Rock Lake support the conclusions of the ELA acidification experiments that lake primary production and biomass are not reduced through a reduction in pH from 6.7 to 5.1.

4.2.4 *Aesthetics*

The acidification of a water body can have two detrimental effects on the aesthetics. *Mougeotia* sp. is referred to as 'elephant snot' by local residents living around acidified lakes (Schindler, pers. comm.). The threshold pH at which *Mougeotia* will become an aesthetic problem is 5.6.

In eastern North America, the planktonic alga *Chrysochromulina breviturrita* has recently been reported to cause strong odours similar to rotten cabbage or a garbage dump (Nicholls et al., 1982). The presence of the alga is linked to lake acidification as 80 percent of the lakes with *C. breviturrita* had a pH less than 6.9 and an alkalinity below 10 mg $CaCO_3$/L.

4.2.5 *Summary*

In summary, the results of the systematic reduction of pH in Lake 223 provide the most comprehensive assessment of the effects of acidification on the phytoplankton community. Although changes in community structure occurred in lakes acidified to as low as pH 5, biomass (including the fraction considered edible to zooplankton) and primary productivity were not affected. Changes in species diversity during the summer months, however, occurred when the pH was< 5.6. The presence of *Mougeotia* at pH 5.6 created an aesthetic problem in lakes used for recreation, while the presence of C. *breviturrita* in acidified lakes produced taste and odour problems. The pH criteria outlined in Section 4.9 consider the aesthetic and taste and odour problems caused by the presence of *Mougeotia* and *C. breviturrita.*

In contrast, the phytoplankton community structure in lakes is influenced by the concentration of carbon dioxide (in association with other nutrient and physical parameters). Cyanobacteria, which can cause water quality problems, appear to dominate systems with carbon dioxide concentrations below 10 µmol CO_2/L. Because carbon dioxide concentrations decrease with increasing pH, lakes with high pH are typically dominated by cyanophyte communities.

4.3 Aquatic Plants

Land plants utilize carbon dioxide from the air as their source of carbon for photosynthesis. Although carbon dioxide is easily dissolved in water, it is converted to bicarbonate (HCO_3^-) above pH 8.2. As a result, aquatic plants have evolved the ability to utilize both CO_2 and HCO_3^- from the water, and have been observed growing in water with a pH as high as 10.5 (Warrington, 1983).

Warrington (1988) completed a survey of the pH tolerance of aquatic plants and concluded that they have an extremely wide pH tolerance range. For example, *Myriophyllum spicatum* has a pH tolerance from 2.9 to 10.2, a range of 7.3 orders of magnitude of hydrogen ion concentration. He concluded that aquatic plants have a very wide pH tolerance, and major shifts in pH (2-3 pH units) would not impact the community structure or production.

4.4 Crustaceans

4.4.1 *Copepods and Cladocerans*

Copepods and cladocerans are two important components of the limnetic zooplankton community. Crustacean zooplankton are an important food supply for fish, particularly juveniles, transferring energy from the primary producers to the higher trophic levels. Surveys in Sweden (Almer et al.,1978), and Canada (Sprules, 1975) determined that the total number of zooplankton species decreased significantly with decreasing pH.

Despite the fact that these surveys did not consider lake morphology or the impact of fish on the zooplankton community, their general conclusions were that crustaceans and the daphnids (cladocerans) were generally intolerant to acidification. and absent from systems with a pH ≤5.

Sprules (1975) noted that the major determinants of the zooplankton community structure in 47 Ontario lakes (pH 3.7-7) was pH, lake area, and lake depth (in decreasing order of 5, many species were eliminated and the acid-tolerant species became progressively rarer. Very acidic lakes had a single species, *Diaptomus minutus* (Sprules, 1975).

The controlled artificial acidification of Lake 223 (Ontario), and the acidified lakes of La Cloche Mountains (Ontario) provide the best examples of the effects of acidification on the zooplankton community and forms the basis for this section.

The acidification of Lake 223 from pH 6.7 to pH 5.1 did not result in a decrease in the zooplankton biomass; in fact in the second year at pH 5.1, the zooplankton biomass was the highest measured in the 8 years of record (Schindler et al.., 1985). There were, however, significant changes in the zooplankton community structure at pH 5.1 (Malley and Chang, 1986).

A major change was the loss of *Mysis relicta* at pH 5.6. *Mysis* is an opportunistic feeder and can play an important role in structuring the zooplankton community. The decline of *Mysis* in Lake 223 was not correlated with the other observed changes in the zooplankton community (Malley and Chang, 1986). Another invertebrate predator, *Chaoborus,* remained rare throughout the acidification process of Lake 223, and was not implicated in the observed changes in the zooplankton community.

At pH 5.1. cladocerans in Lake 223 increased in total biomass, and absolute and relative abundance. Shifts in the cladoceran species were also observed. *Daphnia galeata mendotae* disappeared; *Diaphanosoma birgei* became rare; *Holopediwn gibberwn, Bosmina longirostris,* and *Daphnia catawba* increased in abundance. Calanoid copepods and to a lesser extent cyclopoid copepods decreased in biomass and abundance over the same pH range (Schindler et al., 1985). The calanoid copepod *Epischura lacustris* disappeared at pH 5.6 (Schindler et al., 1985), while the acidophilic copepod *Diaptomus minutus* declined slightly (Malley and Chang, 1986).

The most important event in Lake 223 affecting the cladoceran community was the increase in cladocerans and the dramatic decline in small fish due to reproductive failure (Malley and Chang, 1986). Lake trout fry and fathead minnows were virtually absent from the lake after 1979 (pH 5.9), while the more acid-tolerant pearl dace and white sucker were severely reduced in numbers in 1981-1983 (pH 5.1). The increase in the abundance of the large cladoceran zooplankton *(D. catawba* and *H. gibberum)* from 1980-1983 was probably the result of reduced predation by small fish (Schindler et al., 1985).

Conclusions:

A decrease in zooplankton community structure was evident with decreased pH. Between pH 6.5 and 5, many non-acid-tolerant species were eliminated, and the acid-tolerant species became progressively rarer below pH 5. Changes in the zooplankton biomass of Lake 223 were not large down to pH 5.1. The reproductive failure of the planktivorous fish species (due to low pH) had the most significant impact on the zooplankton community structure.

4.4.2 *Amphipods*

The information on the effects of pH on the amphipod community is sparse. Stephenson and Mackie (1986) determined that the 96-h and 10-d LC50 of *Hyalella azteca* were pH 4.4 and 4.5, respectively. They also plotted the distribution of *H. azteca* in 79 Ontario lakes. Their survey showed that *H. azteca* was not found in lakes with a pH less than 5.5, indicating that acute toxicity at low pH was not determining the distribution of the species. They implicated reproductive failure as the cause, noting that recruitment was delayed in a lake that underwent short-term acidification.

France and Stokes (1987) concluded that the resistance of *H. azteca* to low pH was directly related to size and development stage. Exposure of adults to pH 5.0 or juveniles to pH 5.5 could result in population decline.

4.4.3 *Crayfish*

As with most aquatic organisms, there appears to be a wide range of pH tolerance among crayfish species. Berrill et al., 1985 studied three common crayfish found near Sudbury, Ontario. In the nine soft-water lakes which ranged between pH 4.7 and 5.6, *Cambarus robustus* was abundant, while C. *bartoni* and *Orconectes propinquus* were absent. The potential impact of heavy metals from the smelter was not discussed by Berrill et al. (1985).

Acid-sensitive species (e.g., *Orconectes propinquus* and *O. rusticus)* experienced 25% mortality between pH 5.6 and 6.1, and 100% mortality at pH 4.3 (Benill et al., 1985). Between pH 5.6 and 6.1, only 50% of the broods of the same species molted from stage I to stage II, and the survival of stage III juveniles was 35% lower than the circumneutral control. In contrast, the pH-tolerant species (C. *robustus)* was able to successfully reproduce at pH 4.5. Like most other freshwater organisms, reproductive failure in crayfish species occurred· at a higher pH than mortality.

France (1984) found that for *Orconectes virilis* (the most common crayfish species in Canada) the adult was quite resistant to low pH, with complete survival at pH 3.5 for one month. In contrast, acidification below pH 5.5 for young and 5 for juvenile *O. virilis* caused progressively increased mortality. For all_ three life stages, mortality was often delayed after initial exposure.

Borgstrom and Hendrey (1976, in Malley 1980) suggested that low pH may affect crustaceans by blocking the uptake of Ca^{++} during molting. At pH 5.0, the crayfish *Orconectes virilis* progressed slower through its molt stages, and the rate of calcification was retarded as compared to the controls (Malley, 1980). For *O. virilis,* the rate of Ca^{++} uptake was reduced at pH 5.75, and completely inhibited at pH 4.

France (1987) compared carapace rigidity (a measure of strength) and calcium levels in *O. virilis* from Lake 223, which had been artificially acidified to pH 5.4. He concluded that the median carapace rigidity and calcium content from Lake 223 were lower than from the adjacent reference lakes.

The inhibition of calcium uptake and the associated soft exoskeletons of crayfish has resulted in elevated loss of chelae and limbs, increased cannibalism, predation by fish, and parasitism by the fungus *Thelohania contejeani* (Mills et al., 1976; France and Graham, 1985). The reduced strength of the exoskeleton is thought to have caused a 50% reduction in the annual survival rate of adult crayfish in Lake 223 at pH 5.1 (Mills et al., 1976).

Conclusions:

The effects of acidification on crayfish are similar to other aquatic organisms in most respects. Some species (e.g., *Cambarus robustus)* survived in acidic conditions; however, reproductive failure was the principal cause of species extinction. Crayfish are different from other aquatic organisms in that they also experienced increased mortality above the critical pH because of reduced strength of the exoskeleton. The increased mortality above the critical pH suggests that, for crayfish, the use of the critical pH may not be adequate for the protection of the species.

4.5 Insects

Insects are the most diverse group of freshwater invertebrates. They are primarily found in the littoral zones of lakes or the benthos of rivers. Insects such as mayflies, caddisflies, chironomids, etc. are very important in the ecosystem, controlling excessive algal growth in rivers (Bothwell et al., 1989), or as a food source for fish.

In general, adult aquatic insects are tolerant of acidic conditions (Table 2).

Table 2. Effects of pH on Aquatic Insects

Species	Group	Result	Reference
Brachycentrus americanus	Caddisfly	pH 1.5 =TLm96	Bell and Nebeker, 1969
		pH 2.5 =30-d TL50	Bell, 1971
		pH 4.0: emergence reduced by 50%	Bell, 1971
Hydropsyche betteni	Caddisfly	pH 3.2 = TLm96	Bell and Nebeker, 1969
		pH 3.4 = 30-d TL50	Bell, 1971
		pH 4.7: emergence reduced by 50%	Bell, 1971
Ischnura verticalis	Damselfly	pH 3.5: no mortality of nymphs or eggs	Berrill et al., 1987
Boyeria vinosa	Dragonfly	pH 3.3 = TLm96	Bell and Nebeker, 1969
		pH 4.4 = 30-d TL50	Bell, 1971
		pH 5.2: emergence reduced by 50%	Bell, 1971

Species	Group	Result	Reference
Libellula lydia	Dragonfly	pH 3.5: no mortality of nymphs or eggs	Berrill et al., 1987
Ophiogomphus rupinsulensis	Dragonfly	pH 3.5 = TLm96	Bell and Nebeker, 1969
		pH 4.3 = 30-d TL50	Bell, 1971
		pH 5.2: emergence reduced by 50%	Bell, 1971
Taeniipteryx maura	Stonefly	pH 3.3 = TLm96	Bell and Nebeker, 1969
		pH 3.7 = 30-d TL50	Bell, 1971
		pH 5.0: emergence reduced by 50%	Bell, 1971
Acroneuria lycorias	Stonefly	pH 3.3 = TLm96	Bell and Nebeker, 1969
		pH 3.9 = 30-d TL50	Bell,1971
		pH 5.0: emergence reduced by 50%	Bell, 1971
Isogenus frontalis	Stonefy	pH 3.7 = TLm96	Bell and Nebeker, 1969
		pH 4.5 = 30-d TL50	Bell, 1971
		pH 6.6: emergence reduced by 50%	Bell, 1971
Pteronarcys dorsata	Stonefly	pH 4.3 = TLm96	Bell and Nebeker, 1969
		pH 5.0 = 30-d TL50	Bell, 1971
		pH 5.8: emergence reduced by 50%	Bell, 1971
Ephemerella subvaria	Mayfly	pH 4.7 = TLm96	Bell and Nebeker, 1969
		pH 5.4 = 30-d TL50	Bell, 1971
		pH 5.9: emergence reduced by 50%	Bell, 1971
		pH 4.0: recruitment severely reduced	Fiance, 1978
Leptophlebia cupida	Mayfly	pH 3.5: no mortality to nymphs or eggs	Berrill et al., 1987
Stenonema femoratum	Mayfly	pH 3.5: no mortality to nymphs or eggs	Berrill et al., 1987
Stenonema rubnum	Mayfly	pH 3.3 = 1Lm96	Bell and Nebeker, 1969
Tanytarsus dissimilis	Midge	pH > 5.5: no effect on reproduction	Bell; 1970
		pH 5.5: adults failed to emerge	Bell, 1970
		pH 4.0: larvae died	Bell, 1970

Bell (1971) concluded that caddisflies were very tolerant to low pH conditions; stoneflies and dragonflies were moderately tolerant, while mayflies were fairly sensitive to low pH conditions. Berrill et al. (1987) determined that no mortality or loss of sodium or chloride ions occurred in nymphs of aquatic insects that were tolerant or intolerant when exposed to pH 3.5.

The pH at which reproduction was affected (critical pH) was substantially higher than the acute pH (Table 2). The critical pH ranged between 4 for the caddisfly *B. americanus* to 6.6 for. the stonefly *I.frontalis,* indicating a wide range of pH tolerance among insects species.

Whole-stream acidification studies have taken two forms; comparison of acidic and non-acidic streams, and the acidification of reaches or tributaries. Two Swedish streams with similar environmental characteristics, but different acidities, were studied by Friberg et al. (1980). Organic debris decomposed much faster in the non-acidic stream (pH 6.5-7.3) and invertebrate biomass per leaf litter pack was higher. Forty-six invertebrate taxa were found in the reference stream, but only 18 were found in the acidified stream (pH 4.3 - 5.9). Scraper species were three times more abundant in the circumneutral stream than in the acidic stream. Ephemeropterans (mayflies) and elminthid beetles (both scrapers) were absent in the acidic stream. It was unclear from the study whether the absence of scrapers was due to physiological inadequacies or to a changed composition of the detritus.

A stream, Norris Brook, located in the Hubbard Brook Experimental Forest in New Hampshire, was manually acidified with sulphuric acid to pH 4.0 from a pH that was never recorded below 5.4 (Hall et al., 1980). The total number of emerging insect adults was reduced by 37% in the acidified portion of the stream as compared to the reference section. Although the numbers of emergent shredders and predators did not differ, there was a significant decrease in the number of collector insects in the acidic section.

Relative to the reference area, macroinvertebrate drift increased 4- fold after one day of. acidification, and 13-fold after two days. After one week there was no difference in drift. *Epeorus* and *Ephemerella* had the highest drift density of the Ephemeroptera. *Epeorus* responded immediately after the addition of acid, while *Ephemerella* showed the greatest drift increase on the second day (Hall et al., 1980).

Based on feeding functional group classification, the collector taxa responded most to acidification with a 17-fold increase in drift on. the first day of acidification. Scrapers increased 9-fold on the first day, predators 4-fold on the second day, and shredders showed no significant increase in drift (Hall et al., 1980).

Sutcliffe and Carrick (1973) concluded that the invertebrate abundance in the River Duddon was indirectly depressed from low pH by a decreased food supply. In Norris Brook, the decreased invertebrate abundance was caused by an immediate response to acidification, not decreased food supply (Hall et al., 1980). The experiment at Norris Brook was not long enough to determine if the benthic community would become recolonized with acid-tolerant species; however, it showed the immediate response of the insect community to low pH which may result from a brief industrial discharge or spill.

Conclusions:

The pH which is acutely toxic to aquatic insects appears to be very low (pH <4.0), with caddisflies the most tolerant group, followed by stoneflies and mayflies. The critical pH for reproduction was higher than the acute levels, and ranged between 4 and 6.6. This indicated that among insect species there is a wide range of pH tolerance. The results of the whole-stream acidification studies indicated that the rapid reduction in pH, through the addition of acid, resulted in increased drift of insects and decreased invertebrate abundance in the river. It was unclear from the whole-stream acidification experiment if the benthic community would become recolonized with acid-tolerant species.

The near neutral pH at which the emergence of *I. frontalis* was affected is significant considering the lower limit of the CCREM guidelines is 6.5. However, the species *I. frontalis* , or the genus *Isogenus* has not been recorded in British Columbia (Hummel, pers. comm.; Ricker and Scudder, 1975) indicating that for aquatic insects, the lower range of the CCREM should be adequate for the protection of aquatic life in British. Columbia.

4.6 Molluscs

4.6.1 *Freshwater*

Freshwater molluscs are an important food source for fish, waterfowl, and small mammals. In British Columbia, their distributions are quite extensive in lowland lakes, but more sparse in alpine systems, presumably because of the difficulty of post-glaciation colonization (Grant, pers. comm.).

Molluscs are potentially more susceptible to the effects of acidification through the reduction in the carbonate concentration in the water, or the dissolution of their carbonate exoskeleton. Surveys of mussel populations in Norway indicated that the number of species decreased at a constant rate with pH (Okland, 1980). For Norwegian lakes with a pH ≥7.0, there were over 15 species recorded; however, the number of species decreased to *5* at pH 6.0, and zero at pH 4.5. Okland (1980) concluded that the lower tolerance limit for the six most common species was between pH 5.7-6.3.

High densities of molluscs were observed iq. neutral lakes in Ontario with very low alkalinity (0.24-3.17 mg/L) and calcium concentrations (Rooke and Mackie, 1984). Servos et al., (1985) demonstrated that the gastropod *Amnicola limosa* experienced impaired egg development below pH 5.0, and delayed development at pH 5.5. They concluded that below pH 6.0, *A. limosa* would experience reproductive failure. In contrast, the bivalve *Pisidium* spp. did not appear to experience any reproductive effects in study lakes with a pH of 5.8.

4.6.2 *Marine*

In the marine environment, molluscan reproduction has a much narrower pH range. Calabrese and Davis (1966) determined that for clams and oysters, the development into normal straight-hinged larvae was very sensitive to pH conditions. Clam eggs developed normally when the pH ranged between 7 and 8.75, while oyster eggs had a slightly wider pH range (pH 6.75-8.75). Survival of both the clam and oyster larvae occurred over a wider pH range. Between pH 6.25 and 8.75 survival of both mollusc groups was normal. Beyond these ranges the mortality of the larvae increased dramatically.

Conclusions:

The extent of literature on the effects of pH on the freshwater molluscs is very limited. Based on surveys in Norway and Ontario, molluscan diversity was not affected by low alkalinity or calcium concentrations in circumneutral lakes, but decreased with decreasing pH. Experiments with *Amnicola limosa* indicated that reproductive failure would occur below pH 6. The lack of literature for other mollusc species prevents an assessment of the pH range that affects reproduction.

Molluscs are the only taxonomic group for which there are data on the effects of pH in the marine environment. Normal development of clam and oyster eggs occurred between pH 7 and 8.75, which is within the normal pH range of British. Columbia. marine waters (Section 3.2).

4.7 Fish

The freshwater fish found in British Columbia are listed by common and scientific names in Appendix 1. For this publication, native fish are referred to by their common names, while introduced species are referred to by their scientific names. Marine fish are not discussed in this section because of the absence of literature on the effects of low pH on fish in the marine environment.

4.7.1 *Acid Toxicity to Fish*

The primary functions of the gill are the exchange of respiratory gases (oxygen and carbon dioxide), anions and cations (calcium, sodium, chloride, etc.), and ammonia excretion. For gills to be effective, fish require large surface areas that are in immediate contact with the external environment. As a consequence, the gills are susceptible to most environmental contaminants, including elevated concentrations of hydrogen ions (low pH).

The following sections outline the mechanisms of hydrogen ion (H+) toxicity, the physiological responses of fish to low pH, and the ameliorative effects of external calcium concentrations and other polyvalent cations.

Elevated H^+ concentrations have three general impacts on fish physiology causing the "hydrogen ion toxic syndrome" (Wood and McDonald 1982). Components of the toxic syndrome include: 1) reduced oxygen uptake and transportation in the blood; 2) loss of ionoregulation (influx and efflux of ions); and 3) changes in acid-base balance of intracellular and extracellular fluids. This section will also discuss the ameliorative effects of calcium on hydrogen ion toxicity, and the effects of acidification on behaviour, reproduction, and inter- and intra-species adaptations to low pH.

4.7.2 *Oxygen Uptake and Transportation*

The first component of the toxic syndrome is decreased oxygen uptake and transportation resulting in hypoxia (Ultsch, 1978). Exposure to low pH can theoretically cause hypoxia through the induction of excess mucus production, destruction of gill tissue, and the alteration of the oxygen carrying capacity of blood pigments.

4.7.2.1 *Ventilation*

The first studies on the effects of acidification focused on the induction of hypoxia caused by respiratory dysfunction. The basic assumption of these studies was that increased ventilation was the result of reduced oxygen transfer across the gills or carrying capacity of the blood. Other factors such as stress on increased ventilation rates were rarely considered.

Eddy (1976) injected acid directly into the blood stream of rainbow trout and observed increased breathing frequency, gape, ventilation volume, and in some cases the fish struggled vigorously. Most of the injected acid was buffered by the tissues, while only 20% was buffered by bicarbonate in the blood. In a more sophisticated experimental design, Neville (1985) exposed juvenile rainbow trout to acute and chronic pH conditions. No responses in ventilation rate, gape, cough rate, or activity were observed at pH 6.5, 5.5, and 5. However, there was a moderate increase in ventilation parameters and cough rate for 1 h when rainbow trout were exposed to pH 4.5, and a moderate increase in activity and a severe increase in ventilation parameters and cough rate for a least 1 to 2 hours when exposed to pH 4. Giles et al. (1984) also observed increased ventilation in immature rainbow trout when the pH was lowered below 4.9.

