6.0 REGIONAL-LEVEL ASSESSMENT OF 2004 RESULTS

This part of the RAMP 2004 Technical Report presents regional assessments of the status of aquatic environmental resources and the possible influence of oil sands developments at the level of the RAMP FSA.

6.1 CLIMATE AND HYDROLOGY

6.1.1 Summary of Hydrologic Conditions in the Athabasca River Mainstem

All hydrologic measurement endpoints for the Athabasca River mainstem were determined to be lower than what they would have been in the absence of oil sands development activities (Table 6.1-1). Magnitude of change varied from -0.2% in the case of 2004 maximum daily discharge to -1.7% in the case of mean 2004 winter discharge, because the generally constant withdrawals are proportionately larger during low-flow rather than high-flow periods. This should be regarded as a conservative estimate because clearing and de-watering did occur in some parts of the RAMP FSA in 2004 (Section 2) which likely had an ameliorating effect on Athabasca mainstem flows. These changes would have been assessed as "Negligible" in most oil sands EIAs (Appendix A). Therefore, based on the available hydrological and oils sands development information, it appears that changes in hydrological conditions up to and including 2004 have been negligible in the Athabasca River mainstem.

Table 6.1-1 Summary of hydrologic conditions of the Athabasca River mainstem in 2004 with respect to oil sands developments.

Measurement Endpoint	% Change	Assessment
Mean open-water (1 May to 31 October) season discharge	-0.5%	Negligible
Mean winter (1 November to 31 March) discharge	-1.7%	Low
Annual maximum daily discharge	-0.2%	Negligible
Open-water season minimum daily discharge	-1.1%	Low

6.1.2 Regional Assessment of Hydrologic Conditions at the RAMP FSA Level

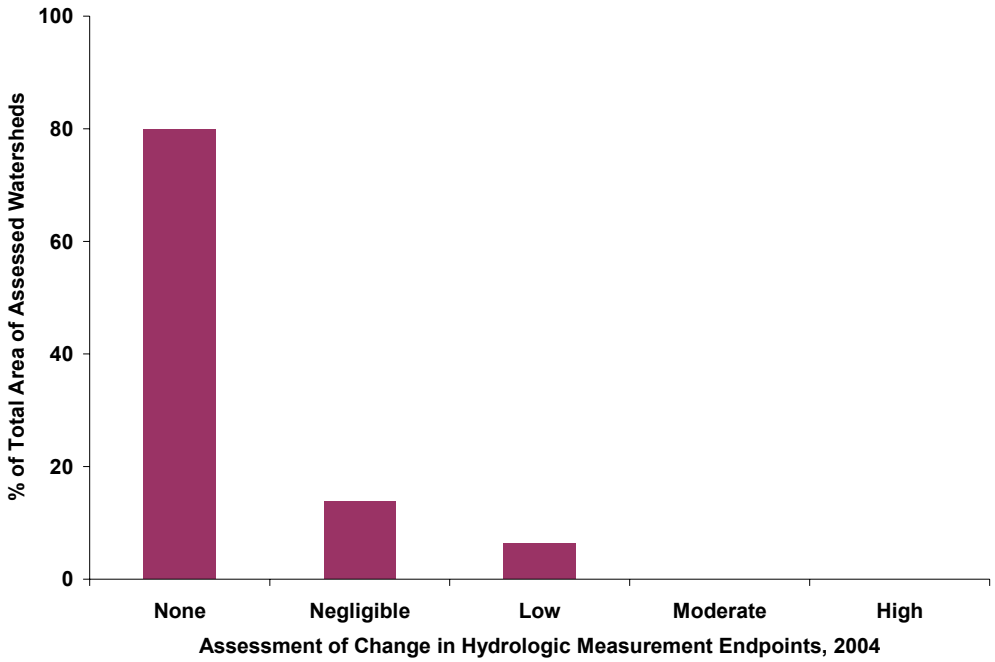
Changes in hydrologic conditions for each exposed watershed in 2004 that may be related to oil sands development activities were assessed using four hydrologic measurement endpoints, specifically:

- mean open-water (1 May to 31 October) season discharge;
- mean winter (1 November to 31 March) discharge;
- annual maximum daily discharge; and
- open-water season minimum daily discharge.

Magnitude of change in each exposed watershed in each of these measurement endpoints was classified using impact criteria presented in various oil sands EIAs, namely: Negligible (<± 5%); Low (± 5 to 10%); Moderate (± 10 to 30%); or High (> 30%). The hydrologic change in each reference watershed was assessed as None. These qualitative assessments were aggregated to the regional level by calculating the total area of watersheds in the RAMP FSA in each of the assessment classes for each of the four hydrologic measurement endpoints.

The assessments at the individual watershed level were the same for all hydrologic measurement endpoints in each watershed and so only one set of regional results on the basis of hydrologic measurement endpoints is provided (Figure 6.1-1). In 2004, the surface water hydrology of the RAMP FSA was relatively unchanged from what it would have been in the absence of oil sands developments; 80% of the area of the RAMP FSA was experienced no hydrologic effect, while 14% was assessed to have experienced a Negligible effect, and 6% a Low effect. Therefore there has been little change in surface water hydrology throughout the RAMP FSA in relation to oil sands developments.

Figure 6.1-1 Regional assessment of hydrologic changes in the RAMP FSA with respect to oil sands developments, 2004.