Other studies have focused on the effects of pH on the rate of oxygen consumption; however, approximately half of the studies were not able to show any change or decrease. At pH 3.5, no decrease in oxygen consumption was observed in rainbow trout (Ultsch et al., 1980), pumpkinseed, or goldfish (Ultsch, 1978). However, the catfish *(Ictalurus punctatus:* Ultsch, 1978), and brook trout (Packer and Dunson, 1972; Packer, 1979) showed a significant decrease in oxygen consumption at pH 3.5, indicating that the reaction to low pH varied among species.

Blood PO_2 (gas tension of dissolved oxygen in the blood) or lactate concentrations are more reliable indicators of tissue hypoxia (Ultsch et al., 1981). Decreased oxygen transfer and reduced available blood oxygen capacity in brook trout could not be detected at pH 4.2 (Dively et al., 1977), but was observed at pH 3.5 (Vaala and Mitchell, 1970; Packer, 1979).

In similar experiments, reduction of ambient pH from 7.4 to 4 did not significantly reduce PO_2 or increase blood lactate concentrations in carp. However, when the pH was further reduced to 3.5, disturbances in gas exchange across the gills and Bohr (decreased affinity of oxygen to haemoglobin with decreased pH) effects caused tissue hypoxia and elevated blood lactate concentrations (Ultsch et al., 1981). The tissue hypoxia induced in the carp at pH 3.5 appeared to be the principal cause of death, although severe acid-base and electrolyte disturbances were also observed.

Based on the literature presented, it is difficult to ascertain whether or not observed changes in ventilation parameters at low pH were the result of stress to the fish or decreased oxygen exchange. It does appear from the studies by Neville (1985) and Giles et al. (1984) that pH 5 represented a threshold for increased ventilation in rainbow trout. Exposure to lethal pH can cause tissue anoxia due to gill and blood dysfunction, which can be a significant component of the toxic syndrome (Ultsch and Gros, 1979).

4.7.2.2 *Mucus Production*

Gills are covered by a thin mucus layer which is a complex of glycoproteins that has a neutral or small net negative charge. Mucus reduces the frictional drag of water passing through the narrow slits of the secondary lamellae (Leivestad, 1982), provides a diffusion barrier to ion and water movements, and by virtue of its negative charge it will tend to concentrate cations (e.g., Na^+, Ca^{2+}, Al^{3+}, etc.) in the gill epithelium (McDonald, 1983).

Ultsh and Gros (1979) observed the increased production of mucus in carp exposed to pH 3.5 and a reduction in the rate of oxygen transport to the blood. They concluded that the mucus formed a non-convective layer over the secondary lamellae reducing oxygen transfer rates.

Daye and Garside (1976) recorded that the threshold for increased mucus production was pH 5.2 for brook trout, and production increased with increasing acid stress. Below pH 4, mucus production in brook trout was sufficient to interfere with oxygen diffusion (Vaala et al., 1969; Plonka and Neff, 1969). Because of the negative ionic charge of the glycoproteins forming mucus, McDonald (1983) concluded that increased mucus production in reaction to H+ was an appropriate physiological response to the inhibitory effects of hydrogen ions on the sodium active transport mechanism (Section 4.7.3).

Recent research by Wood et al., (1988) showed that exposure to aluminum was the principal mechanism for increased mucus production in salmonids and presumably other· freshwater fish. They concluded that exposure to high monomeric aluminum concentrations and low pH induced sufficient mucus production to cause a reduction in the oxygen transfer capability of the gill epithelium.

4.7.2.3 *Epithelial Damage at Low pH*

Daye and Garside (1976) noted that the threshold for gill injury in brook trout (the most acid-tolerant salmonid) was between pH 5.2 and 5.6. The principal effect was a separation of the epithelium layers of the gill lamellae. Damage became progressively greater with decreased pH. Daye and Garside (1976) suggested that mild gill destruction was easily repaired.

Jackson and Fromm (1980) recorded an increase in vascular resistance in the perfused gills of rainbow trout exposed to acutely toxic pH (3.5) and very low calcium concentrations (0.8 mg/L). McDonald (1983) concluded that at acutely toxic pH levels, irreversible gill damage probably does occur.

4.7.2.4 *Effects on Blood Plasma*

Haemoglobin is the blood protein that transports oxygen from the gills to the tissues. The affinity of haemoglobin for oxygen is strongly pH dependent. Under normal conditions the blood pH is lower near the tissues due to the presence of elevated CO_2 concentrations (the result of respiration), and the affinity of haemoglobin for oxygen decreases. As venous blood (low in oxygen) enters the gills, the CO_2 is transferred from the blood through the gills and into the water, resulting in an increase in the blood pH and the affinity of haemoglobin for oxygen. Because the blood pH determines the affinity of haemoglobin for oxygen (known as the Bohr effect), the acid base balance of the blood in very important.

However, fish have very poorly buffered blood (low bicarbonate concentrations) when compared to mammals, and consequently, they are very susceptible to elevated hydrogen ion and carbon dioxide concentrations. The low plasma bicarbonate concentrations in fish are caused by the high solubility of carbon dioxide in water and the low partial pressure of carbon dioxide in the blood (Eddy 1976). Because of the poor buffering capacity of the blood, freshwater fish are very susceptible to acidosis or a change in the acid-base balance of the blood (see Section 4.7.4.1).

Fish exposed to low pH had increased haematocrit (red blood cells and haemoglobin) in the blood (Neville 1979; McDonald, 1983; Giles et al., 1984; Wood et al., 1988). Wood et al. (1988) noted that the increase in red blood cells was rapid, and the spleen was the source of the cells. The threshold for increased haematocrit and haemoglobin for rainbow trout was pH 5.5, and their concentrations increased progressively with decreased pH (Waiwood, 1980; Giles et al. 1984).

Witters (1986) noted that haematological conditions in rainbow trout exposed to pH *5* (Ca =l.1 mg/L) were restored to normal concentrations after 11 days, while Audet and Wood (1988) observed a 25% increase in adult rainbow trout haemoglobin concentrations after 22 days exposure to pH 4.8. The concentration of haemoglobin remained elevated over the 3-month experiment.

The decreased capacity of the blood to carry oxygen is not considered to be a critical component of the toxic syndrome *per se;* however, increased haematocrit, blood volume, viscosity, and pressure (due to exposure to low pH) caused cardiovascular failure in fish exposed to acutely toxic pH conditions, and is thought to be the principal cause of death in the toxic syndrome (Wood and McDonald, 1982: see Section 5.7.6).

4.7.2.5 *Summary*

Wood and McDonald (1982) concluded that the effects of chronic exposure to low pH on oxygen uptake and transport are minimal between pH 4 and 6, but may become an important component of the toxic syndrome at lower pH. Exposure to acutely toxic pH may affect the exchange and transportation of oxygen by damaging gills, modifying the affinity of haemoglobin for oxygen, and increasing mucus production.

4.7.3 *Ionoregulation*

The gills are the major site of ionic exchanges. These involve the passive effluxes of both anions and cations, and slightly higher active uptakes to compensate for the loss of ions in the urine and to maintain steady blood and tissue ionic levels.

The second component of the toxic syndrome is the loss of sodium and chloride ions from the extracellular and intracellular fluids (e.g., blood and tissues, respectively). The principal cause of ion loss is through the inhibition of the active transport of Na^+ and Cl^- ions across the gill epithelium (influx), and an increase in the permeability of the gills to ion loss (efflux) (Wood and McDonald, 1982).

4.7.3.1 *Influx*

The gills of fish serve as the site for the active transport of sodium and chloride ions into the extracellular fluid (Figure 6). McDonald (1983) reviewed the literature and concluded that the sodium and chloride mechanisms for fish gills were separate and independent. However, the chloride cell within the gill epithelium is thought to be the site of active transportation of both ions (Wood and McDonald, 1982).

The active transport mechanism is thought to be the result of electroneutral ion exchanges of Na^+/H^+ or $NH4^+$, and Cl^-/HCO_3- or OH^- (Figure 6). McDonald and Milligan (1988) observed a positive linear relationship under neutral pH conditions between the rate of the active transportation of sodium and ambient sodium concentrations. They concluded that sodium transportation was mediated by a limited number of transportation sites in the gill epithelium.

Wood and McDonald (1982) noted that there was little or no effect of low pH on the influx of chloride ions. Garcia-Romeu et al. (1969) concluded that hydrogen ions did not inhibit the neutrally or positively charged chloride channels in the gill epithelium. In contrast, Audet and Wood (1988) observed significant inhibition of chloride influx in adult rainbow trout exposed to sublethal pH (pH =4.8). They could not offer any explanation for the different results (Wood, pers. comm.).

The inhibitory effect of H^+ on the Na^+ active transport mechanism is species dependent, but begins around pH 6, and is nearly complete at pH 4 for most of the acid-tolerant species (Packer and Dunson, 1972). For salmonids, brook trout are considered to be the most acid resistant, while rainbow trout are the most sensitive (Wood and McDonald 1982).

The inhibition of sodium influx can be explained by the binding of hydrogen ions with the negative charges in the Na^+-specific channels within the gill epithelium. The H^+ binding would act to restrict access of Na^+ ions to the active transport mechanism, hence reducing the influx of sodium across the gills (McDonald, 1983).

The inhibition of sodium uptake is not constant over time. Some recovery occurs, but the degree of recovery is dependent upon time and the ambient pH and calcium concentrations (McDonald, 1983). Recovery of the sodium influx was nearly complete in brown trout after 10 days of exposure to pH 6 (Ca =0.6 mg/L: McWilliams, 1980a and 1980b). At pH 4.6 recovery was limited to 20 percent of the control, and was virtually nil at pH 4.0.

In agreement with McWilliams' studies on brown trout, very little recovery in sodium influx was observed in rainbow trout exposed to pH 4 (calcium =1.2 mg/L; McDonald et al., 1983). Recovery of sodium influx was still not complete when adult rainbow trout were exposed for 30 to 53 days to pH 4.8 (Ca=2 mg/L); however, the fish achieved a new ionic equilibrium through lower sodium efflux, and sodium plasma concentrations (Audet et al., 1988).

Rainbow trout exposed to pH 5 were able to restore completely the ion influx after 3 days, and whole-body concentrations after 11 days (Witters, 1986). In a separate 22-day study on rainbow trout, plasma sodium and chloride concentrations were unaffected by exposure to pH 5.2 (Ca=2.1 mg/L; Giles et al., 1984). Below pH 5.2, the change in plasma Na^+ and Cl^-concentrations decreased linearly with decreasing pH. Figure 7 shows the change and recovery of sodium influx with pH and time (McDonald, 1983). Of particular importance is the relatively slow and small recovery of sodium influx with respect to time compared to sodium efflux. Long-term sodium losses in rainbow trout at low pH were the consequence of the persistent inhibition of the sodium-active-transport mechanism rather than from continuous sodium efflux (McDonald et al. 1983).

Exposure of rainbow trout to acutely toxic pH conditions resulted in the initial efflux of sodium and chloride ions with a gradual recovery (Section 4.7.3.2), and the permanent inhibition of sodium influx

(McDonald, 1983). The result was a continued decrease in whole body sodium concentrations, resulting in death. Exposure of rainbow trout to chronically toxic pH conditions produced similar ionoregulatory problems. Between pH 4.5 and 5 there was a permanent inhibition of sodium influx which resulted in lower sodium plasma and whole body concentrations (Giles et al. 1984; Audet and Wood, 1988), while exposure to pH> 5 resulted in a temporary inhibition of sodium influx with complete recovery over time, and a return of plasma and whole body ion concentrations to control or pre-exposure levels (Giles et al. 1984; Witters, 1986).

This is an important distinction as there seem to be two chronic pH thresholds for rainbow trout: the first is the pH (approximately pH 5 or greater) at which sodium influx is temporarily inhibited but recovery of whole-body and plasma sodium and chloride are complete, and the second (pH 4.5 - 5) where sodium influx is permanently inhibited and lower whole-body and plasma ion concentrations result.

4.7.3.2 *Efflux*

Efflux refers to the loss of sodium or chloride ions through the epithelial cells. Wood and McDonald (1982) described the gill epithelium as tight under neutral or alkaline conditions and leaky under acidic conditions. McDonald (1983) concluded that the H^+ ions increased the efflux of ions from fish gills by displacing Ca^{2+} within the paracellular (between cell) pathway (Figure 6).

The pH threshold of increased sodium and chloride efflux is lower than the threshold of the inhibition of sodium influx (McDonald et al. 1983), because efflux is caused by the passive paracellular diffusion, and influx is the result of active transportation of ions across the gills.

The threshold for increased Na^+ efflux in salmonids is between pH 5 and 6, and the effect is progressive with further pH reduction (Wood and McDonald, 1982). At pH 4, Na^+ efflux can be 10-fold higher than normal (Packer and Dunson, 1972). With influx virtually inhibited at pH 4, the net loss of whole body sodium can approach 10%/h. At pH 3, the net Na^+ loss increased to approximately 50%/h, which rapidly resulted in death (Packer and Dunson, 1972). Wood and McDonald (1982) reported that a loss of 4% total body Na^+ within the first 24 hours of exposure to low pH caused mortality in more than 80% of fish within 5 days.

The effect of low pH on chloride efflux was less than or similar to the sodium efflux, depending on the external calcium concentration (McDonald et al., 1983). In softwater the rate of chloride efflux was similar to the rate of sodium efflux (1:1), while in hardwater the chloride efflux was less than the sodium efflux (0.5:1; McDonald, pers. comm.). In hardwater, the reduced chloride efflux created a charge imbalance within the extracellular fluid. The result is a higher H^+ influx in hardwater and acidosis of the blood (see Section 4.7.4).

Mortality due to ionoregulatory failure in rainbow trout exposed to acutely toxic pH conditions in softwater was studied by McDonald et al., (1983). Prior to death, sodium plasma levels decreased from 150 to 115 mEq/L, and chloride plasma levels decreased from 135 to 90 mEq/L. Similar ionic plasma concentrations were observed in rainbow trout exposed to acutely toxic pH conditions in hardwater; however, the rate of ion loss (and mortality) was slower.

Ionoregulatory failure was usually the key component of the toxic syndrome (Audet and Wood, 1988). Reduction in the salt content of the extracellular fluid caused massive disruptions in cardiovascular and fluid volume homeostasis (Wood and McDonald, 1982). As salts were lost from blood plasma, osmotic and ionic gradients occurred between the intracellular and extracellular fluids causing water to enter the intracellular compartment. The result was a swelling of red blood cells, decreased blood plasma volume, and increased blood viscosity, pressure, and heart rate. Combined with the mobilization of red blood cells from the spleen (see Section 4.7.2.4), mortality was caused by cardiovascular failure (Wood and McDonald, 1982).

4.7.4 *Acid-Base Balance*

The third component of the pH toxic syndrome is the change in the acid-base balance of the blood (Wood and McDonald, 1982). Fish blood is poorly buffered against acid-base disturbances primarily because of the high solubility of carbon dioxide in water. The high solubility causes low concentrations of CO_2 and bicarbonate in the blood (Eddy, 1976). In addition, the ability of the gills and the kidney to excrete hydrogen ions is limited. Consequently, fish are susceptible to blood acid-base imbalance due to the buildup of acid in the blood.

4.7.4.1 *Acidosis*

Acidosis primarily occurs due to the passive influx of H^+ ions from the environment, a build-up of lactic acid following strenuous exercise (Section 4.7.4.3), high carbonic acid concentrations due to elevated ambient carbon dioxide concentrations (Section 4.7.10) and, to a lesser degree, the reduced ability of the gills to excrete H^+ ions by decreasing the Na^+/H^+ active transport mechanism (McDonald, 1983).

The degree of acidosis is a function of ambient pH, external calcium concentration, and the amount of exercise or strenuous activity of the fish. Wood and McDonald (1982) reported a blood pH depression of 0.1 to 0.5 units in rainbow trout exposed to pH > 4. The acidosis caused at pH < 4 can be sufficiently severe (0.6- 1 pH units) to be the direct cause of death (Packer, 1979).

The degree of acidosis also varied with the external calcium concentration (McDonald, 1983). With increased calcium concentrations, the ratio of the net chloride loss relative to the net sodium loss decreased. McDonald (pers. comm.) noted that the ratio of Cl^-/Na^+ loss is approximately 1:1 in softwater and 0.5:1 in hardwater. For fish in hardwater, elevated Na+ efflux will cause a charge imbalance in the extracellular fluids, resulting in elevated H+ influx and severe acidosis (Figure 8).

Wood and McDonald (1982) concluded that for a pH range between 4 and 6, acidosis was not the direct cause of death; however, it may be a contributing factor to fish mortality when coupled with loss of ionoregulation, or aluminum toxicity.

4.7.4.2 *Branchial and Renal Excretion of Hydrogen Ions*

Wood and McDonald (1982) reported that a significant excretion of hydrogen ions occurred in response to the influx of hydrogen ions under low pH conditions. The principal efflux mechanism of H+ ions is with ammonium ions (NH_4^+) excreted by the gills. McDonald (1983) reported that approximately 90% of the ammonium excreted by fish exposed to acidic conditions occurred across the gills. The remaining hydrogen ion excretion was by the kidney as NH_4^+ or $H_2PO_4^-$. Wood and McDonald (1982) noted that renal excretion only served to slow the development of internal acidosis.

4.7.4.3 *Effects of Exercise and Acid Exposure*

Parker and Black (1959) observed a 46 to 86 % mortality of chinook salmon caught in the marine environment by west coast trollers. The cause of death was acidosis, due to the build-up of lactic acid following vigorous exercise. Wood and Randall (1973) noted that the effects of exercise at neutral pH was similar to acid stress. Exercise increased branchial ion loss and blood acidosis through the production of CO_2 and lactic acid.

Acid-stressed rainbow trout appeared to be more sensitive to additional stress (Barton et al., 1985). Juvenile rainbow trout exposed for 5 days to pH 5.7 and 4.7 were more sensitive to 30 seconds of handling stress than were fish in the control (pH 6.6). Plasma cortisol concentrations were twice the level in the control fish, indicating elevated stress levels (Barton et al. 1985).

Rainbow trout that have been successfully restocked into acidic lakes in Ontario do not survive if caught and then released. Acidosis due to handling stress, in conjunction with the low body ionic concentrations due to the effects of acidification, caused mortality in 100% of the fish (McDonald, pers. comm.). Consequently, chronic exposure of fish to low pH may not be toxic in laboratory situations; however, wild fish may suffer mortality under similar conditions due to the build-up of lactic acid following strenuous exercise.

4.7.5 *Effects of Calcium on Hydrogen Ion Toxicity*

The ambient calcium concentration is very important for the regulation of tissue water content (Oduleye, 1975), and for the stabilizing of membranes, cell-to-cell junctions, and ion permeability (McDonald et al., 1983). This is achieved through the binding of calcium to specific binding sites on the gill tissue, resulting in increased tolerance of fish to low pH with increased calcium concentrations (Lloyd and Jordan, 1964; McDonald, 1983; Wood and McDonald, 1982; Booth et al., 1988).

Wood and McDonald. (1982) experimented with rainbow trout in hard- and softwater to determine the effect of ambient calcium on the physiological response to high hydrogen ion concentrations. In hardwater (Ca^{2+} = 40 mg/Land pH between 4 and 4.5), rainbow trout experienced progressive acidosis and slow rates of sodium and chloride loss (Figure 8). In softwater (Ca = 3.5 mg/L) with the same pH, the result was reversed; there was slight acidosis with a rapid loss of plasma sodium and chloride ions.

Mortality of rainbow trout was significantly greater in softwater, with ionoregulatory failure being the main cause of death. Similar sodium and chloride plasma concentrations were observed in hardwater, indicating ionoregulation failure as the cause of death; however, the time to death was longer.

Calcium reduced the impact of acidification by binding to at least two sites on the gill epithelium involved with ionoregulation (McDonald et al., 1983). Firstly, ca2+ binds to the tight junctions between cells within the gill epithelium. The result was a reduced rate of paracellular ion efflux, and increased rate of paracellular-ion-efflux recovery.

The second binding site for calcium is to the sodium-active-transport channels in the apical membrane. Calcium is thought to stabilize the epithelial membrane w ich is important to maintain the sodium active transport mechanism. The influx of Na^+ was significantly greater (almost double; McDonald et al. 1983) in hardwater as compared to softer waters.

External calcium concentrations were important for fish growth. Reduction of external calcium independently of pH caused ionic disturbances. Wood and McDonald (1982) noted that· fish grown at neutral pH and low calcium concentrations had lower growth rates and ionic plasma concentrations. Acute reduction of both Ca^{2+} and pH in brown trout increased the sodium efflux substantially more than that caused by pH reduction alone (McWilliams, 1982). The aggravated plasma ion losses which occurred in acidified softwater accounted for the increased mortality observed for most freshwater fish (McDonald, 1983).

4.7.6 *Summary of pH Toxic Syndrome for Freshwater Fish*

Ionoregulatory disturbance is the main toxic effect of chronic and acute exposure to acidic conditions (Audet and Wood, 1988). The effects of H^+ ions on the intracellular and extracellular compartments of a fish are summarized in Figure 9. Wood and McDonald (1982) concluded that the most important effects of acidification on freshwater fish were:

1) passive acid (H^+) entry along a concentration gradient,
2) inhibition of the active transport of Na^+/H^+ or NH_4^+ across the gill epithelium,
3) elevation of the passive permeability of the branchial epithelium to Na^+, and Cl^-.

Hydrogen ions entering the extracellular fluid (ECF) is initially buffered by protein (mainly haemoglobin) and HCO_3^-. The buffering by carbonates forms CO_2 gas that is easily diffused out of the gills. After the initial exposure of the fish to low pH, H^+ ions penetrate the intracellular fluid· (ICF) resulting in intracellular acidosis. Hydrogen ions may also enter bone where it is buffered by $CaCO_3$ and Ca3(PO_4)2 (Figure 9).

Cations (Ca and K) from the ECF move into the ICF and are lost through the gills and to a lesser extent through the kidney. The result is a depletion of salts from the entire body which, unless reversed, will result in death.

Physiological responses to the reduced salt content include the ability to increase the renal acid excretion, recovery of the branchial active transport of Na^+ (in chronic exposure), and the reduction of the permeability of the gill epithelium to Na^+ and Cl^-. Sodium influx does not fully recover in acute exposure, resulting in progressive sodium loss and mortality.

Low calcium concentrations modifies the toxic syndrome by three factors:

1) a general increase in branchial permeability which exacerbates the ionoregulatory disturbance,
2) a proportionately greater net loss of chloride ions through the gills, resulting in a reduction in the H+ uptake and acid-base disturbance,
3) slower recovery of the Na+ active transport mechanism and the paracellular efflux of Na+ and Cl^- through the gill epithelium.

Although the effects of aluminum on freshwater organisms are outside the scope of this report, it is important to mention the similar action of hydrogen ions and monomeric aluminum on the gills of fish. Aluminum accumulates in the gill epithelium and causes increased ion efflux and mucus production (Audet and Wood, 1989; Butcher, 1988). The result is an additive effect of pH and aluminum.

4.7.7 *Effects on Reproduction*

The elimination of freshwater fish species from a body of water was usually attributed to reproductive failure and the elimination of new age classes from the population (Beamish, 1976; Mills et al., 1987). The following sections describe the effects of low pH on egg development (oogenesis), fertilization, embryonic growth, and hatching success.

4.7.7.1 *Oogenesis*

Reproductive failure in oviparous fish exposed to acid stress during oocyte (egg) formation and development generally occurs from an inability to release all or part of the mature eggs, or from physiological changes preventing the production and maturation of eggs (Beamish, 1976; Peterson et al., 1982).

Extensive reductions in quality and numbers of eggs with decreasing pH have been documented when maturing females were exposed to low pH (Mount, 1973; Craig and Baksi, 1977; Ruby et al. 1977; Lee and Gerking, 1980). Fathead minnow egg production decreased by 50% when the adults were exposed to pH 6 (control =6.8) (Craig and Baksi, 1977), while desert pupfish egg production fell by 60% at pH 5 (control =8.3) (Lee and Gerking, 1980). The few eggs of the desert pupfish produced at pH 5 had a reduced yolk size with opaque areas. Lake herring from an acidified lake (pH 4.5-4.7) had portions of ovaries with no developing eggs, and the eggs that developed had reduced yolk size or no yolk (Beamish, 1974).

Ruby et al., (1977) observed that flagfish exposed to pH 6 had initially higher oocyte concentrations, but a high proportion of the oocytes underwent resorption and degeneration as they developed. Mature oocyte production was 80% and 92% lower than the control (pH 6.7) in females exposed to pH 6 and 4.5, respectively.

Peterson et al. (1982) concluded that the low production of small mature eggs when exposed to low pH was caused by restriction in the synthesis and transportation of yolk proteins. Low serum calcium and hormone concentrations, which are vital to the transportation and deposition of yolk proteins within the oocyte, have been observed in fish exposed to the acid conditions (Beamish et al., 1975; Beamish, 1976; Peterson et al.,1982).

4.7.7.2 *Egg Fertilization*

The volume of sperm and length of time that sperm remain motile is very critical to the success of egg fertilization. Ruby and Craig (1978) observed that the production of mature sperm was reduced in the flagfish *(Jordanella floridae)* below pH 6. The number of sperm produced decreased with decreasing pH. Since most fish eggs must be fertilized within 30 to 90 seconds after leaving the female, the sooner the sperm can reach the egg the greater the chances of reproductive success.

The pH of the milt has been measured between 8 and 8.5, and the activity of sperm decreased with decreasing pH (Mohr and Chalanchuk, 1985; Peterson et al., 1982). Kennedy (1980) observed reduced egg and embryo viability in lake trout captured from Lake 223 (pH 5.8), yet fertilization of the eggs was not affected. He concluded that reproductive failure of the lake trout population was the result of reduced egg and embryonic viability, not reduced fertilization success.

Mohr and Chalanchuk (1985) observed reduced sperm motility in white sucker sperm with decreasing pH. They concluded, however, that the motility of the sperm at pH 5 was sufficient to fertilize viable embryos.

4.7.7.3 *Embryonic Growth and Development*

Investigations regarding the influence of low pH on the growth of fish generally concluded that exposure to low pH will reduce the rate of egg growth or cause abnormal development (teratogenesis) (Kennedy, 1980; Peterson et al., 1982). The effect of pH on the growth of fish was apparently not related to efficiency of food utilization, but to physiological stress imposed by

ionic imbalance within the embryo. Energy normally used for growth is redirected to compensate for body sodium loss and altered metabolic processes within the blood and various organ systems (Peterson et al., 1982; Fromm, 1980).

Kennedy (1980) observed complete reproductive failure of fertilized lake trout eggs collected from adults caught from Lake 223 (pH 5.8). Egg volume was 23% lower compared to the control (Lake 224, pH 6.8), and the incidence of embryonic mortalities and abnormalities was 78% and 28% higher, respectively, than embryos from the control. Typically, the deformed embryos developed caudal segments that became detached from the embryo. After 60 days, 100% of the lake trout embryos were either dead or abnormal from Lake 223, as compared to 7.1% from the control (Lake 224).

Viable eggs from lake trout collected from Lake 223 (pH 5.8) and 224 (pH 6.8) were incubated together in near-neutral waters (Kennedy, 1980). After 31 days, only 24% of the eggs from the Lake 223 fish survived to the eyed stage, while 75% of the eggs from the control lake survived.

The effects of low pH on the developing embryos of Atlantic salmon were similar, but the impact threshold was much lower. The lower lethal level for Atlantic salmon was pH 3.6.during the early developmental stages, pH 3.1 prior to hatching, and pH 4 for newly hatched alevins (Daye and Garside, 1977). In a similar experiment, Daye and Garside (1979) did not observe changes in the rate of embryonic development of Atlantic salmon at pH ≥4 or external deformities in alevins at pH ≥4.3. In contrast they did observe internal deformities in the integument, gill, and vascular system in Atlantic salmon alevins exposed to pH 5 and deformities in the brain, kidney, spleen, and optic retina at pH 4.5.

The effect of low pH on developing embryos is an important component of reproductive failure of a species, and the pH at which reproductive failure occurs is species specific. Based on the work of Daye and Garside, most authors agree that the early embryo and the alevin stages are the most susceptible to low pH.

4.7.7.4 *Hatching Success.*

Successful hatching of embryos requires a softening of the egg capsule, the release of a hatching enzyme, and the physical rupturing of the outer layer by the emerging alevin (Peterson et al., 1980). The softening process can take place as much a one month prior to hatching, while the hatching enzyme is released a day or two prior to hatching. The pH of the perivitelline fluid in which the hatching enzymes are released does not differ by more than 0.5 pH units from the ambient pH. At pH 5, the activity of the hatching enzyme was less than 10% of the norm (Peterson et al., 1980).

The effect of low pH on the hatching success of developed embryos has been documented by Daye and Garside (1977; 1979), Johansson et al. (1977), and Peterson et al., (1980). At pH 4.1, approximately 70% of Atlantic salmon and 17% of the brown trout alevins died as the result of incomplete hatching. Peterson et al., (1980) observed similar results with Atlantic salmon, attributing the reduced hatching success to the-inhibition of the hatching enzyme, chorinase.

Like most other impacts of low pH, the threshold was species specific; however, the typical observation was that at low pH the alevin remained partially encapsulated by the outer egg layer, resulting in increased mortality.

4.7.7.5 *Critical pH for Reproduction*

Beamish (1976) introduced the term “critical pH” to describe the point at which reproduction of a species was unsuccessful. Because the critical pH varies from species to species, the critical pH for a water body would be based on the species most sensitive to low pH.

The critical pH for fish located in the La Cloche Mountains (Ontario, Canada) was species specific, and ranged between 4.5 and 6 (Table 3; Beamish, 1976). Failure to reproduce was indicated by the inability of the females to release ova (unfertilized eggs). After the normal spawning period, the ovaries became flaccid and watery, and the fish appeared to resorb the tissue.

Whole-lake acidification experiments at ELA supported the hypothesis that fish extinction from freshwater systems exposed to acid deposition was due to reproductive failure. Sulphuric acid was added to Lake 223 over 6 years to reduce the pH from 6.7 to 5.1. The fathead minnow was the most sensitive of the fish species with a critical pH of 5.8, while the remaining species (lake trout and white sucker) experienced reproductive failure between pH 5.4 and 5.1 (Table 3; Mills et al., 1987). The pH at which the white sucker and lake trout experienced reproductive failure in the La Cloche Mountains (Beamish, 1976) and Lake 223 (Mills et al., 1987) were similar despite differences in water quality and fish community structures (Table 3).

Table 3. Summary of the Effects of pH on Fish Reproduction and Development

Species	Life Stage	Result	Reference
Atlantic Salmon	embryo	pH 3.1: LL50 prior to hatching	Daye and Garside, 1977
	embryo	pH 3.5: direct mortality	Carrick, 1979
	embryo	pH 3.6: LL50 for embryos in early cleavage	Daye and Garside, 1977
	embryo	pH 3.7: LL50; development not retarded	Daye and Garside, 1979

Species	Life Stage	Result	Reference
	embryo	pH4: hatching suppressed	Peterson et al., 1980
	embryo	pH <4.4: increased mortality at hatching stage	Johansson et al., 1977
	embryo	pH ≥4.5: no effect	Carrick, 1979
	embryo	pH <4.8: increased incidence of partial hatching	Johansson et al., 1977
	embryo	pH ≤5: increased abnormal development	Daye and Garside, 1980
	embryo	pH ≤5.5: reduced rate of embryo development	Peterson et al., 1980
	embryo	pH ≤5.5: hatching delayed and increased mortality	Peterson et al., 1980
	alevin	pH 4: LL50	Daye and Garside, 1977
	alevin	pH 4.3: LL50; no increase in deformities	Daye and Garside, 1979
	alevin	pH ≤4.5: increased injury to brain, kidney, optics	Daye and Garside, 1980
	alevin	pH 5-5.3: increased mortality	Johansson et al., 1977
	alevin	pH ≤5 increased injury to integument, and gills	Daye and Garside, 1980
Brook Trout	embryo	pH ≤5 significant decrease in viable eggs	Menendez,1976
	embryo	pH ≤6.5: reduced embryo hatchability	Menendez, 1976
	alevin	pH ≤6.5: reduced growth	Menendez,1976
Brown Bullhead	embryo	pH 4.7-5.2: reproductive failure	Beamish, 1976
Brown Trout	embryo	pH 3.5: direct mortality	Carrick, 1979
	embryo	pH ≤4.4: increased incidence of partial hatching	Johansson et al., 1977
	embryo	pH ≤4.4: increased mortality at hatching stage	Johansson et al., 1977
	yearlings	pH ≥5: growth similar	Jacobsen, 1977
Burbot	embryo	pH 5.5-6: reproductive failure	Beamish, 1976
Fathead Minnow	oogenesis	pH 6: 50% reduction in egg production	Craig and Baksi, 1977
	oogenesis	pH ≤6.6: reduced egg production	Mount, 1973
	embryo	pH 5.8: reproductive failure	Mills et al., 1987
	embryo	pH 5.9: eggs deformed and reduced hatchability	Mount, 1973
	alevin	pH 5.2: increased deformities	Beamish, 1974
Lake Chub	embryo	pH 4.5-4.7: reproductive failure	Beamish, 1976
Lake Herring	oogenesis	pH 4.5-4.7: reduced yolk and egg production	Beamish, 1974
	embryo	pH 4.5-4.7: reproductive failure	Beamish, 1976
Lake Trout	embryo	pH ≤5.8: increased teratogenesis	Kennedy, 1980
	embryo	pH 5.2-5.5: reproductive failure	Beamish, 1976
	embryo	pH 5.4: reproductive failure	Mills et al., 1987

Species	Life Stage	Result	Reference
Northern Pike	embryo	pH 4.7-5.2: reproductive failure	Beamish, 1974
	alevin	pH ≤5: reduced growth	Johansson and Kihlstrom, 1975
Smallmouth Bass	embryo	pH 5.5-6: reproductive failure	Beamish, 1976
Rainbow Trout	oogenesis	pH 5.5: reduced viability	Weiner et al., 1986
	embryo	pH 5.5 and temp. =5°C 96 h-LC50	Kwain, 1975
	embryo	pH 4.75 and temp. =10°C 96 h-LC50	Kwain, 1975
	alevin	pH 4 and temp. =5°C 96 h-LCS0	Kwain, 1975
	alevin	pH 4.1 and temp. =10°C 96h-LC50	Kwain, 1975
	alevin	pH 4.2 and temp. =15°C 96 h-LC50	Kwain, 1975
	alevin	pH 4.5 and temp. =20°C 96 h-LC50	Kwain, 1975
	yearling	pH 3.4 and temp. =10°C 96h-LC50	Kwain, 1975
Troutperch	embryo	pH 5.2-5.5: reproductive failure	Beamish, 1976
Walleye	embryo	pH 5.5-6: reproductive failure	Beamish, 1976
White Sucker	embryo	pH 4.7-5.2: reproductive failure	Beamish, 1976
	embryo	pH 5.1: reproductive failure	Mills et al., 1987
	embryo	pH <5: decreased hatchability	Trojnar, 1977a
	larvae	pH 5.3: reduction in swim-up fry	Trojnar, 1977a
Yellow Perch	embryo	pH 4.5-4.7: reproductive failure	Beamish, 1976

There were three important observations from the ELA acidification experiments at Lake 223 (Mills et al., 1987). Firstly, the rate of abundance decline for all Lake 223 fish species was inversely related to the number of age groups in each population. The longer-lived species such as lake trout and white suckers declined more slowly following recruitment failure. Secondly, the threshold pH that resulted in reproductive failure was species specific. Thirdly, the growth and condition factor of the piscivorous lake trout declined dramatically due to the recruitment failure and decline of its prey species (fathead minnow and pearl dace). Although reproductive failure for lake trout occurred at pH 5.1, extinction of prey species would in itself result in the extinction of the piscivorous species.

Acid-tolerant species exposed to pH levels above their critical pH can benefit from the acidification process. In Sweden, the roach *(Rutilus rutilus)* and the European perch *(Perca fluviatilis)* were larger for given age classes in lakes with a pH 4-4.5 than those from less acidic lakes (pH 6.3-6.8) (Almer et al., 1978).

Artificial acidification of Lake 223 at ELA resulted in the reproductive failure of the fathead minnow at pH 5.6 and a rapid increase in a reproducing population of pearl dace (critical pH =5.1) due to reduced competition for food (Mills et al., 1987).

Acid-tolerant species found in British Columbia, such as the pearl dace, yellow perch and brown trout, could benefit from the acidification of its habitat (Howells et al., 1983). Acidification of lakes within the La Cloche Mountains (Ontario) resulted in fewer numbers of yellow perch, faster growth rates of the early age classes, and slower growth rates in older age groups. Brown trout in acidic Norwegian lakes were not obviously larger, but were reported to have fuller stomachs and to be in better condition. Reduced competition for food, less predation pressures, and lower population densities have been proposed as explanations for the success of these species at acidic pH levels.

Of the 64 species of freshwater fish found in British Columbia (Appendix 1), 16 have data on critical pH (Table 3). The critical pH selected for each of the 16 species listed in Table 4, was the highest pH at which reproductive failure, reduced oogenesis, or increased abnormal growth was observed. Determination of a critical pH for rainbow trout was difficult, because only one paper has been published (Weiner et al., 1986), and the chemistry of the water used in the experiment was not representative of freshwaters found in British Columbia. Although pH 5.5 was used as the critical pH for rainbow trout in Table 4, the limitations of Weiner's results to British Columbia must be noted.

Table 4. Critical pH for Reproduction of 16 Fish Species Found in British Columbia

Species	Critical pH	Reference
Atlantic Salmon	5.5	Peterson et al., 1980
Brook Trout	6.5	Menendez, 1976
Brown Bullhead	5.2	Beamish, 1976
Brown Trout	4.4	Johansson et al., 1977
Burbot	6.0	Beamish, 1976
Fathead Minnow	6.0	Craig and Baksi, 1977
Lake Chub	4.7	Beamish, 1976
Lake Herring	4.7	Beamish, 1976
Lake Trout	5.8	Kennedy, 1980
Northern Pike	5.2	Beamish, 1974
Rainbow Trout	5.5	Weiner et al., 1986
Smallmouth Bass	6.0	Beamish, 1976
Troutperch	5.5	Beamish, 1976
Walleye	6.0	Beamish, 1976
White Sucker	5.2	Beamish, 1976
Yellow Perch	4.7	Beamish, 1976

4.7.8 *Effects of Acidification on Behaviour*

Behaviour is important in feeding, reproduction, migration, pollution avoidance, and inter and intra-species competition. The avoidance of low pH may be of great importance in avoiding chronically and acutely toxic pH associated with freshet or storm events. Some behaviour changes may in fact constitute adaptive mechanisms to preventing further stress from acid exposure (e.g., reduced activity because exercise exacerbates acid toxicity) (Jones et al., 1977). In addition, chronic exposure to low pH may alter feeding or olfactory responses, resulting in reduced growth, reproduction, or long-term survival.

MacFarlane and Livingston (1983) observed that pH 5 was sufficiently stressful to make the Gulf killifish *(Fundulus grandis)* hyperactive and disrupt their diurnal activity. Jones et al., (1985a) noted that Arctic char avoided plumes of water with a pH of 5.5 or less. Below pH 5, the Arctic char had sharply reduced locomotor behaviour (activity) and chemoreceptive behaviour to food extract (Jones et al., 1985b). The char did not show any sign of compensatory adaptation to pH <5 over a two-week period.

In a more sophisticated experiment, Jones et al., (1987) observed that: 1) the activity of Arctic char was negatively correlated with plasma protein and glucose concentrations; and 2) the attraction to food extract was negatively correlated with haematocrit, glucose, and cortisol levels, and positively correlated with plasma Cl^- concentrations. After the fish were returned to control pH concentrations, blood parameters and behaviour returned to normal.

In contrast; the fathead minnow did not elicit a feeding response below pH 6.5 (Jones et al., 1985b), indicating that the effects of pH on feeding behaviour was species specific and that acid-sensitive species like the fathead minnow are disturbed near neutral pH conditions.

Klaprat et al. (1988) showed a reduced olfactory nerve response to the amino acid L-serine in rainbow trout exposed to pH 4.7 (20 mg Ca/L). Increased mucus production around the olfactory organ occurred following exposure to pH 4.7, but damage to the olfactory epithelium was not detected.

Spawning female brook trout actively avoided interstitial upwelling water with a pH < 5 (Johnson and Webster, 1977). The strong preference of the brook trout for breeding sites with neutral or alkaline upwelling water would assure a suitable environment for the egg and larval stages. In a similar experiment, emergent brook trout actively avoided water with a pH <5

(Ca =l.3 mg/L; Gunn and Noakes, 1986). The avoidance of acidic conditions may delay the emergence of brook trout fry from neutral or alkaline interstitial waters to streams experiencing low pH associated with freshet or snow melt.

Conclusions:

The pH at which behaviour was affected was at or below the critical pH for that species.

For example, the fathead minnow experienced reduced feeding response below pH 6.5 (Jones et al., 1985b), while its critical pH was 6 (Table 4). Rainbow trout and female brook trout had behaviour modifications at pH 4.7 and <5.0, respectively. The critical pH for both species was higher at 5.5 and 6.5, respectively (Table 4). It appears from the few studies that are available, that behavioural modifications will not occur above the critical pH for that species.

4.7.9 *Adaptation of Fish to Low pH*

4.7.9.1 *Morphological Adaptation to Low pH*

The key component to the survival of a species in low pH water is ionoregulation. Several fish species have become adapted to low pH conditions (e.g., mudminnows *(Umbra),* and perch *(Perca)).* For example, at pH 4.5 the mudminnow *(Umbra pygmaea)* has stimulated sodium influx, and no sodium efflux (Flik et al., 1987). The mudminnow has adapted to low pH through well-developed chloride cells (site of sodium influx), expansion of the apical membrane area (location of chloride cells), a relatively small surface of the gill lamellae (to reduce ion loss), low locomotor activity, and a high concentration of haemoglobin (Dederen et al., 1987). The mudminnow is so well adapted to low pH conditions that it grows faster at pH 4.5 than at pH 7 (Flik et al.,1987).

The mechanism that prevents sodium efflux in the acid-tolerant yellow perch is fundamentally different than the more acid- sensitive trout or shiners (Freda and McDonald, 1988). Increased sodium efflux was observed in the yellow perch when exposed to pH <3.5; however, ambient calcium concentrations did not have a protective effect on efflux. Freda and McDonald (1988) concluded that sodium efflux in yellow perch was calcium independent which is in sharp contrast to trout and shiners. In addition to a difference in branchial permeability, the sites for sodium transport in the yellow perch have a high affinity for sodium allowing for increased sodium influx at pH 4 than at pH 7.

Interspecies differences in acid tolerance are related to differences in the ionoregulation mechanism for that species. When exposed to acidic conditions, acid-intolerant species undergo an initial shock phase where influx is inhibited and efflux is rapid. The recovery phase that follows consists of partial or complete recovery of the efflux and a slower and less complete recovery of sodium influx.

Increasing fish sensitivity to low pH was characterized by greater losses of ions from the body, more complete inhibition of sodium influx, greater sodium efflux, and shorter survival times (Freda and McDonald, 1988). The inhibition of sodium uptake reduces plasma and whole-body ion concentrations for two reasons: 1) the threshold for the inhibition of sodium influx occurs at a higher pH than the change in gill permeability (efflux); and 2) after prolonged exposure efflux may be reduced to normal levels, whereas influx only partially recovers (Freda and McDonald, 1988).

Salmonids are moderately sensitive to acidic conditions, while shiners are very sensitive. The lower calcium binding capacity and sodium affinity of the shiner's gills caused elevated net sodium loss, and hence extreme sensitivity to acidic conditions (Freda and McDonald, 1988).

4.7.9.2 *Acclimation to Low pH*

Lloyd and Jordan (1964) postulated that the exposure of trout to chronically toxic pH may provide protection and increased survival to acutely toxic pHs that follow precipitation events, snow melt, or pulses of acid mine drainage. They were unable to show any greater resistance when rainbow trout were exposed to pH 6.5 for five days and then exposed to pH 3 and 3.8. In contrast, Trojnar (1977b) incubated brook trout eggs at pH 4.6, 5, 5.6, and 8, and then exposed the swim-up fry to pH 4, 5, 5.75, and 7.9. Decreased mortality was observed when the fry incubated at low pH (< 5.6) were exposed to pH 4. The differential mortality during egg development indicated an acclimation effect.