6.2 WATER QUALITY

6.2.1 Summary of Water Quality Conditions in the Athabasca River Mainstem

Water quality in the Athabasca River mainstem in fall 2004 was influenced strongly by higher-than-average flows and associated increased sediment loads. Total suspended solids were relatively high at all mainstem stations, although generally within historical

fall values observed upstream of Fort McMurray. Other water quality variables typically associated with TSS, including total aluminum, total copper, total iron, total lead and total phosphorous, typically also were high at all stations in fall 2004, often exceeding CCME water quality guidelines for the protection of aquatic life. Concentrations of these measurement endpoints were high at all stations in 2004, both upstream and downstream of oil sands developments. Dissolved species of these metals and nutrients did not occur at similarly high levels, indicating that these high total metal and total phosphorous values related to high levels of suspended materials in the river in 2004.

Ion balance characteristics generally vary within a narrow range for all stations regardless of sampling year or longitudinal location along a river.

In summary for 2004, there were no discernible or detectable water quality effects of oil sands development activities in the Athabasca River mainstem in 2004, based on available water quality and oil sands development information.

6.2.2 Regional Assessment of Water Quality Conditions at the RAMP FSA Level

The regional assessment of the status of water quality conditions in the RAMP FSA was conducted using the watershed-level results of water quality conditions compared against the regional baselines applied to each watershed; seven selected water quality measurement endpoints were summarized:

- Total suspended solids;
- Total dissolved solids;
- Dissolved phosphorous;
- Total nitrogen;
- Total aluminum;
- Total boron; and
- Total mercury (ultra-trace).

A count was made of the number of times these seven water quality measurement endpoints in 2004 fell within the following regional baseline ranges:

- Within the 25th and 75th percentiles (i.e., the central 50%) of all relevant regional baseline values (i.e., within the Inter-Quartile Range, or IQR) measured by RAMP from 1997 to 2004;
- Outside the IQR but within the 5th and 95th percentiles (i.e., the central 90%) of relevant regional baseline values; or
- Outside the 5th percentile or 95th percentiles of relevant regional baseline values.

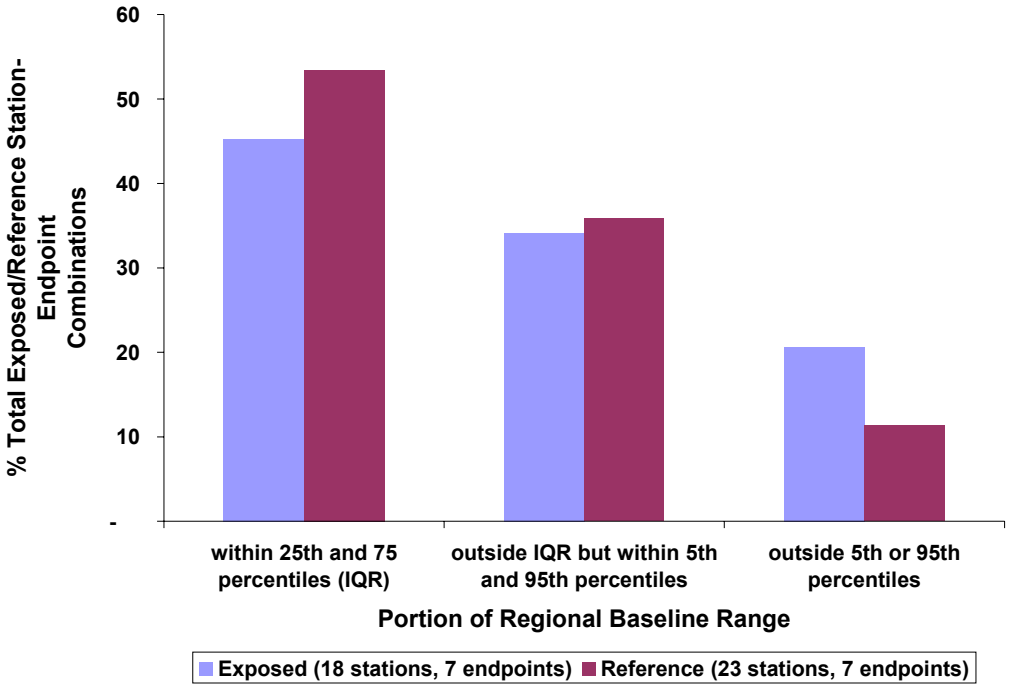
Counts were made for all water quality stations sampled in 2004 in the RAMP FSA; separate counts were made for stations designated as exposed and for stations designated

as reference. The distribution (i.e., proportion) of counts in the exposed stations was then compared to the distribution of counts in the reference stations.

The distribution of counts in exposed and reference stations (Figure 6.2-1) shows a somewhat higher percentage of water quality measurement endpoints in 2004 that fell outside the central 90% of regional baseline values in exposed stations (21%) than at reference stations (11%). Percentages of observations that fell within the central 50% of observations (i.e., the Inter-Quartile Range) were similar for exposed (45%) and reference (53%) stations. Observations that fell outside the Inter-Quartile Range, but within the 5th and 95th percentiles, also were similar for exposed (34%) and reference (36%) stations.

These distributions of results in exposed and reference stations are qualitatively similar and statistically identical (p= 0.5, Kolmogorov-Smirnoff two-sample test with unequal sample sizes), leading to the conclusion that, in 2004, there was little or no difference in water quality between areas of the RAMP FSA designated as exposed and areas designated as reference.

Figure 6.2-1 Distribution of water quality measurement endpoints in RAMP FSA according to position in regional baseline range.



6.3 SEDIMENT QUALITY

6.3.1 Summary of Sediment Quality Conditions in the Athabasca River Mainstem

Sediment quality in the Athabasca River mainstem has been highly variable during RAMP sampling since 1997, between stations in a given year and within stations between years. Sediments in the Athabasca River mainstem typically are composed of high

amounts of sand with variable amounts of silt and clay. Cluster analysis of sediment quality characteristics at mainstem stations from 1997 to 2004 indicated that sediment characteristics—including particle size, organic carbon, metals and PAH concentrations—typically are highly variable between stations and between years.