In similar experiments, Daye (1980) attempted unsuccessfully to acclimate Atlantic salmon and rainbow trout embryos and alevins to low pH. Embryos and alevins were exposed to pH 5, 5.5, 6, and 6.8 for as long as 6 months. The LL50 (Lethal Level) for control and acclimated fish did not change regardless of prior exposure.

Falk and Dunson (1977) exposed brook trout fry (50-80 g) to either pH 5 or 5.8 for 2 or 24 hours, and then to pH 3.15. Increased survival times (albeit small and statistically insignificant in six of the nine tests) were observed in all the tests with fish pre-exposed to the lower pH. Although these results suggest some acclimation of brook trout fry, the results were contradicted by the observation that fry allowed to recover from the sublethal pre-exposure of 2 hours did not survive as long as naive trout when exposed to acutely toxic pH.

The physiological recovery of ionic fluxes in fish after low pH exposure is even less clear. McWilliams (1980a) exposed brown trout to pH 6 for three weeks and observed complete recovery of ionic fluxes. When the pH was lowered to 4, the rates of Na^+ efflux and influx were less in the pre-exposed fish than naive fish. McDonald (1983) noted that although the acclimated brown trout in McWilliams' experiment were able to recover physiologically from low pH (5.2), a change in the lethal pH did not occur.

Unlike the brown trout, physiological studies on brook trout exposed to pH 5.2 showed that they did not recover their rates of sodium uptake after 10 days (Booth et al., 1988) or 10 weeks (McDonald and Milligan, 1988).

Audet and Wood (1988) observed decreased ability of adult rainbow trout to survive severe acid stress (pH=4) after 3 months of sublethal acid exposure (pH=4.8). The pre-exposed trout had elevated sodium plasma losses, plasma glucose concentrations, ammonia excretion, and red blood cell swelling. They concluded that long-term exposure significantly decreased the ability of rainbow trout to survive additional acid stress.

In summary, it appears that pre-exposure of trout to low pH conditions may or may not increase their survival time when exposed to lethal pH conditions, and physiological adaptation or. compensation to low pH conditions does not occur.

4.7.9.3 *Genetic Adaptation to Low pH*

Differences in the acid tolerance of brown and brook trout strains have been documented (Falk and Dunson, 1977; Swarts et al., 1978; Gjedrem; 1980; Robinson et al., 1976; and Rosseland and Skogheim, 1987). When the brook trout were exposed to pH 5.3 (Ca = 3.3 mg/L), the strain from a naturally acidic brook had slower net plasma chloride losses (sodium not measured), than a strain from a pristine non-acidic environment (Rosseland and Skogheim, 1987). A third strain of brown trout, from a genetic breeding program designed to increase resistance to acidic conditions, had a physiological response similar to the acid- tolerant strain. This indicated that increased resistance to acidic waters was genetically linked.

Gjedrem (1980) obtained brown trout brood stock from 250 locations in Norway to test their sensitivity to acidic conditions. He found significant variation in the death rate of eggs and alevins when incubated at pH 4.7 and 5.2. Crosses between acid-resistant and non-resistant strains improved the egg and alevin survival, indicating that selective breeding can significantly improve the acid tolerance of a species.

Robinson et al. (1976) conducted similar experiments and concluded that a program of selective breeding could produce a strain of Norwegian brook trout that would be resistant to a pH below 4.1.

4.7.10 *Effects of High pH*

Ammonia excretion across the gill epithelium is a complicated interaction of carbon dioxide, the carbonic anhydrase enzyme, pH, NH_3, and NH_4^+ (Randall and Wright, 1989). The majority of ammonia in blood is in the form of NH_4^+ (95-99%); however, the gill epithelium is quite impermeable to NH_4^+. Consequently, the majority of the ammonia excreted across the gill is in the form of NH_3.

Under normal conditions, the NH_3 diffuses through the gill epithelium into the mucus and boundary layers, along a concentration gradient, and is then converted to NH_4^+. The rate of the conversion decreases with increasing pH, and will not proceed if the pH is greater than 9.5. Because of the simultaneous excretion of carbon dioxide into these layers and the conversion of carbon dioxide to bicarbonate by the carbonic anhydrase enzyme, the mucus and boundary layers of the gill have a neutral or acidic pH ensuring a rapid conversion of NH_3 to NH_4^+. The rapid conversion is essential to maximize the NH3 concentration gradient across the gill, and maintain a constant excretion of ammonia.

High ambient pH (>9.0) can cause a disruption in the ammonia excretion mechanism across the gill epithelium by increasing the pH of the mucus and boundary layers. The result is a reduction in the concentration gradient of NH_3 across the gill epithelium, and a build-up of NH_4^+ in the blood and body tissues of the fish (Randall and Wright, 1989).

The ammonia excretion mechanism can also be disrupted by high concentrations of NH_3 in the ambient environment with a pH< 9.0 (Nordin, 1986). Because the proportion of NH_3 and NH_4^+ is pH dependent, a small increase pH in an environment with high $NH4^+$ concentrations can result in NH3 toxicity. See Nordin (1986) for complete discussion of ammonia toxicity where the pH is less than 9.5.

Because most fish are unable to form urea, or excrete significant quantities of ammonia through the kidney, the disruption of the ammonia excretion mechanism (pH > 9.5) will result in death. The exception is the Tilapia fish of Africa which has evolved a urea excretory system, and is able to survive in water with a pH exceeding 10 (Randall and Wright, 1989).

Rainbow trout were exposed to gradual and rapid increases in pH to determine the upper limit of pH exposure (Murray and Ziebell, 1984). The rainbow trout raised at pH 8 became acclimated to pH 9.8 when the pH was increased at a gradual rate (0.4-1.0 units per day). Above pH 9.8 the fish continued to feed, but their activity was reduced. Mortality was observed at pH 10.2.

Rainbow trout exposed to rapid increases in pH (pH increased every 15 minutes for 6 hours from 8 to 9.3 or 9.5) exhibited very different responses. When the pH was increased from 8 to 9.3 in 6 hours the trout had a temporary loss of appetite. An increase from pH 8 to 9.5 in 6 hours resulted in stress and approximately 50% mortality (Murray and Ziebell, 1984).

The impact of high pH on the excretion of ammonia in fish suggests that there is an upper pH tolerance. Although differences between species are expected, the upper pH limit appears to be between 9 and 9.5.

4.7.11 *Effects of Carbon Dioxide*

The bicarbonate ion is the most abundant anion in most freshwater systems. The addition of hydrogen ions to a bicarbonate solution forms carbonic acid and carbon dioxide. The amount of CO_2 produced is a function of the bicarbonate concentration and the number of hydrogen ions added to the solution. Supersaturated concentrations of carbon dioxide will be vented to the atmosphere over time. However, the rate of venting will be dependent on the percent . supersaturation, air entrainment, mixing, etc. Lloyd and Jordan (1964) showed that the free carbon dioxide content of fish blood ($PaCO_2$) increased with the PCO_2 content of the water. In most teleost fish, $PaCO_2$ concentrations remained approximately 2 mm Hg above the ambient concentrations (Janseen and Randall, 1975). Consequently, an increase in ambient PCO_2 concentrations will result in a proportional increase in $PaCO_2$ (hypercapnia). A portion of the $PaCO_2$ will form carbonic acid and bicarbonate, releasing H^+ ions into the blood (acidosis). Janseen and Randall (1975) observed a drop in plasma pH (pHa) from 7.93 to 7.39 in rainbow trout exposed to 5 mm $HgCO_2$ for 5 minutes. Increased arterial bicarbonate concentrations ($[HCO_{3-}]a$), and a return to pre-hypercapnic pHa was observed within 72 hours. In a similar experiment, Eddy (1976) subjected rainbow trout to 10 mm Hg, and observed a similar drop in pHa and recovery starting within 8 hours. For fish the recovery from acidosis caused by hypercapnia involves an increase in arterial HCO_{3-} concentrations (Lloyd and Jordan, 1964).

Lloyd and Jordan (1964) exposed rainbow trout to 50 mg CO2/L and pH 7 and 4.5. At pH 7 there were no mortalities. However, mortality was observed when the pH of the water was lowered to 4.5. Under these severe conditions, the trout were unable to maintain arterial bicarbonate concentrations and overcome acidosis. Lloyd and Jordan (1964) also showed that the acute toxicity level for rainbow trout increased with high concentrations of PCO_2. Normally, pH 5.6 would not be toxic to rainbow trout; however, elevation of free CO_2 to 20 mg/L caused mortality to 50 percent of rainbow trout after 15 days. The authors concluded that, below pH 6, 20 mg/L free CO_2 may cause mortality in rainbow trout after 3 months.

Neville (1979) showed that mild hypercapnia (PCO_2 =4:5 mm Hg) at pH 4 was less toxic to fish than pH 4 water with normal PCO_2 concentrations (< 1.5 mm Hg). The explanation is that mild hypercapnia increased the bicarbonate concentrations in the test solutions and the pH adjacent to the fish gills. Neville (pers. comm.) noted this observation was only valid under mild hypercapnia conditions, and the acidosis and toxicity observed by Lloyd and Jordan (1964) with elevated CO_2 concentrations (10-50 mm Hg) were valid.

Alderdice and Wickett (1958) experimented with the effects of free carbon dioxide on chum eggs. Prior to the development of blood pigment and a functional circulatory system, salmon eggs depend on diffusion of respiratory gases across the egg capsule. High ambient CO_2 levels (125 mg/L) may inhibit diffusion of gases causing deformities or mortality. Mortality of the chum eggs appeared to be caused by the prolonged inhibition of oxygen uptake and a deceleration of metabolic rates.

Normally, CO_2 tensions in natural waters are low (<1.5 mg/L); however, they can approach 10 mg/L in salmon rearing ponds and hatcheries (Sigma, 1979). Because hypercapnia causes a drop in arterial pH, a criterion for CO_2 in water must be considered, particularly downstream from an alkaline discharge into an acidic environment or vice versa.

EPA (1973) noted that most fish species were able to extract sufficient oxygen for survival when carbon dioxide levels approached 60 mg/L. The EPA criteria did not consider the effects of hypercapnia on fish or the interaction of sublethal concentrations of H^+ and CO_2. Lloyd and Jordan (1964) observed as much as 50% mortality at pH 5.6 and 20 mg/L free CO_2. They predicted mortality of rainbow trout would occur at pH 6 and 50 mg/L free CO_2 after three months. No mortalities were observed at pH 7 and 50 mg CO_2/L for the same time period. The work of Neville (1979) indicates that mild hypercapnia may decrease pH toxicity under some circumstances, but her results do not contradict Lloyd and Jordan (1964). The British Columbia criteria for pH should take into account the free CO_2 concentration limits recommended below:

pH	CO_2 Concentration
<6	<10 mg/L (230 µmol/L)
6-6.5	10 - 20 mg/L (230-460 µmol/L)
>6.5	60 mg/L (1360 µmol/L)

4.8 Amphibians

Nineteen species of amphibians are known to reside in British Columbia (Table 5). Seventeen of the 19 species deposit eggs and have larval stages in freshwater; the ensatina and clouded salamanders do not have any life stages that utilize the aquatic environment (Orchard, 1984).

Table 5. Amphibians Found in British Columbia (from Orchard. 1984)

Salamanders and Newts	
Ambystoma gracile	Northwestern Salamander
Ambystoma macrodactylum	Long-toed Salamander
Ambystoma tigrinum	Tiger Salamander
Aneides ferreus	Clouded Salamander
Dicamptodon ensatus	Pacific Giant Salamander
Ensatina eschscholtzi	Ensatina Salamander
Plethodon vehiculum	Western Redback Salamander
Taricha granulosa	Roughskin Newt
Frogs and Toads	
Ascaphus truei	Tailed Frog
Bufo boreas	Western Toad
Hyla regilla	Pacific Treefrog
Pseudacris triseriata	Striped Chorus Frog
Rana aurora	Red-legged Frog

Rana catesbeiana	American Bullfrog
Rana clamitans	Green Frog
Rana pipiens	Leopard Frog
Rana pretiosa	Spotted Frog
Rana sylvatica	Wood Frog
Scaphiopus intermontanus	Great Basin Spadefoot Toad

The majority of studies on amphibians have focused on the effect of low pH on embryonic development because it is the most sensitive life stage. The critical pH in Table 6 was described by Freda (1986) as the pH at which hatching success decreased below levels normally occurring in neutral conditions, while Pierce (1985) used 50% embryo mortality as a criterion for critical pH.

Table 6. Lethal and Critical pH for Amphibians Found in British Columbia

Species	Lethal pH	Critical pH	Reference
Western Toad	----	4.0	Freda, 1986
Striped Chorus Frog	4.2	----	Freda, 1986
American Bullfrog	3.9	4.3	Gosner and Black, 1957
Green Frog	3.8	3.8-4.1	Freda, 1986
	3.7-3.8	4.1	Gosner and Black, 1957
Leopard Frog	3.7	4.1	Gosner and Black, 1957
	4.0-4.5	4.5-<5.8*	Freda and Dunson, 1985
Wood Frog	3.5	3.9	Gosner and Black, 1957
	3.5-4.0	4.0.-4.5	Freda and Dunson, 1985

*The calcium content of this study was 1 mg/L, a condition not expected for leopard frog habitat in British Columbia.

Amphibian embryos exposed to lethal pH displayed a mottled appearance of the surface layer and a shrunken rubbery texture of the egg jelly and membranes. The majority of embryos exposed to a pH above the lethal pH, but below the critical pH, experienced the “curling effect.” Through the activity of the hatching enzyme the vitelline membrane normally lifts off the embryo, creating the perivitelline space. Below the critical pH, the perivitelline space never enlarges, forcing the elongating embryo to fold over itself. The curling effect is thought to be caused by the deactivation of the hatching enzyme by hydrogen ions.

The hatching enzyme also facilitates the rupture of the vitelline membrane at hatching. Curled embryos that do manage to hatch often have curved spines, and no chance of survival. Other less commonly observed abnormalities induced by low pH include swelling of the thoracic region, stunted gills, failure to retract the yolk plug, and deformation of the posterior trunk.

Amphibians as a group appear to be relatively tolerant of low pH. Most species have a lethal pH ≤4 (Pierce, 1985); however, as with most other aquatic organisms, low pH impacts the egg and larval stages resulting in reproductive failure (Freda, 1986). The critical pH for the 5 endemic species listed in Table 6 is less than pH 4.5. The only exception was the experiment with the leopard frog at different calcium concentrations by Freda and Dunson (1985). The critical pH with the calcium concentration of 1 mg/L ranged between pH

4.5 (90% mortality) and 5.8 (0% mortality). while the critical pH at 10 mg Ca/L ranged between 4 and 4.5. The leopard frog is typically found in the interior of B.C. (Orchard, 1984), while most of the lakes in British Columbia with a calcium concentration less than 1 mg Ca/L are located on or near the coast (Swain, 1987). Consequently, the leopard frog is not expected to be found in water with low calcium concentrations (<1 mg/L). As a result, the high critical pH (4.5-<5.8) for the leopard frog at 1 mg Ca/L should not be considered in the British Columbia pH criteria.

4.9 Summary

The effects of pH on aquatic life range from impairment of reproduction to direct toxicity. Typically, the pH threshold that will impact reproduction (critical pH) is higher than the pH that will cause direct toxicity to an individual organism. Changes in community structure are simply changes in the reproductive success of species within a changing environment and the dominance of a different species better adapted the new environmental conditions. The effects of low and high pH on the aquatic community are summarized in Figure 10.

Bacteria are important in fresh water systems as a food source, the recycling of nutrients, the decomposition of organic matter. and the generation of alkalinity through denitrification or sulphate reduction. Kelly et al., (1984) observed that the decomposition of newly sedimented material decreased below pH 5.3, while the decomposition rates of residual carbon were unaffected at pH 4.

The phytoplankton community was strongly affected by pH. At high pH (> 8), the dominance of the limnetic phytoplankton community by cyanobacteria has been linked to high nutrient conditions and low carbon dioxide concentrations. Cyanobacteria can cause taste and odours, clog filters, or form aesthetically unpleasant surface scums.

Under acidic conditions, the effects of acidification on the phytoplankton community has been well documented. Kelso et al., (1986) used discriminant analysis to determine that a large portion of the variation in the phytoplankton community between lakes in eastern Canada was explained by the lake's elevation, location, and chloride, sulphate, alkalinity, and magnesium

concentrations. No single variable dominated the discriminant analysis, and pH was determined not to influence the phytoplankton community of a geographic area.

Undesirable algal species can dominate the algal community under low pH conditions. The taste and odour causing alga, *Chrysochromulina breviturrita* occurred typically in low alkalinity lakes with a pH< 6.9, and the filamentous alga *Mougeotia sp.* (elephant snot) caused aesthetic problems in lakes with a pH < 5.6.

Decreased species diversity was observed in the phytoplankton community when the pH was lowered below pH 5.6. Despite a change in community structure, phytoplankton biomass and productivity were not affected adversely.

The response of the zooplankton community to acidic conditions was similar. Decreased community complexity was evident with decreased pH. Below pH 5, many species were eliminated and the acid-tolerant species became progressively rarer. Whole-lake acidification experiments showed that the zooplankton biomass was controlled by the presence of small fish, and that the zooplankton biomass increased when the small fish were eliminated (by reproductive failure) from the lake.

Crayfish species were either acid-tolerant or acid-intolerant. Acid-tolerant species have been found in water with a pH as low as 4.7. while acid-intolerant species experienced reproductive failure between pH 5.6 and 6.1. Low pH also reduced the calcium uptake during molting of the crayfish which produced a soft exoskeleton. The soft exoskeleton resulted in a reduction in annual survival rate of the adult crayfish in Lake 223 through the increased loss of limbs, cannibalism, predation by fish, and parasitism by a fungus.

Insects were also influenced by low pH conditions. Although insects have a high toxicity tolerance (pH< 5.5), reproductive failure (measured as reduced emergence) and pH avoidance would be the primary factors governing the distribution of aquatic insects. Of the insects tested, the stonefly *Isogenus frontalis* had the highest critical pH (6.6); however, this sensitive species has not been recorded in British Columbia.

The rapid decrease in the pH (5.6 to 4) in a stream resulted in a massive increase in drift during the first day of acidification. Although the pH was not toxic, the avoidance of the low pH resulted in the rapid depopulation of the stream community.

The literature for freshwater molluscs is limited. Surveys suggest that the diversity of molluscs decreases with decreasing pH. The surveys were not sufficiently sophisticated to distinguish if the decreased diversity was the result of reproductive failure or direct hydrogen ion toxicity.

The pH tolerance of marine molluscan larvae is well defined. Clam eggs developed normally when the pH ranged between 7 and 8.75, while oyster eggs had a slightly wider pH range (6.75 to 8.75).

The largest information base available is for the effects of pH on fish. The acutely lethal pH level for a species is typically less that the critical pH. However, there is a wide range of critical pH among species. There is information on the critical pH for 17 out of the 64 freshwater species of fish found in British Columbia. Brook trout have the highest critical pH (6.5), while brown trout the lowest (4.3). The critical pHs of the other 15 species were evenly distributed between these two extremes.

High pH (>9) reduces the ammonia transfer across the gill epithelium. Prolonged exposure to.high pH (>9) can cause mortality due to the build-up of ammonia in the blood.

Amphibians appear to be less affected by low pH. The critical pH of 5 of the 15 aquatic species found in British Columbia ranges from a low of 4 for the western toad, to 4.5 for the wood frog. It is unclear if the critical pH for the remaining 10 species is in this range.

4.10 Criteria for Aquatic Life

4.10.1 *Criteria for Aquatic Life: Other Jurisdictions*

The water quality criteria for aquatic life for other jurisdictions are summarized in Table 7.

Table 7. Summary of Selected Water Quality Criteria for Aquatic Life in North America and Europe

Agency	Reference	Criteria
Canadian Council of Resource and Environment Ministers*	CCREM, 1987	6.5-9
Environmental Protection Agency (USA)	EPA, 1986	6.5-9
Ministry of the Environment, Ontario, Canada	MOE-ONTARIO, 1984	6.5-8.5
European Inland Fisheries Advisory Commission	EIFAC, 1982	See Table 8

*Now Canadian Council of Ministers of the Environment - CCME

The range of criteria from different jurisdictions is quite small. The Ontario Ministry of the Environment has the narrowest pH range (6.5-8.5), while the EPA and CCREM guidelines allow a slightly higher range (6.5-9). The EIFAC pH criteria, based on the work of Alabaster and Lloyd (1982), stated that there was no definite pH range within which a freshwater fishery would be unharmed or damaged. They concluded that there would be a gradual deterioration in the fishery as the pH values deviated from the normal range (Table 8), and that the scientific data were insufficient to establish pH criteria for each important fishery and for different environmental conditions.

The British Columbia pH criteria for aquatic life are designed to protect all aquatic life in a wide range of water quality conditions. In areas with important freshwater fisheries, water quality objectives for pH should be developed on a site specific basis using the information presented in this report.

Table 8. Summary of EIFAC pH Ranges for the Protection of Aquatic Life (from Alabaster and LIoyd, 1982)

3-3.5	Unlikely that any fish can survive for more than a few hours.in this range, although some plants and invertebrates can be found at pH values lower than this.
3.5-4	This range is lethal to salmonids. There is evidence that roach, tench, perch and pike can survive in this range, presumably after a period of acclimation to slightly higher, non-lethal levels, but the lower end of this range may still be lethal for roach.
4-4.5	Likely to be harmful to salmonids, tench, bream, roach, goldfish, and common carp which have not previously been acclimated to low pH values, although the resistance to this pH range increases with the size and age of the fish. Fish can become acclimated to these levels, but of perch, bream, roach, and pike, only the last named may be able to breed.
4.5-5	Likely to be harmful to the eggs and fry of salmonids, and to adults particularly in soft water containing low concentrations of calcium, sodium, and chloride. Can be harmful to common carp.
5-6	Unlikely to be harmful to any species unless either the concentration of free carbon dioxide is greater than 20 mg/L, or the water contains iron salts which are freshly precipitated as ferric hydroxide, the precise toxicity of which is not known. The lower end of this range may be harmful to non-acclimated salmonids if the calcium, sodium, and chloride concentrations or the temperature of the water are low, and may be detrimental to roach production.
6-6.5	Unlikely to be harmful to fish unless free carbon dioxide is present in excess of 100mg/L.
6.5-9	Harmless to fish, although the toxicity of other poisons may be affected by changes within this range.
9-9.5	Likely to be harmful to salmonids and perch if present for a considerable length of time.
9.5-10	Lethal to salmonids over a prolonged period of time, but can be withstood for short periods. May be harmful to developmental stages of some species.
10-10.5	Can be withstood by roach and salmonids for short periods but lethal over a prolonged period.
10.5-11	Rapidly lethal to salmonids. Prolonged exposure to the upper limit of this range is lethal to carp, tench, goldfish and pike.
11-11.5	Rapidly lethal to all species of fish.

4.10.2 *British Columbia pH Criteria for Aquatic Life*

4.10.2.1 *Freshwater*

The British Columbia pH criteria to protect aquatic life must take into account the wide variability of the natural pH found in the freshwaters of British Columbia (Section 3) and the most sensitive aquatic organisms. The proposed criteria are summarized in Table 9.

Natural pH less than 6.5

Acidic conditions are commonly found in the high precipitation areas on the west coast of British Columbia. Waters in these areas are typically acidic, and in boggy areas water can have a pH as low as 5.0 (e.g., Queen Charlotte Lowlands, Section 3). These areas may have a fauna and flora that are at the low end of their pH range. To protect the aquatic communities from further acidification and possible elimination of species from the system, one component of the pH criteria for freshwaters is: no statistically significant decrease from background or upstream values (Table 9). See Section 4.10.2.3 for definition of a statistically significant decrease in pH.

In boggy areas where the fauna and flora are considered unique (e.g., ecological reserve, park, nature walk, etc.), an increase in pH could allow less acid-tolerant species to inhabit the body of water. Under these circumstances, site specific ambient water quality objectives for pH are required in order to preserve the integrity of the bog's unique fauna and flora.

Natural pH 6.5 to 9.0

For natural freshwaters with a pH between 6.5 and 9.0, one component of the pH criteria is : no restriction on change within this range. Note that a pH change in freshwaters containing carbonate and bicarbonate ions will alter the carbon dioxide concentration. An increase in pH that causes the carbon dioxide concentrations to decrease below 10 µmol/L may cause a shift in the phytoplankton community structure to cyanobacteria (Section 4.2.2.2). High concentrations of cyanobacteria can cause taste and odour problems in drinking water supplies, a muddy flavour in game fish, aesthetically unpleasant surface scums and, under rare circumstances, toxicity to livestock, dogs, or wildlife. A decrease in pH that causes the carbon dioxide concentrations to exceed 1360 µmol/L may be toxic to aquatic life. Consequently, this component of the pH criteria should be used cautiously in situations where the carbon dioxide concentrations could exceed a 10 µmol/L minimum or a 1360 µmol/L maximum. Carbon dioxide concentrations should be calculated using the formulae outlined in Appendix 2.

Natural pH greater than 9.0

For systems with a pH greater than 9.0, toxicity to fish is a concern. Above pH 9.0, fish have difficulty excreting ammonia across the gill epithelium (Section 4.7.10). Although it is uncommon to have pH 9.0, it can occur in very productive lakes, streams, and aquatic plant beds during the day because of the pH shift caused by the uptake of carbon dioxide for photosynthesis. During the night the pH of these waters can decline as much as 1 pH unit due to the dissolution of carbon dioxide from the atmosphere, the respiration of the biota, and the cessation of carbon dioxide uptake by plants. Despite these extreme diurnal pH fluctuations, fish are capable of surviving pH levels 9.0 for short periods of time (Section 4.7.10).

The addition of lime or calcium carbonate to lakes and reservoirs has been an effective lake restoration technique to reverse the eutrophication process (Murphy, pers. comm.). Liming temporarily increases the calcium and carbonate concentrations as well as the pH of the water causing a precipitation of calcium carbonate. During the precipitation of calcium carbonate, dissolved and suspended phosphorus as well as living algal cells are incorporated within the calcium carbonate crystal and deposited on the lake bottom. The result is an improvement in water quality through a reduction in algal biomass and phosphorus concentrations. Because of the potential importance of liming as a lake restoration technique, short term increases in pH to 9.5 are acceptable as long as the elevated pH is not toxic to aquatic life.

For freshwaters with a natural pH above 9.0, one component of the pH criteria is: no statistically significant increase over background, except for short periods of time (2-3 days maximum) in lakes or reservoirs for restoration purposes. See section 4.10.2.3 for definition of a statistically significant change in pH.

4.10.2.2 *Marine Waters*

The need for water quality criteria for pH in marine waters has not been addressed by other jurisdictions. Based on the narrow pH tolerance of marine molluscs, and the importance of marine molluscs in British Columbia, the pH criterion for marine waters is 7.0 to 8.7.

4.10.2.3 *Sampling Requirements for Aquatic Life Criteria.*

1) Streams: Statistical comparison of background (upstream) and downstream results should use a I-tailed, two sample t-test, at the 0.05 probability level. The minimum sampling requirement is *5* measurements collected weekly in 30 days. The two sample t-test requires the different stations to have similar variances (use the F-test). If, at the downstream site, data from spills or discharge events are pooled with steady state data, the variance may increase and become dissimilar to the upstream site invalidating the two sample t-test. To reduce the variance, consider the data from the steady state and the event as independent data sets. Additional pH measurements, or a pH sensor with an automatic recorder are recommended for sites subject to event-driven pH fluctuations.
2) Lakes: Same as streams or, if background stations are not available, predischarge data should be collected near the zone of influence, once every three weeks for one or two years to determine the temporal variation. A pH sensor with an automatic recorder would collect more data and provide a better understanding of the temporal variability than normal field sampling.

4.10.2.4 *Summary of Freshwater and Marine Criteria*

The British Columbia freshwater pH criteria are compatible with the CCREM guidelines (i.e., 6.5 to 9.0) but contain refinements in several areas. The B.C. criteria recognize that the pH of freshwaters can naturally drop below 6.5; however, anthropogenic decreases in pH below pH 6.5 are not permitted. Increases in pH for natural waters with a pH < 6.5 is permitted as long as the water body does not have an unique acidophilic fauna or flora (e.g., bog). Under these circumstances, site specific ambient water quality monitoring and objectives are required to set limits on the permissible increase in pH.

Between pH 6.5 and 9.0, the B.C. criteria and the CCREM guidelines are similar. The only difference is that the B.C. criteria recognize the importance of low carbon dioxide concentrations on the phytoplankton community structure and high carbon dioxide concentrations and its potentially toxic effects to aquatic life.

For pH> 9.0, the CCREM guidelines suggest that short term increases to pH 9.5 are permitted; however, the B.C. criteria do not permit any statistically significant increases because of the limited data on the tolerance of fish to pHs between 9.0 and 9.5. The B.C. criteria recognize that the elevation of pH in lakes to cause calcium carbonate precipitation is an effective and important lake restoration technique. Consequently, the criteria permits short-term increases (2-3 days) to pH 9.5 provided the treatment is not toxic to aquatic life. See Section 4.10.2.3 for definition of statistically significant change in pH.

The CCREM guidelines do not include marine criteria, whereas the B.C. criteria do (7.0-8.7). The marine criteria are based on the effects of pH on the development and survival of molluscan larvae.

Table 9. Summary of the pH Criteria for the Protection of Aquatic Life

Freshwater	
pH< 6.5	No statistically significant* decrease in pH from background. No restriction on the increase in pH except in boggy areas that have a unique fauna or flora Site specific ambient water quality objectives to restrict the pH increase in areas with a unique fauna and flora are recommended.
pH 6.5-9.0	Unrestricted change permitted within this pH range. This component of the freshwater criteria should be used cautiously if the pH change causes the carbon dioxide concentrations to exceed a 10 µmol/L minimum or a 1360 µmol/L maximum. Carbon dioxide concentrations below 10 µmol/L can cause a shift in the phytoplankton community to cyanobacteria (Section 4.2.2.2), while CO_2 concentrations above 1360 µmol/L can be toxic to fish (Section 4.7.11). See Appendix 2 for the method to determine CO_2 concentrations.
pH >9.0	No statistically significant* increase in pH from background. Short-term increases (2-3 days) to pH 9.5 are permitted for lake restoration projects. Decreases in pH are permitted as long as carbon dioxide concentrations are not elevated above 1360 µmol/L. CO_2 concentrations above 1360 µmol/L may be toxic to fish (Section 4.7.11). See Appendix 2 for the method of determining CO_2 concentrations.
Marine Water	
pH 7.0-8.7	Unrestricted change within this range (or the protection of mollusc embryo development- Section 5.6).

*See Section 4.10.2.3 for definition of statistically significant change.

5. WILDLIFE

While birds and mammals are not affected directly by acidic deposition, they are vulnerable to changes in their habitat caused by acidification, particularly to changes affecting the availability and quality of food. Almer et al., (1978) reported that fish-eating birds, such as mergansers and loons, had been forced to migrate from acidic lakes with decreasing fish stocks. Nilsson and Nilsson (1978) found a positive correlation between pH and bird species richness. They suggested that a reduction in young fish, an important food component for aquatic birds, may lead to low reproductive success and local extinction. Losses of other aquatic organisms such as clams, snails, amphibians, and crayfish can have an impact on food availability for aquatic birds and semi-aquatic mammals.

Several studies have observed reduced fish-eating bird populations in acidic lakes. The common merganser *(Mergus merganser)* and the kingfisher *(Megaceryle alcyon)* were observed only on lakes with a summer pH>5.6 (McNicol and Ross, 1982). In the vicinity of Schefferville (Quebec), a third as many species and a quarter of the total number of aquatic birds were observed on lakes with a pH less than 4.5. The acidic lakes contained fewer piscivorous birds and a larger number of invertebrate-feeding ducks (McNicol and Ross, 1982).

Although the effects of acidification on birds and mammals is indirect, they are not considered the most sensitive species. Presumably, the protection of fish and invertebrate species from acidic conditions will result in the protection of birds and mammals, consequently no criteria for the protection of wildlife are required.

6. LIVESTOCK WATER SUPPLY

6.1 Effects

The literature regarding the effects of pH of water on livestock is scant. The reasons being that pH, by itself, is not considered to affect the palatability of water or to have an adverse effect on growth and development of livestock. The following discussion is based on the few studies found in the literature.

In 1983, Galyean et al. undertook a study to evaluate the effect of drinking water pH (pH ranging from 5.5 to 6.0, and 9.0 to 9.5) and dietary nitrogen sources (natural versus NPN, in which 25% of the crude protein was derived from urea) on the growth, water intake, and metabolism of lambs. A high roughage diet was fed in a dry-lot in an effort to simulate the dietary conditions encountered by the ruminants grazing range grasses. Their results were as follows:

(i) No differences in performance or water intake by the animals were observed due to the pH of the drinking water;
(ii) The drinking water with pH between 9.0 and 9.5 resulted in higher ($P<0.05$) digestion coefficients for dry matter, organic matter, and cellulose than the pH 5.5-6.0 water. It was argued that the added Ca^{++} in the alkaline water might have enhanced cellulose digestion; and
(iii) Drinking water had little effect on nitrogen metabolism, except that lambs supplied with pH 9.0-9.5 water digested more nitrogen than lambs with pH 5.5-6.0 water.

These investigators concluded that the pH of drinking water was not a major concern in the management of rangeland ruminants fed with a high roughage diet.

Horvath and Wendt (1980) observed that livestock rejected water that was grossly polluted with acid mine drainage (AMD). To identify characteristics of AMD that caused this rejection, Horvath (1985) exposed sheep to (a) unaltered AMD water from two sources (pH 2.4 and 2.8), (b) neutralized AMD water, (c) simulated AMO water, and (d) tap water (pH 6.3). It was concluded that neutralizing the two AMD waters with $Ca(OH)_2$ did not make either one as acceptable to sheep as unpolluted tap water. Also, exposure to simulated AMO water suggested that ferric ion as ferric sulfate was the principal contributor to reduced short-term intake of AMO water by sheep.

In the Netherlands, the Committee on Mineral Nutrition (1973) suggested that waters with pH ranging between 2 and 11 were acceptable for dairy cattle watering.

6.2 Criteria from the Literature

Table 10 lists the pH criteria for livestock water supply from various jurisdictions. In general, water supplies having pH between 5.0 and 9.0 are considered to be acceptable for livestock watering. However, this range is quite narrow compared to that (pH 2 to 11) suggested for dairy cattle by the Dutch Committee on Mineral Nutrition (1973).

The Alaska Department of Environment Conservation (1979) proposed a criterion (pH 6.8 to 8.5) which was primarily concerned with the sanitation of dairy cattle. However, no details were provided in their publication with regard to problem(s) which might result if the pH of a livestock water supply fell beyond the given range of 6.8 to 8.5.

6.3 Recommended Criteria

Assuming that the constituents of water do not interfere with the palatability or the health of livestock, it is recommended that the pH of livestock water supplies should not fall below 5.0 or exceed 9.5.

A pH criterion for livestock water supplies was not proposed by the Canadian Council of Resource and Environment Ministers (1987).

6.4 Rationale

While water with pH as low as 2.4 may not have a direct effect on growth and development of livestock, it may contain undesirable levels of ferric sulfate, thus making it unpalatable for livestock (Horvath, 1985). High pH water, on the other hand, may be associated with a high salt content, which is known to cause adverse effects on livestock. Experimental evidence suggests that waters with pH 5.5 to 9.5 will not affect adversely livestock development (Galyean et al., 1983).

Based on these data and suggested criteria from various jurisdictions (Table 10), livestock water supplies with pH ranging between 5.0 and 9.5 should pose no threat to livestock.

Table 10. pH Criteria for Livestock Water Supply from Various Jurisdictions

Criteria Statement	Criteria Value (pH)	Jurisdiction	Date	Reference
For dairy sanitation pH of water should not < 6.8 or > 8.5	6.8 - 8.5	Alaska	1979	ADEC, 1979
Acceptable pH range for livestock watering is 5.5 to 9.0	5.5 - 9.0	Manitoba	1983	MDEWSH, 1983
Recommended pH in livestock water supply: 6.0- 9.0 as the 95th. percentile range and 5.0 - 9.5 as the 99th. percentile range	6.0 - 9.0 (95th percentile) 5.0 - 9.5 (99th percentile)	United Kingdom	1983	Anglian Water Authority, 1983

7. IRRIGATION

7.1 Effects

7.1.1 *Soil pH and Plant Growth*

Natural soils differ considerably in their pH. In general, soils in humid regions of the world are acid (pH<7) in reaction. In arid regions of low precipitation, soils are saline to alkaline in reaction (pH>7). In addition, sources internal to an ecosystem and long-term use of large amounts of nitrogen fertilizer have been recognized to affect soil pH (Mahler and McDole, 1987; Van Miegroet and Cole, 1985).

The harmful effects of a soil pH are due primarily to secondary effects. Soil factors such as nutrients distribution and their availability to crops, soil water characteristics, microbial activity, which is responsible for such processes as nitrogen mineralization, nitrification, denitrification, etc., are all affected by the soil pH. It has been found that several essential elements (e.g., Fe, Mn, Cu, and Zn) tend to become less available as soil pH is raised from 5 to 8, whereas the availability of others (e.g., molybdenum) increases at higher pH. In acid soils (pH<5), Al, Fe, and Mn are often soluble in sufficient quantities to be toxic to some crops (Brady, 1974; Russell, 1973; Foy, 1984). On the other hand, saline and alkaline conditions (pH≥8.5) are undesirable for crop growth due to their adverse effects on both physical (e.g., osmotic pressure, structure, etc.) and chemical (e.g., nutrient availability) characteristics of soils. The effects of pH on soil physical, chemical, and biological properties, and on plant growth have been the subject of several investigators (Chiang et al., 1987; Suarez et al., 1984; Weier and Gilliam, 1986; Mahler and McDole, 1987).

To study the effect of pH (as an independent variable) on saturated hydraulic conductivity (K), Suarez et al. (1984) subjected several soils to solutions having the same sodium adsorption ratio (SAR 20 and 40) and electrolyte concentration (EC ranging from 1.0 to 500 mmol/L) at pH 6, 7, 8, and 9. The saturated conductivities at pH 9 were lower than at pH 6 for a montmorillonitic and a kaolinitic soil, at all ECs < 100 mmol/L. For a vermiculitic soil with lower organic carbon and higher silt content, pH changes did not cause large changes in K. These investigators also found that decreases in K were (i) more severe at SAR 40 than at SAR 20, and (ii) not reversible on application of waters with higher electrolyte concentrations. Soils with large amounts of variable charge were most susceptible to pH effects.

Mahler and McDole (1987) found that, among cereals, lentil *(Lens culinaris,* cv. Tekoa) and spring pea *(Pisum sativum,* cv. Columbia and Alaska) were the least tolerant to soil acidity; minimum pH of 5.65 and 5.52, respectively, were required for maximum yields. Spring barley *(Hordeum vulgare,* cv. Advance and Steptoe) was relatively more tolerant, yielding a minimum acceptable soil pH of 5.23 (for both cultivars). The three winter wheat *(Triticum aestivum)* cultivars used in their tests, however, reacted differently as Daws, Hill 81, and Stephens yielded minimum acceptable pH values of 5.19, 5.31, and 5.37, respectively. In earlier experiments, Mahler and McDole (1985) and Mahler (1986) noted that most forage and pulse legume crops grown in northern Idaho showed reductions in yield when soil pH was below 5.6.

Denitrification is an important mechanism of loss of nitrogen (N) from soils. Nitrogen gas, NO, and N_2O are produced during biochemical reduction of NO_3-N. Recently, concerns have been expressed regarding detrimental effects of N_2O-N evolved during denitrification on the stratospheric ozone layer. It has been shown that as the soil acidity increases below pH 6, N_2O becomes the major product of denitrification (Tisdale and Nelson, 1975; Weier and Gilliam, 1986; Koskinen and Keeney, 1982; Knowles, 1981).

7.1.2 *Irrigation Water Quality and Soil*

Traditionally, concerns for the quality of irrigation water are expressed not in terms of pH but salinity (e.g., electrical conductivity, salt concentration), alkalinity (e.g., sodium adsorption ratio), and trace ion concentration as it affects soil properties and plant growth (Wilcox and Durum, 1967). However, guidelines for pH levels have been considered when irrigating, for example, with pulpmill effluent (Blosser and Owens, 1964) and sewage or reclaimed water (Bouwer and Idelovitch, 1987; Westcot and Ayers, 1984). More recently, concerns from possible adverse effects of acid precipitation (caused by sulphur dioxide and oxides of nitrogen emissions from industry and automobiles, respectively) on terrestrial and aquatic ecosystems have stimulated a great deal of interest in evaluating the impact of the pH of water on agriculture.

Acid rain may affect terrestrial environments by causing chemical alterations (e.g., lowering of soil pH, leaching of cations, solubilization of heavy metals, etc.), biological alterations (e.g., microbial growth and activity), and biochemical alterations (e.g., N mineralization, N fixation, denitrification, etc.). The sensitivity of a soil system to an acid input depends upon influent (e.g., precipitation) chemistry, soil characteristics (e.g., soil pH, anion adsorption capacity, cation adsorption capacity, base saturation, texture, and organic carbon), as well as the vegetation supported by the soil (Abrahamsen et al., 1976). A soil process may be unaffected, stimulated, or depressed by the acidity of water (Table 11).

Soils are well buffered below pH 4 and above pH 7. Whereas organic matter content plays

a dominant role in acid soils, a lime reaction mechanism may explain the strong pH buffering in saline and alkaline soils. Within the pH range of 4.5 to 6.5, changes in soil pH in response to acid input are linear (Magdoff and Bartlett, 1985; James and Riha, 1986). While investigating the effects of acid precipitation (250 cm at pH 3.7) on microbial activity in an organic soil (pH 7.32), Bitton and Boylan (1985) noted that the pH of the soil was unaffected by the acid rain treatments; however, the microbial activity (e.g., phosphatase and dehydrogenase activities, and soil respiration) was significantly reduced compared to the control (precipitation pH 4.5 to 5.2). The resistance to showing a change in pH in response to the acid rain was attributed to the high cation exchange capacity (CEC) of the organic soil. These results also demonstrated that the absence of an obvious change in soil pH in response to acid rain did not mean that acid rain had no effect on the soil system.

The leaching of cations from soils is a complex phenomenon and depends on soil type and the physico-chemical characteristics (e.g., ionic composition, duration of exposure, etc.) of the percolation water. In general, an increase in acidity of the influent (e.g., acid precipitation) will result in increased rates of cation leaching, while the presence of neutral salts in rainwater counteracts the leaching process (Likens et al., 1977; Winkler, 1976; Wiklander, 1975). In studying leaching of soils by acid rain with varying NO_3^-/SO_4^{--} ratios, Huete and McColl (1984) noted that soil cation leaching varied directly with NO_3^- content of the rain water in an alfisol, which had a high sulfate adsorption capacity. However, in soils dominated by negative charge constituents, anion composition of the rain water had little effect on cation leaching. In two deciduous forest ecosystems, Richter et al. (1983) found that soil cations that were exchanged with H^+ in acid precipitation (pH 4.3) were almost entirely supplied by forest canopies and litter layers, and did not come from exchangeable mineral soil pools. It was also suggested that even in sensitive and infertile soils (CEC <7.2 meq/100 g), exchangeable bases were more than two orders of magnitude greater than the annual H^+ input in bulk precipitation (pH 4.6). Therefore, it was concluded that leaching would affect soil cation reserve and soil development only over a very long term.

In a Sierran forest soil (pH 6.42, CEC = 19 meq/100 g) exposed to acid precipitation (pH 3.0 and 4.0) for 12 weeks, Killham et al. (1983) noted that the overall microbial response was one of stimulation. It was suggested that the microbial activity in the soil was limited by available nitrogen, and the nitric acid in the acid precipitation (HNO_3 : H_2SO_4 = 3:2) helped stimulate this activity. Respiration and enzymatic activities, however, were inhibited in the soil when exposed to acid precipitation of pH 2.0.

Among all the soil microbiological parameters studied (e.g., soil respiration, hydrogenase, phosphatase, urease and protease activity, N mineralization, and N fixation), Bitton and Boylan (1985) and Bitton et al. (1985) found that nitrification was the most sensitive to acid precipitation under field conditions. Whereas nitrification rates were significantly reduced at both pH 3.7 and 3.0, mineralization of nitrogen was impacted by the acid precipitation only at pH 3.0. These conclusions were in agreement with those from other studies (Francis, 1982; Strayer et al., 1981).