Although highly variable, sediment quality in the Athabasca River in 2004 was within the range of previous years' observations. Carbon-normalized concentrations of total recoverable hydrocarbons, total PAHs and naphthalene since 1997 have not exhibited any consistent trends in the Athabasca River since 1997.

6.3.2 Regional Assessment of Sediment Quality Conditions at the RAMP FSA Level

The regional assessment of the status of sediment quality conditions in the RAMP FSA was conducted in a similar fashion to the regional water quality assessment (above). Watershed-level results of sediment quality conditions were compared against the regional baselines applied to each watershed, and three selected sediment quality measurement endpoints were summarized:

- Total recoverable hydrocarbons (normalized to total organic carbon);
- PAHs (normalized to total organic carbon); and
- naphthalene.

A count was made of the number of times these three sediment quality measurement endpoints in 2004 fell within three regional baseline ranges:

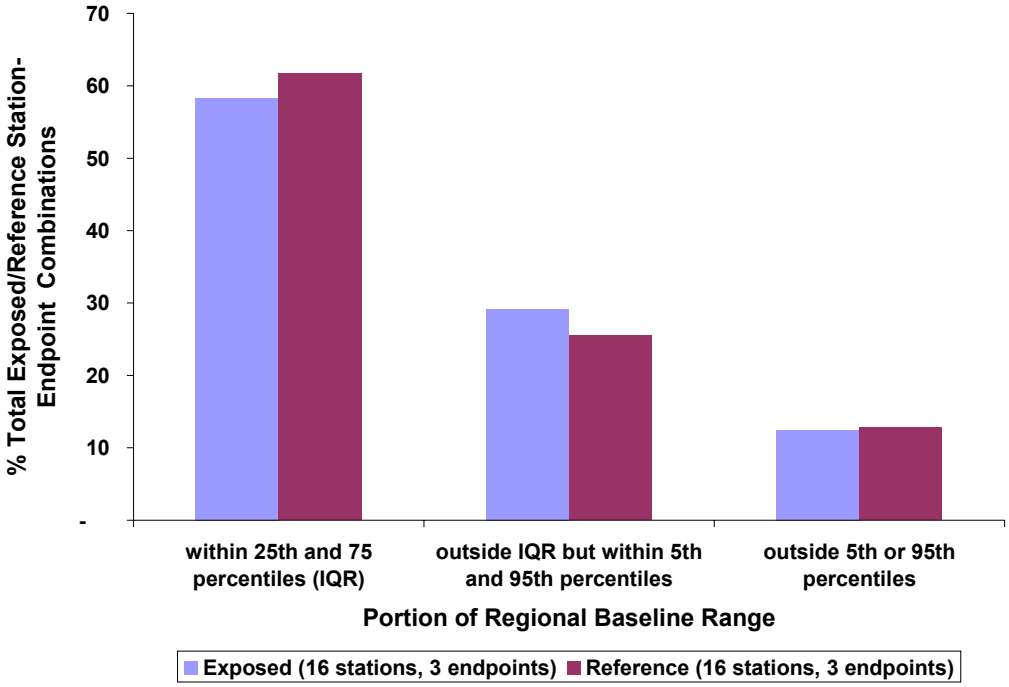
- Within the 25th and 75th percentiles (i.e., the central 50%) of all relevant regional baseline values (i.e., within the Inter-Quartile Range, or IQR) measured by RAMP from 1997 to 2004;
- Outside the IQR but within the 5th and 95th percentiles (i.e., the central 90%) of relevant regional baseline values; or
- Outside the 5th percentile or 95th percentiles of relevant regional baseline values.

Counts were made for all sediment quality stations sampled in 2004 in the RAMP FSA; separate counts were made for stations designated as exposed and for stations designated as reference. The distribution (i.e., proportion) of counts in the exposed stations was then compared to the distribution of counts in the reference stations.

The distribution of counts in exposed and reference stations (Figure 6.3-1) shows that, in 2004, there was practically no difference in the percentage of sediment quality measurement endpoints whose observed values that fell outside the central 90% of regional reference values (i.e., outside the 5th or 95th percentiles) between exposed stations (12.5%) as compared to reference stations (12.8%). A lower percentage of observations from exposed stations (58%) relative to reference station (62%) fell outside the regional reference Inter-Quartile Range but within the 5th and 95th percentiles. Similar percentages of observations from both exposed (29%) and reference (26%) stations fell within the regional reference Inter-Quartile Range.

These distributions of results in exposed and reference stations are qualitatively the same, and are statistically identical (p= 1.0, Kolmogorov-Smirnoff two-sample test with unequal sample sizes). It is concluded that in 2004, there was no difference in sediment quality between areas of the RAMP FSA designated as exposed and areas designated as reference.

Figure 6.3-1 Distribution of sediment quality measurement endpoints in RAMP FSA according to position in regional baseline range.



6.4 BENTHIC INVERTEBRATE COMMUNITIES

6.4.1 Regional Assessment of Benthic Invertebrate Community Conditions at the RAMP FSA Level

The regional assessment of the status of benthic invertebrate community conditions in the RAMP FSA was conducted in a similar fashion to the regional water and sediment quality assessments (above). Watershed-level results of benthic invertebrate community indices were compared against the regional baselines applied to each watershed, and five selected benthic invertebrate community measurement endpoints were summarized:

- Abundance;
- Taxon richness;
- Simpson's Diversity Index;
- Evenness; and
- Percent EPT.

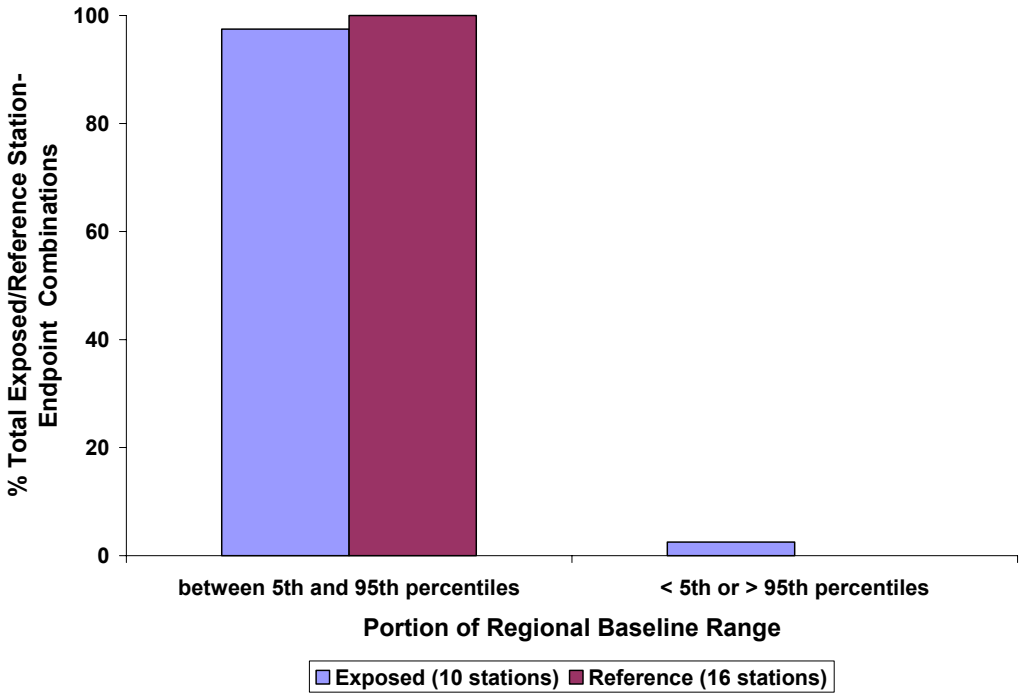
A count was made of the number of times these five benthic invertebrate community measurement endpoints in 2004 fell within two regional baseline ranges:

- Between the 5th and 95th percentiles of the distribution of regional baseline values; or
- Either less than 5th percentile or greater than 95th percentile of the distribution of regional baseline values.

The counts were made for all benthic invertebrate community locations sampled in 2004 in the RAMP FSA; separate counts were made for locations designated as exposed and for locations designated as reference. The distribution (i.e., proportion) of counts in the exposed locations was then compared to the distribution of counts in the reference locations.

In 2004, the percentage of benthic invertebrate community indices whose observed values were greater than 2 standard deviations from their regional baseline median in exposed locations was low and basically the same as for reference stations (Figure 6.4-1). The distributions in exposed and reference stations are qualitatively almost identical, and they are statistically identical as well (p= 1.0, Kolmogorov-Smirnoff two-sample test with unequal sample sizes). It is concluded that in 2004, there was no difference in benthic invertebrate communities between areas of the RAMP FSA designated as exposed and areas designated as reference.

Figure 6.4-1 Distribution of benthic invertebrate community measurement endpoints in RAMP FSA according to position in regional baseline range for similar sites (depositional, erosional) in 2004.



6.5 FISH POPULATIONS

Assessing the status of fish populations at a regional level in the RAMP FSA and possible relationships to oil sands development activities at a regional level is challenging due to the limited spatial coverage of the programs within the Fish Populations component, limited number of years of information gathered and alterations to the sampling design between years for some elements. These factors make it difficult to establish the level of natural variability at the regional level associated with impact parameters or measurement endpoints defined for the Fish Populations component.

6.5.1 Regional Assessment at the RAMP FSA Level of Fish Inventory Results

2004 fish inventory results from the Athabasca River mainstem and the Muskeg River/Jackpine River indicate:

- While there is some species-specific variability in fish population measurement endpoints (i.e., relative abundance and condition factor), there are no significant trends in this regard, and there is little evidence to suggest that characteristics of key indicator fish populations have changed during increasing development in the oil sands region; and

- Species diversity and overall catch when compared to previous RAMP data were higher in the Jackpine Creek and lower in the Muskeg River during the 2004 inventory. However, fish population measurement endpoints (i.e., percent composition, condition factor and size distributions) were similar to those recorded in previous RAMP inventory years, and data analysis results indicate there is little evidence to suggest that these characteristics of key indicator fish populations have changed during increasing development in the oil sands region.

Insufficient data have been collected to date from the Clearwater-Christina Rivers to include results from that watershed here.

Based on results from the Muskeg River (including Jackpine Creek), it may be tentatively concluded that, regionally, fish population parameters in the RAMP FSA, as measured in the RAMP fish inventory programs, exhibit expected natural variability in relative abundance and condition, little of which to date appears to be in relation to oil sands development activities.

6.5.2 Regional Assessment at the RAMP FSA Level of Fish Tissue Results

2004 fish tissue results from the Muskeg/Jackpine Rivers, the Clearwater River, and Winefred Lake indicate uniformly:

- Concentrations of mercury in fish tissues are naturally high in this region, occurring at levels that pose a high risk to subsistence fishers, a variable risk for recreational fishers, and variable risk for general consumers;

- Concentrations of metals (other than mercury) and tainting compounds in tissues of sampled fish generally pose a low risk to human health, with the exception of arsenic in some cases that poses a high risk for subsistence use;

- Tissue mercury concentrations that pose a generally high risk for fish and wildlife; and
- Concentrations of other chemicals in tissues of sampled fish that pose a generally low risk for fish and wildlife.