Will et al (1986) observed that in a sandy soil subjected to 200 cm of simulated acid precipitation (pH 3.0 and 3.6), soil pH, respiration, and phosphatase activity levels were generally lower in covered plots (protected from natural rainfall of pH 4.6) than uncovered plots. It was also noted that 24 weeks after the last acid precipitation treatment there was no difference in any of the measured parameters between pH treatments in uncovered plots, suggesting that the microbial population was able to readjust when the treatment stress was removed.

In the long term, probably the most serious ecological effect of acid precipitation is the removal of basic cations and the mobilization of Al in soils (Reuss, 1983). While modelling the soil response to acidic precipitation, however, Reuss (1983), and Bloom and Grigal (1985) concluded that changes in soil pH and base saturation, and the change from a Ca- to Al-dominant soil system in response to naturally occurring acid rain, are very slow even in very poorly buffered soils.

7.1.3 *Irrigation Water Quality and Vegetation*

Many crops would grow satisfactorily in solutions with pH ranging from 4 to 8 and containing a liberal supply of all the important nutrients. Plant roots were definitely injured in solutions as acid as pH 3 and were unable to sorb phosphate at pH 9 (Russell, 1973). Therefore, the effect of pH on crops in most agricultural soils (pH between 4 and 8.5) is due to secondary effects brought about by changes in soil pH (Russell, 1973), except in extreme cases of low pH rain.

The results of the effect of pH of applied water (e.g., precipitation) on agricultural and forest vegetation are tabulated in Tables 12 and 13.

Upon reviewing published data, Irving (1983) concluded that the majority of crop species studied exhibited no effect on growth or yield from an exposure to simulated acidic rain (pH≤4.2). Whereas a few crops in some studies were negatively affected by the acidic rain, others exhibited a positive response. It was suggested that the net response of a crop to acidic precipitation was dependent upon: (a) the interaction between the positive effects of S and N associated with acid rain, (b) the negative effects of acidity, and (c) the interaction between these factors (i.e., (a) and (b)) and other environmental conditions such as soil type and the presence of other pollutants.

It has been shown that while some crops appear to be influenced by the SO_{4--}/NO_{3-} ratio in acid precipitation (Irving, 1985; Johnston et al., 1982), no effect of the concentration or ratios of SO_{4--}, NO_{3-}, and Cl^- ions has been found on other crops (Jacobson et al., 1986; Adaros et al., 1988).

Adaros et al. (1988) exposed broad bean *(Viciafaba* L. cv. 'Con Amore') plants grown in a standard fertilized soil (ED 73) and quartz gravel (0.7-1.2 mm dia) to acid rain at pH 3.0 to 4.0. The plants grown in the soil did not show any detectable effects of four acid rain treatments in 34 days. On the other hand, those in gravel showed a remarkable positive effect on biomass production. These positive effects, however, diminished during later stages. Their results also indicated a cumulative effect of acid rain in plants grown in soil; only in the two final harvests (stages of filling the fruits) were negative effects expressed. Not only was the total biomass reduced, but also there was reduction of the marketable products like pods and seeds.

In studying pollen germination in corn *(Zea mays* L.), Wertheim and Craker (1987) indicated that germination of pollen was significantly reduced (~ 13%) on silks treated with acid rain of pH≤4.6 as compared with silks receiving a pH 5.6 rain treatment before pollination. This reduction in the germination exposed to low pH could result in fewer kernels leading to reduced yield, especially under conditions of environmental stress such as drought (Banwart et al., 1986). Craker and Waldron (1986) had demonstrated that acid rain at pH 3.6 reduced the number of kernels/ear when the supply of pollen was limited.

The sensitivity and the extent of injury to leaves exposed to acidic rain have been related to the wettability of the leaf surface (Keever and Jacobson, 1983; Haines et al., 1985; Caporn and Hutchinson, 1986). It has been reported that rainfall acidity enhances (a) leaching of inorganic ions from leaves of various species (Keever and Jacobson, 1983; Evans et al., 1986), and (b) retention of pesticides on leaves (Troiano and Butterfield, 1984; vanBruggen et al., 1986). Working with leaves of dwarf bean *(P. vulgaris* L. cv. Prince), pea (P. *sativum* L. cv. Meteor), and rape *(B. napus* L. cv. Rafal) plants, Percy and Baker (1988) found that retention of fluorescein increased, whereas droplet leaf contact angle decreased in all species on exposure to precipitation at pH S 4.6, relative to those exposed pH 5.6. This behaviour was attributed to decreases in surface roughness of the leaves.

7.2 Criteria from the Literature

Table 14 lists pH criteria for irrigation waters from various jurisdictions. In most cases, irrigation water with pH between 4.5 and 9.0 is not considered to be a problem in plant growth, provided care is taken to detect the development of harmful indirect effects. The most stringent criterion was proposed for horticultural crops by Manitoba (MDEWSH, 1983), which was based on best professional judgement. It states that “to provide protection for intensive horticultural crop production where irrigation is the sole source of water, pH of water should lie between 6.0 and 8.5”.

7.3 Recommended Criteria

Assuming that the indirect effects of soil acidity, salinity, and alkalinity are identified and properly taken care of by the use of soil amendments, the recommended criterion for irrigation waters is a pH ranging between 5.0 and 9.0.

No criterion for pH for irrigation waters was proposed by the Canadian Council of Resource and Environment Ministers (1987).

7.4 Rationale

The criterion proposed here is based on information presented in section 6.1, Tables 12 and 13, and data found elsewhere in the literature. In the acid range (pH<7), pH 4.6 water may affect plant growth by reducing germination of pollen on com silks and by altering leaf characteristics (Percy and Baker, 1988; Wertheim and Craker, 1987). It has been recognized that in soils with pH below 5.0, aluminum, iron, and manganese are often soluble in sufficient quantities to be toxic to some crops (Russell, 1973; Foy, 1974). The question then is, how would pH 4.6 irrigation water affect the pH of a given soil? In studying effects of acid rain on terrestrial ecosystems, Reuss (1983) and Bloom and Grigal (1985) concluded that changes in soil pH in response to naturally acidic precipitation are very slow even in poorly buffered soils. It is well known that management practices such as liming are quite common for bringing the pH of an acid soil to a desirable level readily and economically. It was therefore considered that acidic waters with pH greater than 4.6 should be acceptable for irrigation purposes.

Plants supplied with adequate nutrients grow well in solutions with pH 4 to 8. In solutions of pH 9, no harmful effects, other than a deficiency of phosphorus, were noted in plants (Russell, 1973). However, pH>7.0 waters are generally associated with high total dissolved solids (or salinity) or alkalinity (or sodium content). The data from British Columbian lakes suggest that, even at pH 9, the total dissolved solids content or the sodium content (in terms of sodium adsorption ratio) of the water would not exceed the lower limit of the range recommended by the CCREM (1987). It was therefore, recommended that pH 9.0 be accepted as the upper limit of the acceptable pH range for irrigation water.

Table 11. Effect of Acid Precipitation on Soils

Acid Rain Characteristics						Soil (Vegetation)	Effects	Reference
pH	**No. of events**	**Duration**	**Rate**	**Amount**	**H_2SO_4: HNO_3**			
3, 3.6, and 4.6 (Control)	20	20 wk.	2.5 cm/h for 4 h	200cm	7:3	Sandy; pH < 5; O.M = 0.79% CEC =3.86 meq /100 g; (Turkey Oak; Longleaf pine)	pH, respiration, arylsulphatase activity unaffected; phosphatase activity decreased at pH 3; urease activity enhanced at pH 3.6; reduced N mineralization of organic N at pH 3	Will et al., 1986
3, 3.7		112 d	2.54 cm per7 d	40.6 cm	7:3	4 sandy and one organic (O.M=38%) soil; pH=3.91-7.65	Soil pH decreased by pH 3 rain; reduced N2 fixation in a mineral soil at pH 3 but unaffected in others; no change in enzymic activity	Bitton and Boylan, 1985
4, 3.7, 4.5- 5.2 (Control)		1st 330d at pH 4; 690 d total	same as above		same as above	same as above	pH for two sandy soils decreased but unaffected for Organic soil; decreased dehydrogenase activity in one sandy and organic soil;	same as above
3, 3.7, 4.6 (Control)		153 d (1981); 182 d (1982)		50cm (1981); 100cm (1982)	7:3	sandy; pH=4.48	No change in urease, dehydrogenase, phosphatase or respiration activity; slight increase in protease activity at pH 3; decreased nitrification at oH 3 and 3.7	Bitton et al., 1985
2, 3, 4, 5.6 (Control)		12 wk.	twice-weekly	15cm	2:3	loamy; pH=6.4; CEC=19 meq/100 g; O.C=5.24%; (Ponderosa nine)	Reduced respiration and enzyme activity at pH 2; overall stimulated microbial response at pH 3 & 4; decrease in soil pH by pH 2 rain	Killham et al., 1983
3.2 to 4.1			5 cm/h continuous to 5 cm/h for 1 hour 3 times/wk	100cm		7 silt loams; 1 gravelly loamy sand; pH=4.4-7.1	Glucose mineralization inhibited in all soils from continuous exposure to pH 3.2 rain; reduced mineralization in one soil from intermittent exposure; acid rain effects mainly at surface except in acid soils	Strayer and Alexander, 1981
3.2 to 4.1			5 cm/h continuous to 1.2 cm/1.5 h twice/wk for	100cm		2 silt loams; 1 gravelly loamy sand; pH =4.4-6.3	Reduced nitrification of added $NH4^+$ from continuous exposure to acid rain; production of N in absence of added $NH4^+$ unaffected or stimulated at pH 3.2; partial inhibited of nitrification of	Strayer et al., 1981

Acid Rain Characteristics						Soil (Vegetation)	Effects	Reference
pH	No. of events	Duration	Rate	Amount	H_2SO_4: HNO_3			
			19wk				added NH_4^+ from intermittent exposure	
3.5		5d	20 mL/h	200mL	0.0:1.0 0.25:0.75 0.45:0.55 and 1.0:0.0	2 sandy loams; 1 clay; pH = 4.9--7.3; CEC =6.7-7.4 meq/ 100 g; O.C. =2- 6 g/kg; Fe_2O_3 = 3-12 g/kg	Cation leaching in alfisol (pH =4.9; Fe_2O_3=12) affected by NO_3 level in rain; leaching unaffected by H_2SO_4: HNO_3 ratio in entisol (pH =7.3; Fe_2O_3 =3); effect on oxisol intermediate	Huete and McColl, 1984
2.4 to 5.5		25-30d	0.74-0.85 cm/0.5 h, twice/wk	22.2 cm	7:3	sandy clay loam; pH =5.8 -5.9; CEC =4-4.5 meq/ 100 g; O.C.=1.5-2%; (Soybean)	Nematode unaffected; significant changes in soil pH, Ca, Mg, and K at rain pH 2.4	Heagle et al., 1983
2 to 4.7		75d	0.85 cm 3 time/wk			sand; pH =4.5; CEC = low; (Jack pine)	Soil pH significantly lowered at the surface by pH 3 rain; indications of Al toxicity and deficiencies of P and Mg at pH 2.5 (rain)	MacDonald et al., 1986

Table 12. Effect of Acid Precipitation on Plants (Field Studies)

Acid Rain Characteristics						Vegetation (soil)	Effect	Reference
pH	SO_4^{++} -µg/L-	NO_3^- -µg/L-	Events	Rate -cm/h-	Duration -h/event-			
3.0-5.5	530- 46 190	753	26	0.67	1.5	'Vernal' alfalfa	Yield greater than or equal to than at control (pH =5.6)	Lee & Neely, 1980
-ditto-	530- 34 000	753- 23 290	58	-ditto-	-ditto-	'Pioneer 3992' corn	9% lower yield at pH 4 than control (pH=5.6); no effect on growth & yield at pH 3 and 3.5	-ditto-
-ditto-	530- 46 190	753- 23 290	26	-ditto-	-ditto-	'Alta' tall fescue	Yield unaffected or greater than control (pH=5.6)	-ditto-
-ditto-	-ditto-	753	16	-ditto-	-ditto-	'So. Giant Curled' mustard green	No effect on growth or yield compared with control (pH = =5.6)	-ditto-
-ditto-	530- 34 000	753- 23 290	-ditto-	-ditto-	-ditto-	-ditto-	24-33% lower yield at pH<4 than at pH=5.6	-ditto-
-ditto-	53- 46 190	753	12	-ditto-	-ditto-	'Cherry Belle' radish	Yield unaffected or greater than control (pH=5.6)	-ditto-
-ditto-	-ditto-	753- 23 290	15	-ditto-	-ditto-	'Thick Leaf spinach	No effect on growth or yield compared with control	-ditto-
2.3-4.0	100- 100 000	1400- 265 000	41	35	0.001	'Amsoy' soybean	Lower seed wt. (15%) & pod/plant ratio at pH=3.4 than control (pH=4.1); yield unaffected at pH 2.3 & 3.1	Evans et al., 1981
3.1, 5 6	4 800, 39 100	2 480, 4960	11	2.0	0.33	'Wells' soybean	Yield & seed weight unaffected or greater at pH 3.1 than pH=5.6	Irving & Miller. 1981
3.2, 6 0	20, 50 000	120	27	3.0	0.17	'Red Kidney' beans	No effect on growth & yield compared with pH 6	Shriner & Johnson, 1981
2.7-5.7	1260- 106 600	3 040	9	35	0.001	'Cherry Belle' radish	Growth & yield unaffected by pH	Evans et al., 1982
2.7-5.7	-ditto-	-ditto-	19	-ditto-	-ditto-	'Perfected Detroit V- 904' garden beet	Lower number of marketable roots at all pHs than pH = 4.1 (ambient) and 5.7 (control); 16% greater yield at control pH than ambient	-ditto-
2.8-5.6	720- 55 600	310- 27 600	5-6	1.0	1.0	'Champion' radish	Higher yield at all levels than pH 5.6; ambient pH = 3.8	Troiano et al., 1982
2.8-4.0	4 321- 59 180	2180 30450	18	1.27	1.0	'Beeson' soybean; 'Williams' soybean	Yield unaffected or greater at pH 2.8 & 3.4 than that at ambient (pH=4.0)	Troiano et al., 1983
2.8-5.2	1 550- 80 300	150- 9 650	30	1.48	0.5	'Davis' soybean (sandy clay loam)	Foliar injury at pH≤2.8; yield & growth unaffected by pH	Heagle et al., 1983

Acid Rain Characteristics						Vegetation (soil)	Effect	Reference
pH	SO_4^{++} -µg/L-	NO_3^- -µg/L-	Events	Rate -cm/h-	Duration -h/event-			
2.4-5.4	200-248 000	150-21 000	25	1.70	0.5	-ditto-	-ditto-	-ditto-
3.0-5.6			92	1.95	0.53	'Amsoy 71' soybean (Flanagan silt loam)	Decrease in yield at lower pH in 1 of 3 years; 3-yr average yield 3% lower at pH 3 than control (pH 5.6)	Porter et al., 1987

Table 13 Effect of Acid Precipitation on Plants (Controlled Studies)

Acid Rain Characteristics						Vegetation (soil)	Effect	Reference
pH	SO_4^{++} -µg/L-	NO_3- -µg/L-	Events	Rate -cm/h-	Duration -h/event-			
3.2, 6.0	20- 50 000	120	24	3.0	0.17	'Red Kidney' kidney beans	Pod number, shoot wt., & root wt. showed both positive & negative response to low pH	Shriner, 1978
3.0- 5.6	480- 28 820	620- 32 200	3	0.8	2.0	'Oakland' lettuce	No effect on growth and yield	Jacobson et al.,1980
2.5- 5.7	5 000- 151 000	800	45	0.72	0.33	'Univ. Idaho' pinto beans	Yield unaffected at pH 3.1; 29-39% lower yield at pH ≤ 2.9 compared to pH *5.7*	Evans & Lewin, 1980
-ditto-	-ditto-	-ditto	78	0.72	0.17	'Amsov' soybean	11% lower yield at pH 2.5 the control (pH=5.7)	-ditto-
3.0- 5.6	960- 42 000	530- 14 000	10	21.2	0.33	'Wells' soybean	Yield at low pHs unaffected or greater than at pH 5.6	Irving & Sowinski, 1981
3.0- 5.6	530- 98 070	740	80	0.67	1.5	'Quinalt' strawberry	Greater yield at lower pH compared to control (pH 5.6)	Cohen et al.,1981; Lee et al., 1981
-ditto-	-ditto-	-ditto-	32	-ditto-	-ditto-	swiss chard	Market yield & growth unaffected by pH	-ditto-
-ditto-	-ditto-	--ditto-	33	-ditto-	-ditto-	'Climax' timothv	Yield at lower pHs unaffected or greater than pH 5.6	-ditto-
-ditto-	-ditto-	-ditto-	24	-ditto-	-ditto-	'Burley' tobacco	No effect of pH on growth or yield	-ditto-
-ditto-	-ditto-	--ditto-	51	-ditto-	-ditto-	'Patio' tomato	Yield at lower pHs unaffected or greater than pH 5.6	-ditto-
-ditto-	-ditto-	-ditto-	46	-ditto-	-ditto-	'Fieldwin' wheat	Yield unaffected: lower root growth at lower offs	-ditto-
-ditto-	-ditto-	-ditto-	56	-ditto-	-ditto-	'Vernal' alfalfa	Yield unaffected or greater at low pHs than pH 5.6	-ditto-
-ditto-	-ditto-	-ditto-	45	-ditto-	-ditto-	'Steptoe' barley	Yield & growth unaffected by pH	-ditto-
-ditto-	-ditto-	-ditto-	26	-ditto-	-ditto-	'Detroit Dark Red' beet	43% decrease in yield & lower root/shoot ratio at lower pHs than control (pH 5.6)	-ditto-
-ditto-	-ditto-	-ditto-	9	-ditto-	-ditto-	'Limestone' bibb lettuce	Yield & growth unaffected by pH; lower root growth at pH 3.0	-ditto-
-ditto-	-ditto-	-ditto-	22	-ditto-	-ditto-	'Italian Green Sprouting' broccoli	25% lower market yield at pH 3 than pH 5.6	-ditto-
-ditto-	-ditto-	-ditto-	72	-ditto-	-ditto-	'Newport'	Market yield & growth unaffected by pH	-ditto-

Acid Rain Characteristics						Vegetation (soil)	Effect	Reference
pH	SO_4^{++} -µg/L-	NO_3^- -µg/L-	Events	Rate -cm/h-	Duration -h/event-			
						grass		
-ditto-	-ditto-	-ditto-	51	-ditto-	-ditto-	'Golden Acre' cabbage	Market yield & growth unaffected by pH	-ditto-
-ditto-	-ditto-	-ditto-	44	-ditto-	-ditto-	'Danvers Half Long' carrot	27-45% lower market yield & decreased shoot weight at pH ≤ 4	-ditto-
-ditto-	-ditto-	-ditto-	23	-ditto-	-ditto-	'Early Snowball' cauliflower	Yield unaffected or greater at lower pHs than control (pH 5.6)	-ditto-
-ditto-	-ditto-	-ditto-	20	-ditto-	-ditto-	'Golden Midget' corn	Yield & growth unaffected by pH	-ditto-
3.0-5.6	530-98 070	740	59	-ditto-	-ditto-	'Alta' fescue	Market yield unaffected; decreased root growth	Cohen et al., 1981; Lee et al., 1981
-ditto-	-ditto-	-ditto-	28	-ditto-	-ditto-	'Marvel' green pea	Market yield & growth unaffected by pH	-ditto-
-ditto-	-ditto-	-ditto-	14	-ditto-	-ditto-	'So. Giant Curled' mustard green	Lower market yield at pH 4 & 3; yield unaffected at pH 3.5 compared to control (pH 5.6)	-ditto-
-ditto-	-ditto-	-ditto-	38	-ditto-	-ditto-	'California Wonder' green pepper	Yield unaffected or greater than that at pH 5.6	-ditto-
-ditto-	-ditto-	-ditto-	48	-ditto-	-ditto-	'Cayuse' oats	Market yield & growth unaffected by pH	-ditto-
-ditto-	-ditto-	-ditto-	65	-ditto-	-ditto-	'Sweet Spanish' onion	Market yield & growth unaffected by pH	-ditto-
-ditto-	-ditto-	-ditto-	35	-ditto-	-ditto-	'Potomac' orchardgrass	Yield unaffected or greater than that at pH 5.6	-ditto-
-ditto-	-ditto-	-ditto-	52	-ditto-	-ditto-	'White Rose' potato	8% lower market yield at pH 3 than pH 5.6	-ditto-
-ditto-	-ditto-	-ditto-	12	-ditto-	-ditto-	'Cherry Belle' radish	Lower market yield at pH ≤3 than pH 5.6	-ditto-
-ditto-	-ditto-	-ditto-	56	-ditto-	-ditto-	'Kenland' red clover	Market yield & growth unaffected by pH	-ditto-

Acid Rain Characteristics						Vegetation (soil)	Effect	Reference
pH	SO_4^{++} -µg/L-	NO_{3-} -µg/L-	Events	Rate -cm/h-	Duration -h/event-			
-ditto-	-ditto-	-ditto-	14	-ditto-	-ditto-	'Improved Thick Leaf' spinach	Growth & yield unaffected by pH; lower root/shoot ratio than control (pH 5.6)	-ditto-
-ditto-	-ditto-	-ditto-	58	-ditto-	-ditto-	'Linn' ryegrass	Yield unaffected; lower root growth at lower pH	-ditto-
3.2-5.6	600-30700	830-750	16	1.64	0.67	'Blue Lake 274' bush bean	No effect of pH on pod weight	Johnston et al., 1982
2.0-4.7				2.55 cm/wk	75d	Jack pine seedlings (Grayling sand)	45-95% mortality of seedlings at pH 2.5 & 2-13% in other treatments;	MacDonald et al., 1986
2.6-5.0			4-10	1.0	1-2	'Cherry Belle' radish	Reduced mass of hypocotyls at pH 3.4 than control (pH 5.6); No effect of anion composition of rain on shoot or hypocotyl mass	Jacobson, et al., 1986
2.6-5.6			1	10	0.025-1	'Pioneer3747' com	Reduced germination of pollen on silks exposed to pH ≤4.6 regardless of acidifying agent	Wortheim & Craker, 1987
2.5-5.6				6.7		Winter barley; White clover; Rye mass	Leaf lesion in clover after 18 wk at pH 2.5; reduced barley & clover yield at pH < 5.6; rye grass shoot yield highest at pH 2.5	Ashenden & Bell, 1987
2.6-5.0		.	10	1.0	1	'Saxafire' & 'Cherry Belle' radish	Reduced growth at pH 2.6; hypocotyl growth unaffected by $S0_4^{-2}/NO_{3-}$ ratio; fertilization increased shoot grow at all pHs	Jacobson et al., 1987a
2.6-5.4						'Patio Pick' & 'Peppi' cucumber	Visible necrosis at pH ≤ 3.4; no significant reduction in vegetative or reproductive tissue at pH 2.6; no reduction in fruit number or weight	Jacobson et al., 1987b