However, mercury concentrations present in water and sediment in the oil sands development area are generally at or below detection limits. Furthermore, fish tissue mercury concentrations observed in 2004 were similar to those observed historically. These findings indicate that mercury concentrations in fish tissue are naturally high in this region and are not related to oil sands developments.

6.5.3 Regional Assessment at the RAMP FSA Level of Sentinel Species

2004 sentinel species results from the lower Muskeg River and the Steepbank River Lake indicate:

- A virtual absence of YOY at the Steepbank exposure site; and
- Poor YOY survival recorded for both the Steepbank and Muskeg exposure sites.

Because of the limited regional scope of the sentinel species program, it is not possible at this time to extrapolate these results to the level of the RAMP FSA. The 2004 population data do provide some indication of potential effects at two sites designated as exposed, and effort to further quantifying these results and expanding the spatial scope of the sentinel species program is warranted.

6.6 ACID SENSITIVE LAKES

As discussed in Section 3.6.7, analyses of the 2004 monitoring data for the ASL component involved the following tasks:

- Comparisons of the chemical characteristics of the RAMP lakes to the general characteristics of lakes within the oil sands region;
- Calculations of organic anion concentrations and charge densities of dissolved organic materials in each lake;
- The analysis of the contribution of strong acid anions to the acid-base status in each lake;
- Analysis of the degree of buffering attributable to weak organic anions in each lake;
- Calculations of critical loads of acidity for each lake and comparison with modelled PAI; and
- Analysis of potential trends in water quality parameters that would indicate increased acidification.

6.6.1 Comparison of RAMP Lakes to Regional Lake Characteristics.

In a continuation of the analyses started in 2003, the chemical characteristics of the RAMP lakes were compared to those of lakes contained in the database on regional lakes created by the NOxSOx Management Working Group (NSMWG). The NSMWG database contains chemical and hydrological data on 450 lakes within the oil sands region. Additional analyses this year included the statistical testing of the mean chemical parameters in the two lake populations and two visual techniques (box plots and Piper plots) to illustrate graphically the similarities and differences between the two lake populations.

Table 6.6-1 summarizes the chemical characteristics of the 50 RAMP Lakes compared to regional lakes. The detailed chemical data for the RAMP lakes for all years can be found in Appendix I. Included in Table 6.6-1 are the range, mean and median values for each parameter. Significantly different means ($p<0.05$) are indicated by shading.

The RAMP lakes fit well within the ranges of each parameter in the regional lakes. The regional lakes described in Table 6.1-1 and the NSMWG report (WRS 2004) as:

- Exhibiting a large range in pH (4.2 to 9.59; median: 7.71);
- Exhibiting a large range of titration alkalinity (non-detectable to 4797 µeq/L). The major source of acid neutralizing capacity (ANC) are bicarbonates of calcium and magnesium;
- Exhibiting a wide range of conductivity 11 µS/cm to 481 µS/cm (median: 117 µS/cm);
- High in colour and dissolved organic carbon (median: 19.4 mg/L); and
- Unusually high in nutrient content especially in total phosphorus (range: non-detectable – 495 µg/L). Nitrates were often low (median: 2µg/L) except for several individual lakes where concentrations as high as 1860 µg/L were observed.

While the 50 RAMP lakes display similar characteristics to lakes in the regional database, there were distinct differences between the two populations:

- The RAMP lakes cover a slightly narrower pH range (4.24 to 8.92) with a lower median value (6.78 vs. 7.69). The mean pH in the RAMP lakes is significantly less than that of the regional database ($p<0.005$);
- Titration alkalinity ranged from non-detectable to 1570 µeq/L with a median of 228 µeq/L, again much lower than the regional median (1000 µeq/L). The mean titration alkalinity in the RAMP lakes (357 µeq/L) was significantly less that that of the regional lakes ($p<0.05$);
- Conductivity was relatively low in the RAMP lakes and ranged from 13 µS/cm to 165 µS/cm (median: 37.1 µS/cm). The regional median for conductivity was 118 µS/cm. The mean conductivity of the RAMP lakes (48.8 µS/cm) was significantly less than that of the regional lakes (140 mg/L);

- Consistent with the lower conductivity in the RAMP lakes, the mean and median concentrations of the principal cations (calcium, magnesium, sodium and potassium) and the sum of base cations (SBC) were all less than the values in the regional database. SBC in the RAMP lakes was 446 μeq/L compared with 1177 μeq/L in the regional lakes. The mean values of these parameters were all significantly less in the RAMP lakes ($p<0.05$);

- Consistent with the lower conductivities in the RAMP lakes, the mean and median concentrations of the major anions (chloride, sulphate and titration bicarbonate) were all less than those in the regional database;

- Colour and DOC were significantly greater in the RAMP lakes ($p<0.05$). DOC in the RAMP lakes ranged from 8.91 mg/L to 50.5 mg/L (median: 22.3 mg/L);

- As in the regional lakes, total phosphorous was exceptionally high in individual lakes attaining concentrations as high as 263 μg/L. The median concentration of total phosphorous was similar in both lake populations (median 39.8 μg/L; vs. 47.3 μg/L);

- As observed in the regional lakes, nitrate concentrations were generally low (median: 8.8 μg/L), although several lakes had exceptionally high values (e.g., 733 μ/L in 2003). Nitrate concentrations were significantly greater in the RAMP lakes after a logarithmic transformation was applied to the data to render the variances homogeneous; and

- Ammonia concentrations in the RAMP lakes were significantly greater than those in the regional lake population (median 27.9 μg/L vs. 11.4 μg/L), although reduced forms of nitrogen in total (total Kjeldahl nitrogen) were not significantly different. Total dissolved nitrogen (TDN) was also not significantly different in the two lake populations.

Table 6.6-1 Comparison between RAMP lakes and 450 regional lakes in the NOxSOx database. The shaded parameters represent significantly different means ($p<0.05$).

Parameter	Units	RAMP Lakes (all years)				Regional Lakes				
		Min	Max	Median	Mean	N	Min	Max	Median	Mean
Lake area	km^2	0.031	431	1.45	18.8	449	0.011	431	1.61	7.81
Net catchment area	km^2	0.62	2137	14.6	92.5	450	0.083	2245	16.8	95.6
Drainage ratio		0.223	88.6	10.1	15.7	449	1.22	1177	12.6	25.5
Runoff	m^3/s	0.001	8.57	0.041	0.298	450	0.0003	8.57	0.041	0.274
Lab pH		4.24	8.92	6.78	6.66	450	4.2	9.59	7.69	7.6
Total alkalinity	µeq/L	0.0	1570	228	357	450	0.0	4797	1000	1201
Gran alkalinity	µeq/L	0.0	1554	202	332	NA	NA	NA	NA	NA
Specific conductivity	µS/cm	13	165	37.1	48.8	417	11	481	118	140
Total dissolved solids	mg/L	31.7	165	62.7	71.8	230	1	261	56.8	72
Turbidity	NTU	0.51	21.4	2.21	3.84	373	0.17	58	2.1	5.6
Suspended solids	mg/L	0.445	128	4.64	10.0					
Colour	TCU	10.2	436	128	141	193	2.7	347	54	79.5
Dissolved inorganic carbon	mg/L	0.268	16.6	2.16	3.49	NA	NA	NA	NA	NA
Dissolved organic carbon	mg/L	8.91	50.5	22.3	23.8	398	0.2	59.5	19.4	20.4
Sodium	mg/L	0.517	9.2	1.24	2.005	450	0.277	49.1	2	3.98
Potassium	mg/L	0.067	1.72	0.511	0.582	450	0.05	13.6	0.6	0.925
Calcium	mg/L	0.572	21.5	4.97	5.92	450	0.25	63.7	14	16.4
Magnesium	mg/L	0.168	7.47	1.47	1.96	450	0.05	27.7	4.09	5.18
Sum of base cations	µeq/L	81.9	1778	446	547	450	46	5770	1177	1442

Table 6.6-1 (cont'd.)

Parameter	Units	RAMP Lakes (all years)				Regional Lakes				
		Min	Max	Median	Mean	N	Min	Max	Median	Mean
Titration bicarbonate	mg/L	0	95.4	14.4	20.6	416	0	262	61.3	73.3
Chloride	mg/L	0.094	2.49	0.201	0.361	447	0.01	18	0.47	1.058
Sulphate	mg/L	0.277	14.2	1.18	2.36	449	0.025	99	2.5	6.528
Ammonia	µg/L	4.12	388	27.9	61.3	338	0.22	650	11.4	31.2
Nitrate + Nitrite	µg/L	0.63	304	8.79	23.6	348	0.02	1,860	2	21
Total Kjeldahl N	µg/L	327	4,834	1,229	1,332	212	276	5,900	1,000	1,193
Total dissolved N	µg/L	302	2,578	796	921	152	183	19.4	863	871
Total Nitrogen	µg/L	383	4,307	962	1,251	NA	NA	NA	NA	NA
Total Phosphate	µg/L	5.22	263	39.8	56.8	444	3	495	47.3	66.3
Dissolved phosphate	µg/L	2.26	107	11.7	19.6	NA	NA	NA	NA	NA
Chlorophyll *a*	µg/L	2.24	182	11.3	20.5	NA	NA	NA	NA	NA
Dissolved Aluminum	µg/L	0.925	539	23.5	74.0	NA	NA	NA	NA	NA
Iron	mg/L	0.003	2.41	0.151	0.346	NA	NA	NA	NA	NA

The box plots (Figure 6.6-1) graphically display many of the population differences noted above. One feature that emerges immediately in the box plots is the degree of skewness of many parameters in the regional database. For many parameters (e.g., conductivity, total alkalinity, sodium and sulphate) the data are highly skewed to the lower values with a small number of very high, extreme values. This degree of skewness was not evident in the RAMP lakes.

6.6.1.1 RAMP Lakes vs. Regional Lakes using Piper Diagrams

The chemical characteristics of the RAMP lakes were also compared to those of the regional lake database diagrams in Piper diagrams (Figure 6.6-2). The Piper diagram for the regional lakes (Figure 6.6-2a) show quite clearly that the vast majority of the regional lakes are of the Ca-Mg-Bicarbonate type with a smaller number having a significant contribution of sulphate/chloride to the anion charge and sodium/potassium to the cation charge. The RAMP lakes (Figure 6.6-2b) are similarly dominated by Ca-Mg-Bicarbonates with fewer of the more extreme lake types exemplified in the large database. This observation is consistent with the smaller range of data in the RAMP lakes evident in the box plots. The one point along the sulphate axis represents lake L29, Clayton Lake, a RAMP lake having virtually no titration bicarbonate whose anion chemistry is controlled entirely by sulphate and chloride.