Acid Rain Characteristics						Vegetation (soil)	Effect	Reference
pH	SO_4^{++} -µg/L-	NO_3^- -µg/L-	Events	Rate -cm/h-	Duration -h/event-			
2.6-5.6				0.2		'Prince' Dwarf beans 'Rafal' rape, 'Meteor' pea, 'Maris bead' field bean	Droplet leaf contact angle decreased at pH ≤ 4.6 compared to control (pH 5.6); increased retention of rain on leaves at pH ≤ 4.6	Percy & Baker, 1988
3-4 & 5.6			25	0.99-1.1	0.13-0.15	'Con Amore' beans (Standard fertilized soil ED73; sand)	Decrease in fresh wt., dry wt., & fruit production in soil grown plants at pH 3-4 rain	Adros et al., 1988
2.5-5.6			520	6.7	0.08-0.12	Silver birch (Brown earth, brown earth w/ gleying, podzol with high available Al, brown sand w/ free $CaCO_3$, dune top sand, John InnesNo.2	Visible leaf injury after 18 wk of exposure to pH 2.5 rain in all soil types; symptoms less apparent later in the growing season; no significant interaction of soil and rain treatment on plant height	Ashenden & Bell, 1988
-ditto-			-ditto-	-ditto-	-ditto-	Sitka spruce (same as above)	Visible leaf injury after 20 wk of exposure to pH 2.5 rain; 16-30% plant mortality after 2 yr of exposure	-ditto-

Table 14. pH Criteria for Irrigation Water Supply from Various Jurisdictions

Criteria Statement	Criteria Value (pH)	Jurisdiction	Date	Reference
pH 4.5 to 9.0 in irrigation water should not present problem	4.5 - 9.0	Australia	1974	Hart, 1974
Water with pH in the range of 4.5 to 9.0 should be usable provided care is taken to detect the development of harmful indirect effects	4.5 - 9.0	U.S. EPA	1973	U.S. EPA, 1973
Recommended pH in water for spray irrigation of field crops: 5.5-8.5 as the 95 percentile range & 4.5-9.0 as the 99 percentile range	5.5 - 8.5 (90th percentile) 4.5 - 9.0 (99th percentile)	United Kingdom	1983	Anglian Water Authority, 1983
pH of irrigation water should not be <5. 0 or>9.0	*5.0* - 9.0	Alaska	1979	ADEC, 1979
pH 6-8.5 is the acceptable range for intensive horticultural crop production where irrigation is the sole source of water; the acceptable range for field crops is 5.0-9.0 where irrigation is used to supplement natural precipitation	6.0 - 8.5 (horticultural crops) 5.0 - 9.0 (field crops)	Manitoba	1983	MDEWSH, 1983

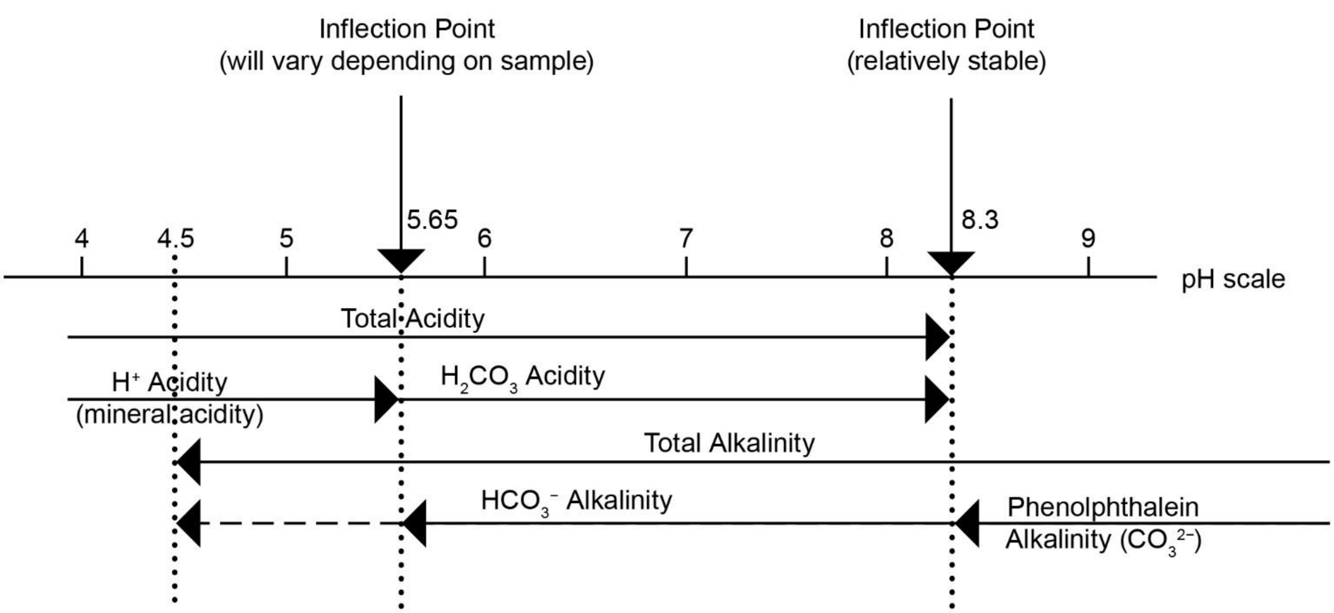


Figure 1. pH Scale with Acidity and Alkalinity Terminology.

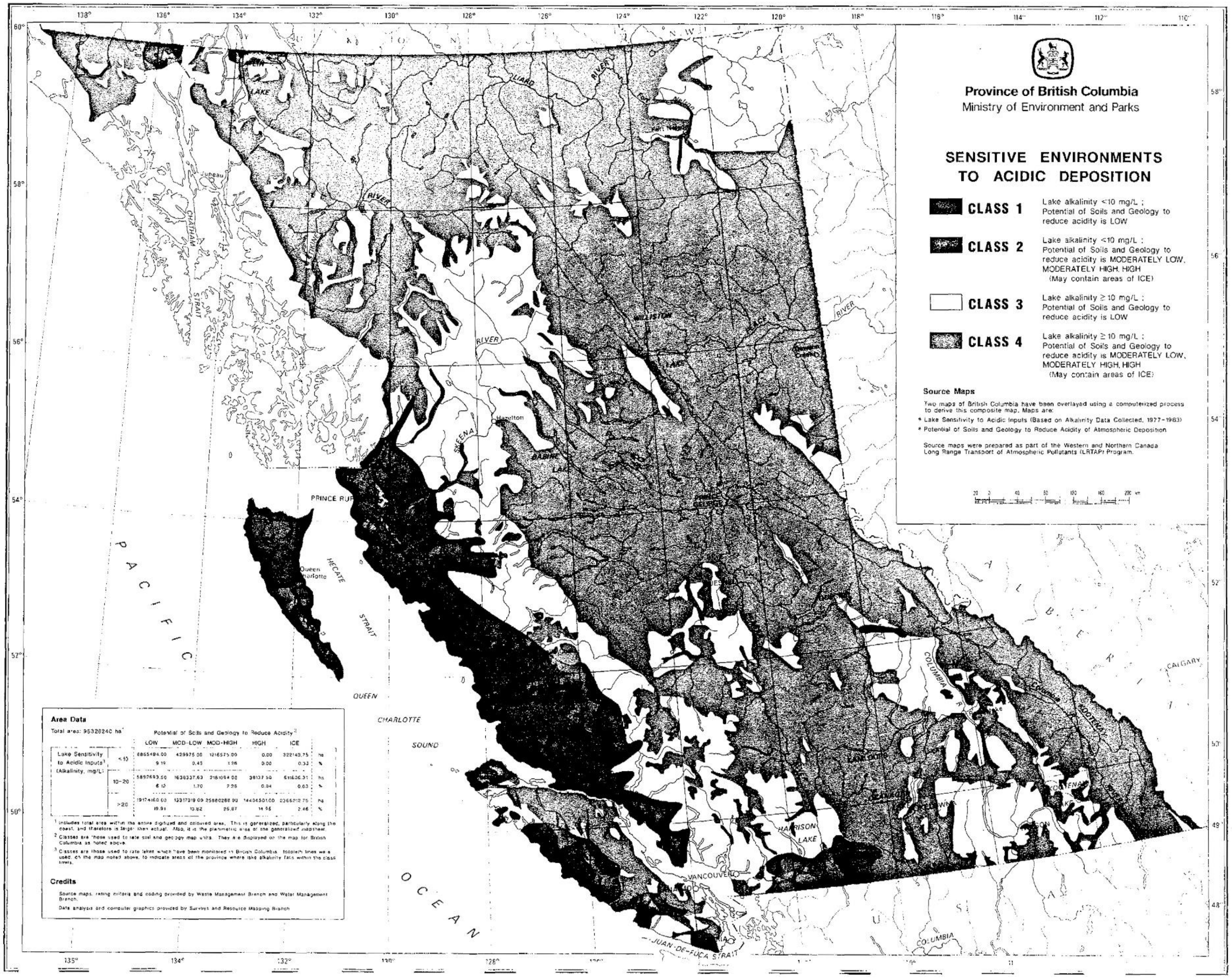


Figure 2. Sensitive Environments to Acidic Deposition in B.C.

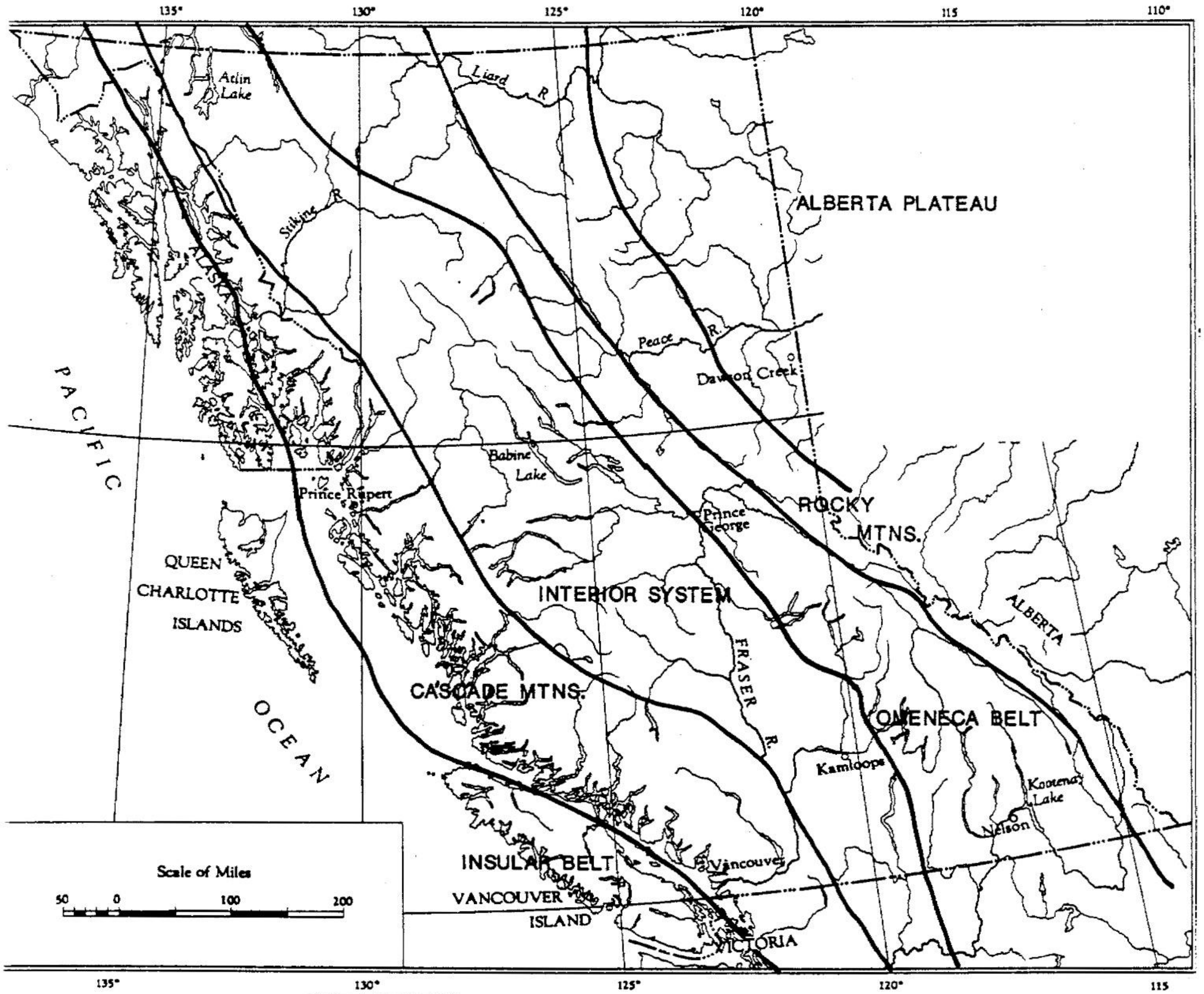


Figure 3. Tectonic Regions in British Columbia (From Farley,1979)

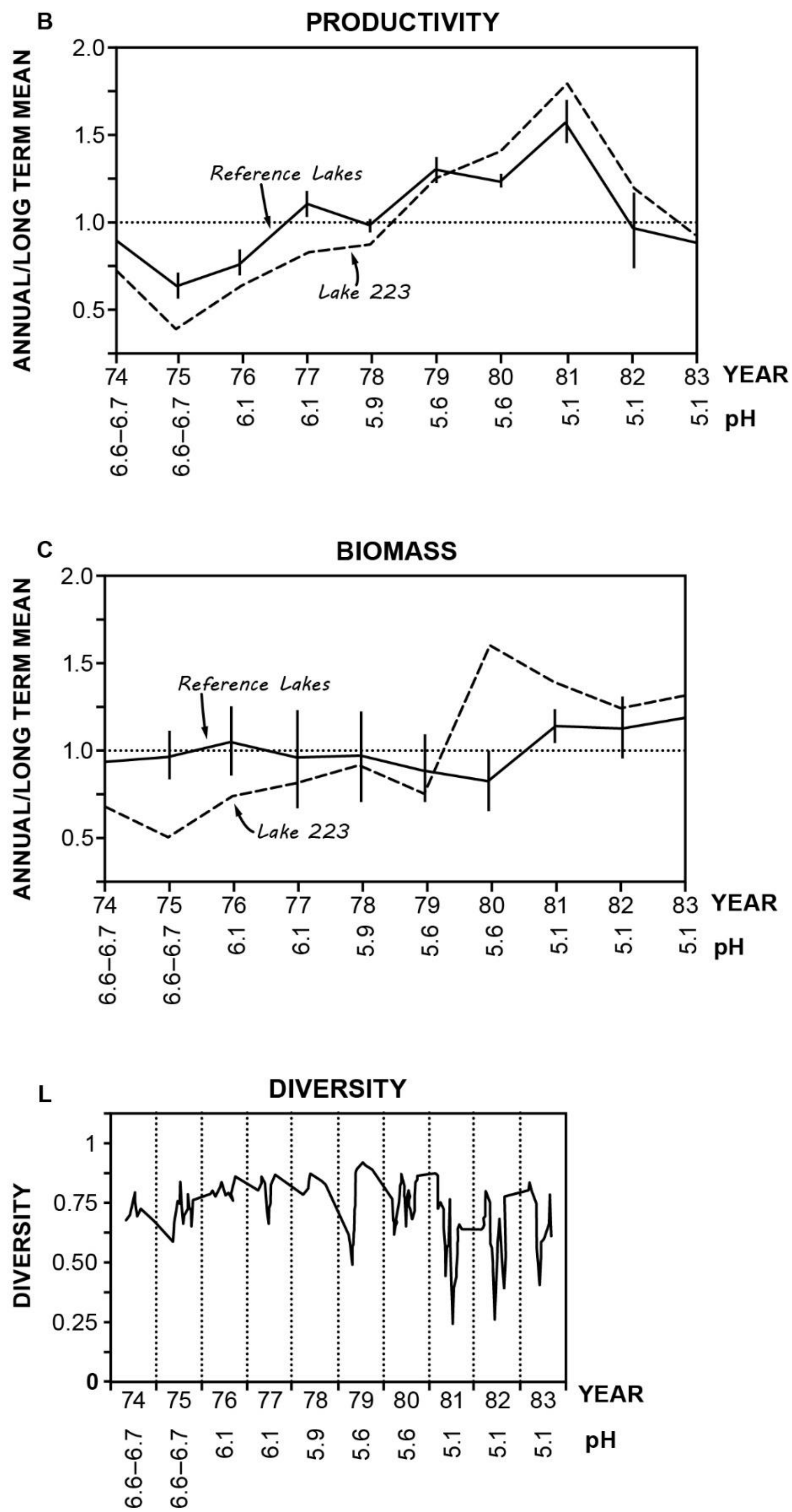
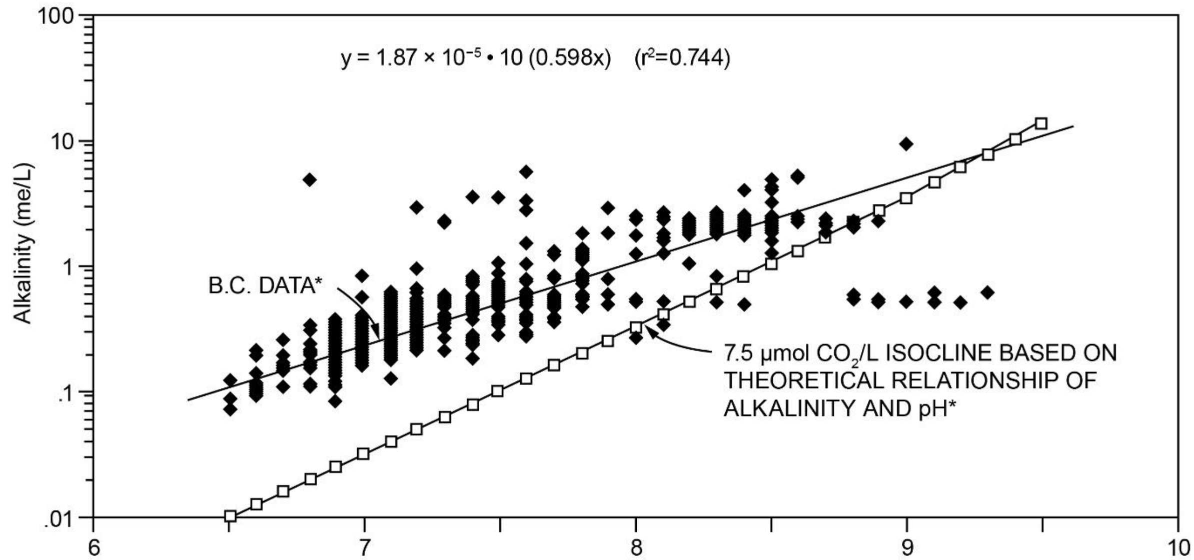


Figure 4. Phytoplankton Productivity, Biomass, and Diversity in Artificially. Acidified ELA Lake 223. (From Schindler et al.,1985)



* CORRECTED FOR TEMPERATURE : 1 ATMOSPHERE PRESSURE ASSUMED.

* SEE APPENDIX 2 FOR CALCULATIONS.

Figure 5. Changes in Carbon Dioxide Concentration as a Function of pH and Alkalinity: Theoretical Relationship and Ambient Data from British Columbia.

*Corrected for Temperature: 1 Atmosphere Pressure Assumed.
*See Appendix 2 For Calculations.

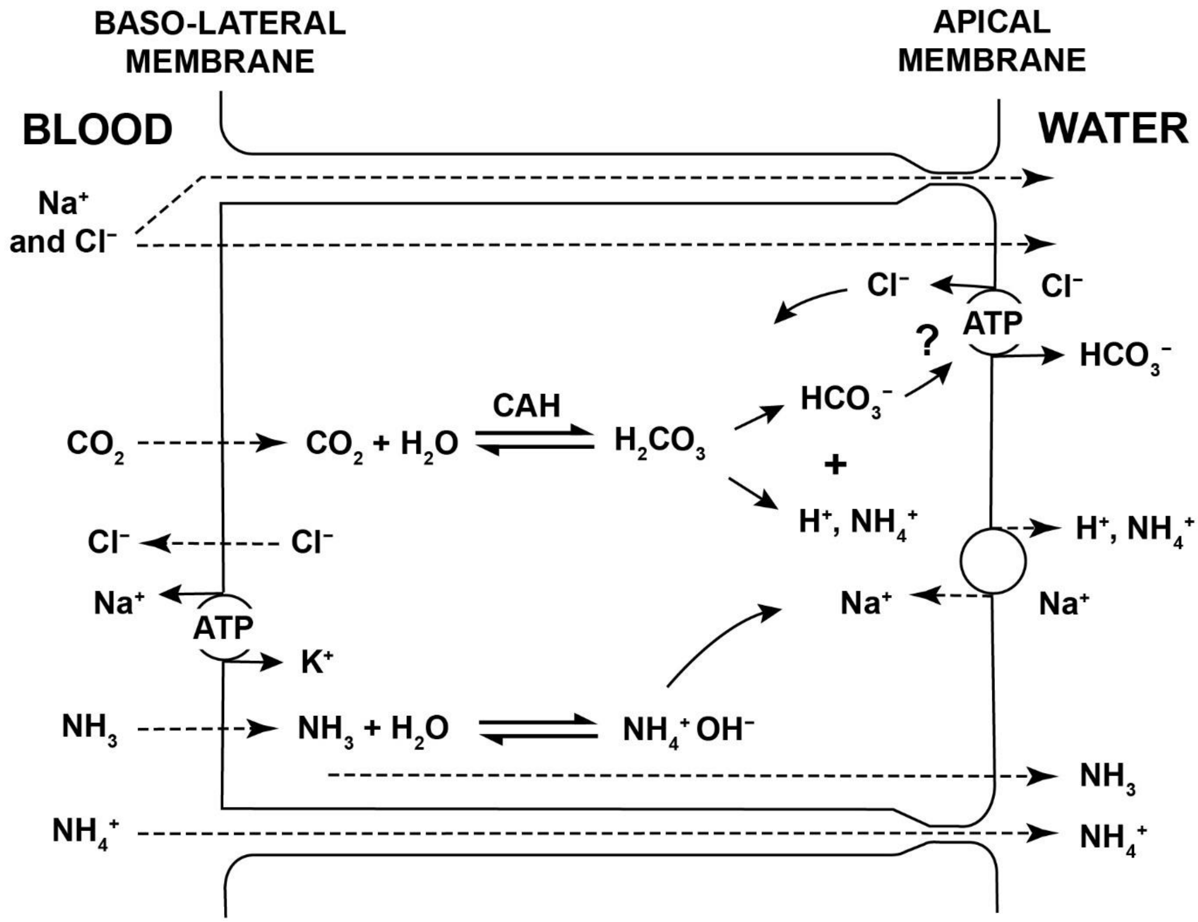


Figure 6. Active Transport Mechanisms in a Fish Gill. (From McDonald,1983)

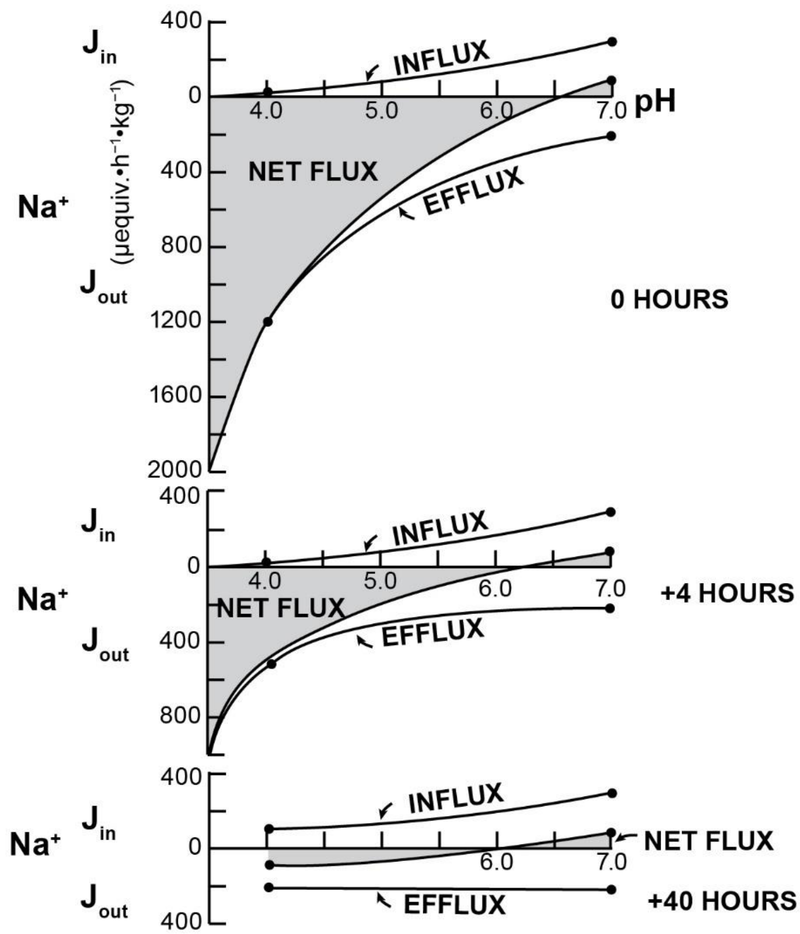


Figure 7. Sodium Influx, Efflux, And Net Flux in Rainbow Trout at pH 7 And pH 4 as a Function of Time in Hardwater. Ca 2+ = 101 mg/L (From McDonald et al.,1983)

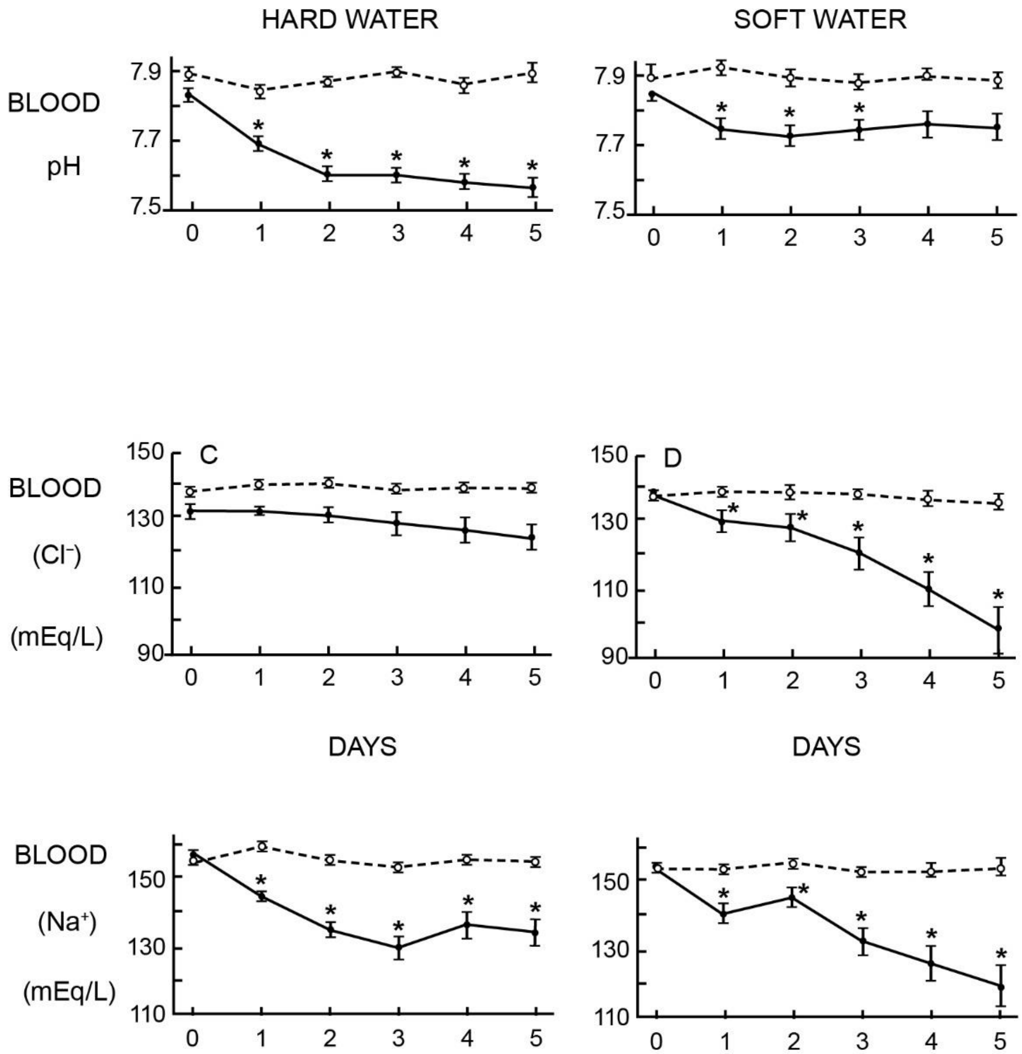


Figure 8. A Comparison of the Blood Ionic Responses of Rainbow Trout Subjected to 5 Days of Acid Exposure in Hard and Soft Water. (From Wood and McDonald,1982)

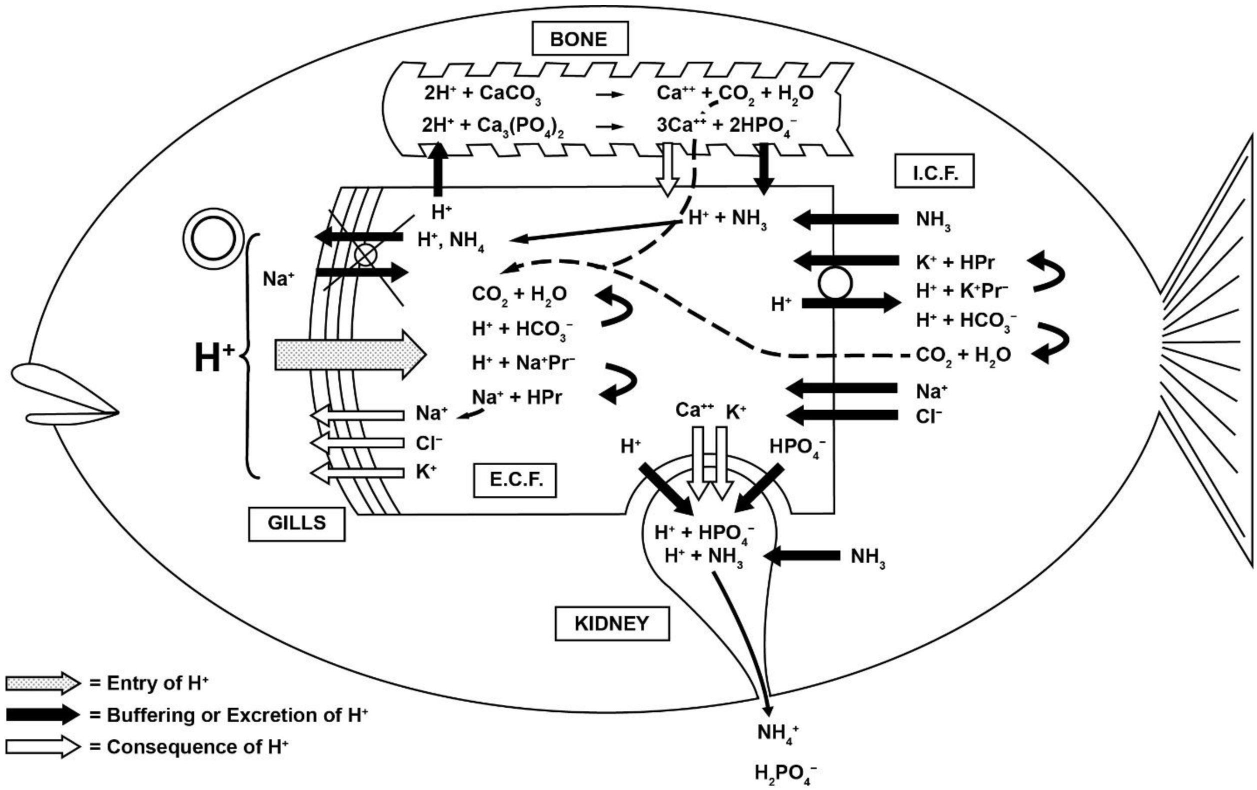


Figure 9. Proposed Model for the Effects of Environmental Acid Exposure on the Acid-Base and Ionoregulatory Physiology of the Rainbow Trout. (From Wood And McDonald, 1982)

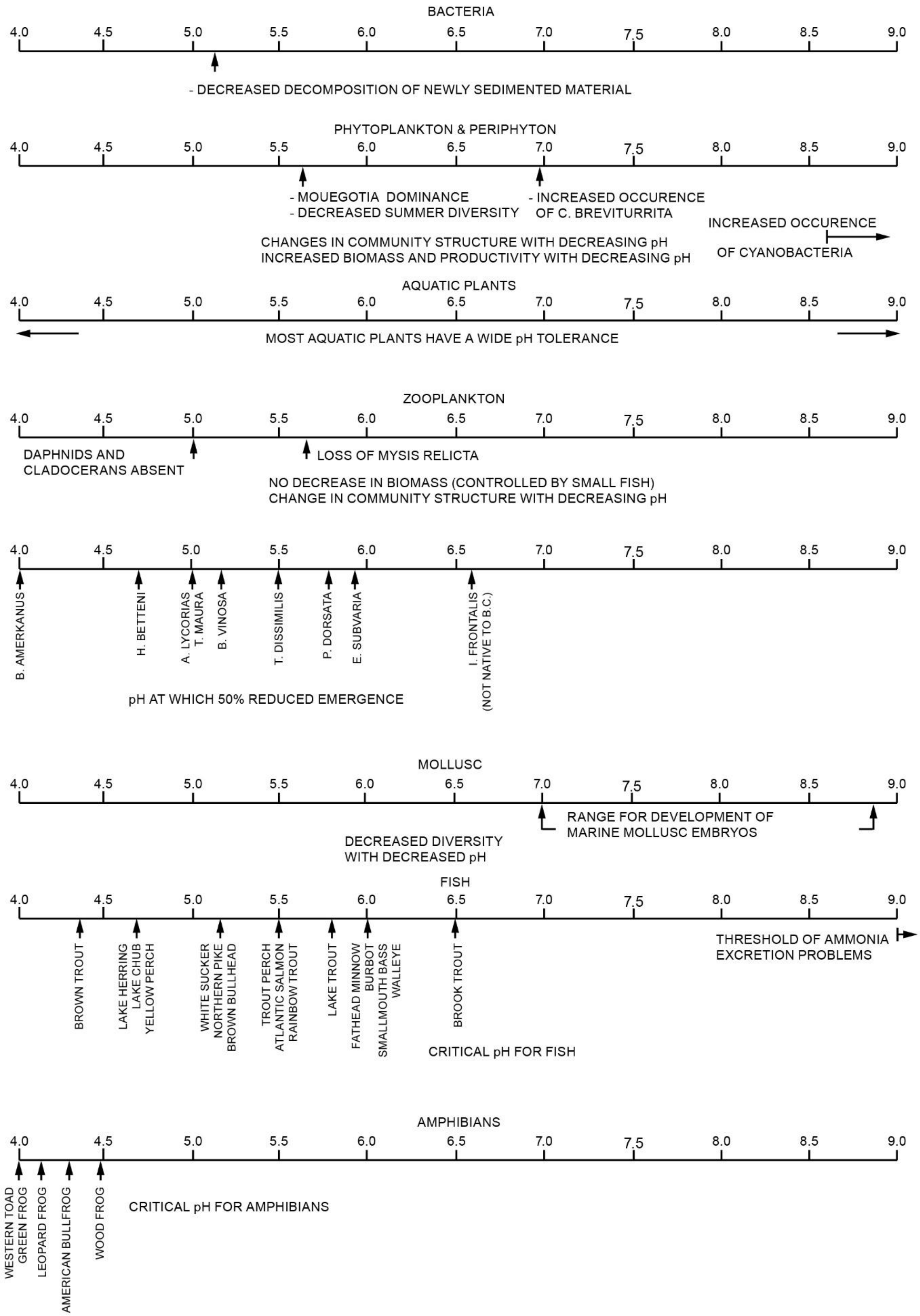


Figure 10. Summary of pH Effects on Aquatic Life.

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9. APPENDIX

Appendix 1. Freshwater Fish of British Columbia (from Cannings and Harcombe 1990)

Carps and Minnows	Chiselmouth	*Acrocheilus alutaceus*
	†Goldfish	*Carassius auratus*
	Northern Redbelly Dace	*Chrosomus eos*
	Finescale Dace	*Chrosomus neogaeus*
	Lake Chub	*Couesius plumbeus*
	Carp	*Cyprinus carpio*
	Brassy Minnow	*Hybognathus hankinsoni*
	Peamouth Chub	*Mylocheilus caurinus*
	Emerald Shiner	*Notropis atherinoides*
	Spottail Shiner	*Notropis hudsonius*
	Fathead Minnow	*Pimephales promelas*
	Flathead Chub	*Platygobio gracilis*
	Northern Squawfish	*Ptychocheilus oregonensis*
	Longnose Dace	*Rhinichthys cataractae*
	Leopard Dace	*Rhinichthys falcatus*
	Speckled Dace	*Rhinichthys osculus*
	Umatilla Dace	*Rhinichthys umatilla*
	Redside Shiner	*Richardsonius balteatus*
	Pearl Dace	*Semotilus margarita*
	Trench	*Tinca tinca*
Catfishes	†Black Bullhead	*Ictalurus melas*
	†Brown Bullhead	*Ictalurus nebulosus*
Cods	Burbot	*Lota lota*
Herrings	†American Shad	*Alosa sapidissima*
Lampreys	River Lamprey	*Lampetra ayresi*
	Lake Lamprey	*Lampetra macrostoma*
	Brook Lamprey	*Lampetra richardsoni*
	Pacific Lamprey	*Lampetra tridentata*
Mooneyes	Goldeye	*Hiodon alosoides*
Perches	Yellow Perch	*Perea flavescens*
	Walleye	*Stizostedion vitreum*
Pike	Northern Pike	*Esox lucius*
Salmonids	Chinook Salmon	*Oncorhynchus tshawytscha*
	Chum Salmon	*Oncorhynchus keta*
	Coho Salmon	*Oncorhynchus kisutch*
	Cutthroat Trout	*Oncorhynchus clarki*
	Pink Salmon	*Oncorhynchus gorbuscha*
	Rainbow Trout	*Oncorhynchus mykiss*
	Sockeye Salmon	*Oncorhynchus nerka*
	††Atlantic Salmon	*Salmo salar*
	†Brown Trout	*Salmo trutta*
	Bull Trout	*Salvelinus confluentus*
	†Brook Trout	*Salvelinus fontinalis*
	Dolly Varden Char	*Salvelinus malma*

	Lake Trout	*Salvelinus namaycush*
	Cisco	*Coregonus artedii*
	Lake Whitefish	*Coregonus clupeaformis*
	Broad Whitefish	*Coregonus nasus*
	Least Cisco	*Coregonus sardinellla*
	Pygmy Whitefish	*Prosopium coulteri*
	Round Whitefish	*Prosopium cylindraceum*
	Mountain Whitefish	*Prosopium williamsoni*
	Inconnu	*Stenodus leucichthys*
	Arctic Grayling	*Thymallus arcticus*
Sculpins	Coastrange Sculpin	*Cottus aleuticus*
	Prickly Sculpin	*Cottus asper*
	Mottled Sculpin	*Cottus bairdi*
	Slimy Sculpin	*Cottus cognatus*
	Shorthead Sculpin	*Cottus confusus*
	Torrent Sculpin	*Cottus rhotheus*
	Spoonhead Sculpin	*Cottus ricei*
	Staghorn Sculpin	*Leptocottus armatus*
Smelts	Longfin Smelt	*Spirinchus thaleichthys*
	Eulachon	*Thaleichthys pacificus*
Sticklebacks	Brook Stickleback	*Culaea inconstans*
	Threespine Stickleback	*Gasterosteus aculeatus*
	Ninespine Stickleback	*Pungitius pungitius*
Sturgeons	Green Sturgeon	*Acipenser medirostris*
	White Sturgeon	*Acipenser transmontanus*
Suckers	Longnose Sucker	*Catostomus catostomus*
	Brigelip Sucker	*Catostomus columbianus*
	White Sucker	*Catostomus commersoni*
	Largescale Sucker	*Catostomus macrocheilus*
	Mountain Sucker	*Catostomus platyrhynchus*
Sunfishes	†Pumpkinseed	*Lepomis gibbosus*
	†Smallmouth Bass	*Micropterus dolomieui*
	†Largemouth Bass	*Micropterus salmoides*
	† Black Crappie	*Pomoxis nigromaculatus*
Troutperches	†Troutperch	*Percopsis omiscomavcus*

† Introduced species

†† Introduction unsuccessful in the Cowichan River, but potential reintroduction exists from salmon farm hatchery and smolt operations (Hall, pers. comm.).

Appendix 2. Protocol for the Determination of Carbon Dioxide Content of Freshwater (from Kelts and Hsu, 1978)

Parameters to be sampled: Alkalinity (total and phenolphthalein), and pH (preferably field measurement) at 1 metre. Note that a rigorous QA/QC program should accompany these measurements to determine accuracy and precision.

Formula: X = (aH2fK1(H+(2*K2)))/1OO

X = micromoles of H_2CO_3 (includes free CO^2)

a = milliequivalents of carbonate alkalinity (see formula below)

H = hydrogen ion activity equivalence (see Table A-2.1)

K_1 = First dissociation constant of carbonic acid ($4.3*10^{-7}$)(@ 25°C)

K_2 = Second dissociation constant of carbonic acid ($5.61*10^{-11}$)(@25°C)

(note that K_1 and K_2 are temperature dependent)

alkalinity (me/L) = ((T−alkalinity−(2 * P−alkalinity))*1.22)*0.164 + (P− alkalinity*0.0333)

Table A-2.1. pH-Hydrogen Ion Activity Equivalence

pH	H^+ equivalence	pH	H^+ equivalence
6.5	$3.16 * 10^{-7}$	8.0	$1.00 * 10^{-8}$
6.6	$2.51 * 10^{-7}$	8.1	$7.94 * 10^{-9}$
6.7	$1.99 * 10^{-7}$	8.2	$6.31 * 10^{-9}$
6.8	$1.58 * 10^{-7}$	8.3	$5.01 * 10^{-9}$
6.9	$1.26 * 10^{-7}$	8.4	$3.98 * 10^{-9}$
7.0	$1.00 * 10^{-7}$	8.5	$3.16 * 10^{-9}$
7.1	$7.94 * 10^{-8}$	8.6	$2.51* 10^{-9}$
7.2	$6.31 * 10^{-8}$	8.7	$1.99 * 10^{-9}$
7.3	$5.01 * 10^{-8}$	8.8	$1.58 * 10^{-9}$
7.4	$3.98 * 10^{-8}$	8.9	$1.26 * 10^{-9}$
7.5	$3.16 * 10^{-8}$	9.0	$1.00 * 10^{-9}$
7.6	$2.51 * 10^{-8}$	9.1	$7.94 * 10^{-10}$
7.7	$1.99 * 10^{-8}$	9.2	$6.31 * 10^{-10}$
7.8	$1.58 * 10^{-8}$	9.3	$5.01 * 10^{-10}$
7.9	$1.26 * 10^{-8}$	9.4	$3.98 * 10^{-10}$
		9.5	$3.16 * 10^{-10}$