The chemical differences between the RAMP lakes and the population of regional lakes reflect a bias in the selection process for the RAMP program. Most of the RAMP lakes were selected for study because they were thought to represent lakes that are potentially sensitive to acid deposition. In practice, this meant selecting lakes that were the most poorly buffered and had low pH values. Low ANC, low conductivity, low base cation concentrations, and low anions concentrations are associated with these characteristics. These types of lakes are also often the smallest lakes and are often located in the upland regions. The higher values of dissolved organic carbon (DOC) and colour in the RAMP lakes may reflect the extensive networks of fens in the catchment basins of lakes in the upland regions. The fens are known to export the humic acids that are responsible for the DOC and colour of these lakes (Gorham *et al*. 1984, Kortelainen and Mannio 1990, Kortelainen 1993).

Several lakes stand out as exceptional in their chemistry and are summarized in Table 6.6-2. In general, these lakes were chosen to have both the highest and lowest values of pH, ANC (Gran alkalinity), and DOC. They represent the extremes in chemistry for the RAMP lake population. Three lakes (168, 169, and 448) had virtually no measurable ANC and very low values of pH (4.91, 4.87 and 4.27 respectively). Kearl Lake (436) had the highest measure of Gran alkalinity (1548 μeq/L) and a pH of 8.04. Lakes 270 and 271 had the highest values of pH (8.28 and 9.44). Lake 444 (Legend Lake), while not having as low a pH and ANC as the other low ANC lakes, had an usually low DOC concentration (13.04 mg/L), atypical of the majority of Birch Mountain lakes. As Legend Lake is unusually deep (10 m), the clearer water in this lake may reflect a greater water retention time than in the majority of Birch Mountain Lakes. DOC is known to decrease with water retention time in a number of studies (Engstrom 1987, Rasmussen *et al*. 1989).

Figure 6.6-1 Box plots comparing the chemical characteristics of the RAMP lakes to those of the NOxSOx regional database.

The boundaries of the shaded Box indicate the 25th and 75th percentiles.
The whiskers indicate the 10th and 90th Percentiles.
The line within the box is the Median Value (50th percentile)

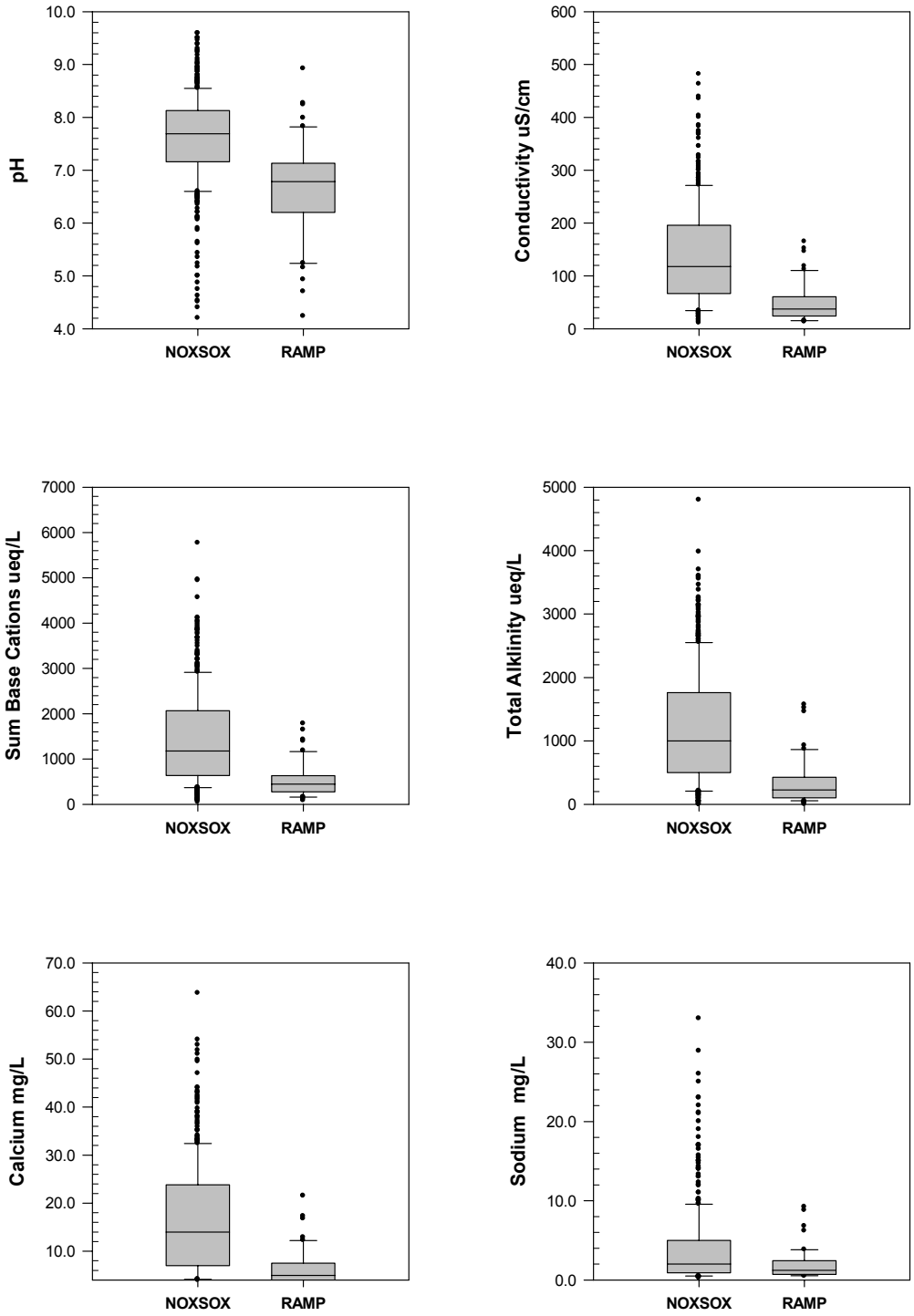


Figure 6.6-1 (cont'd.)

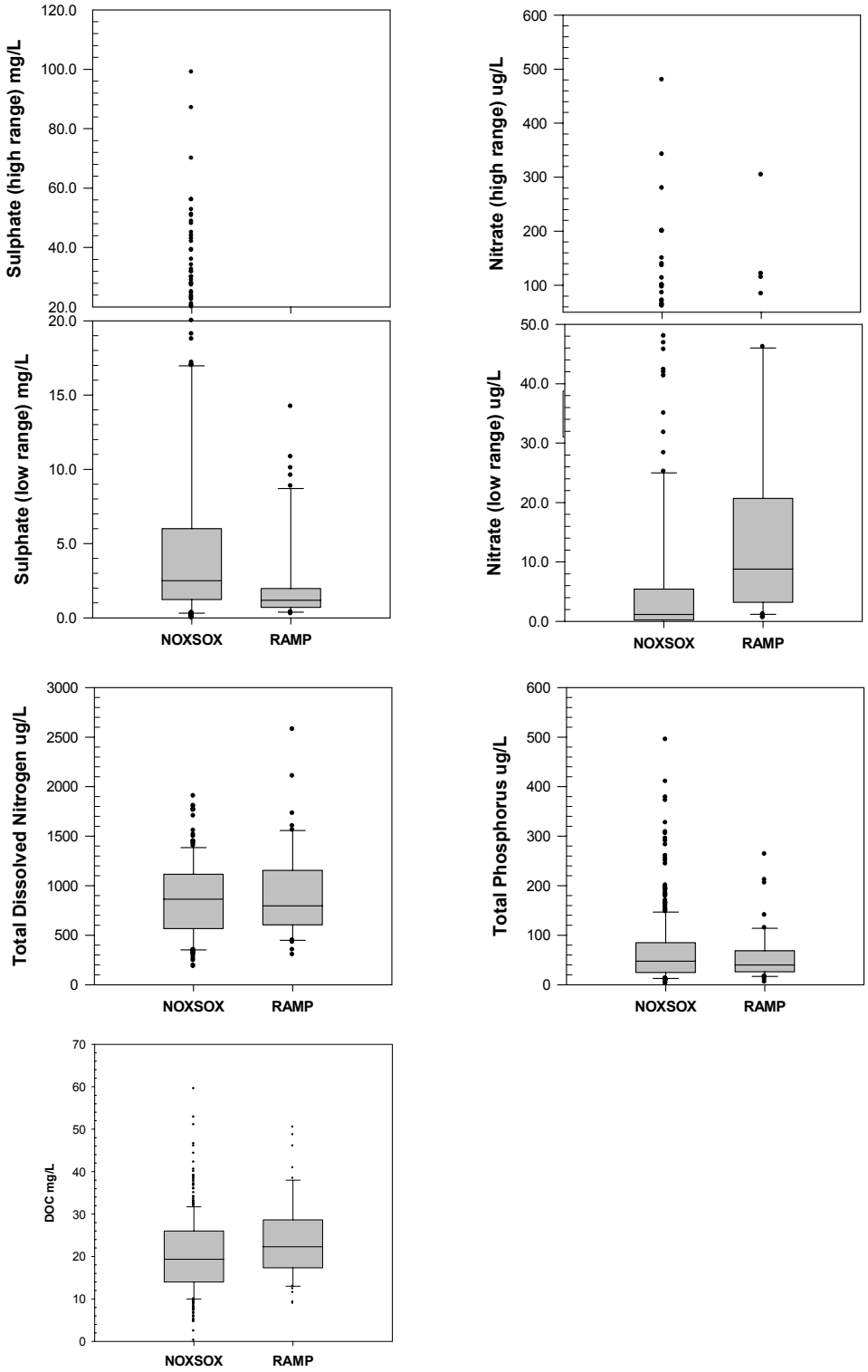
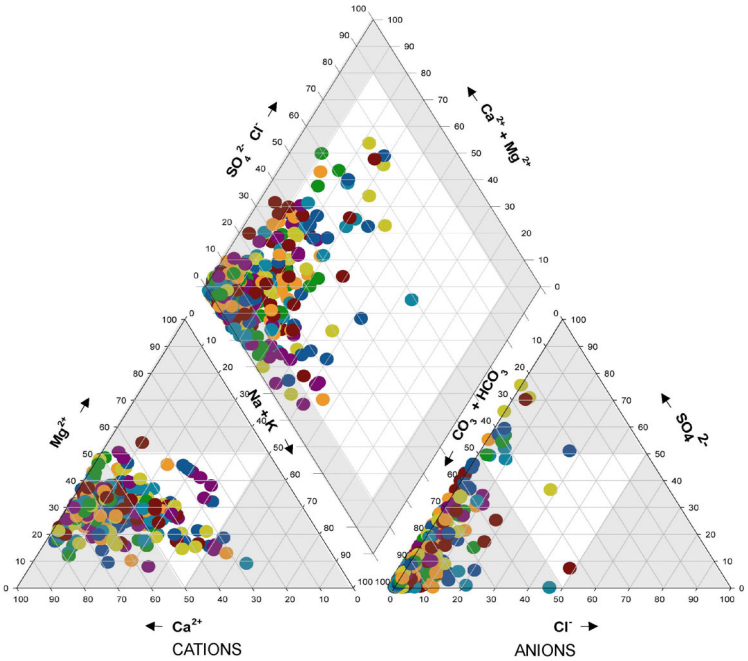


Figure 6.6-2 Piper plots showing major ion composition of the regional lakes (A) and the RAMP lakes (B).

(A)



(B)

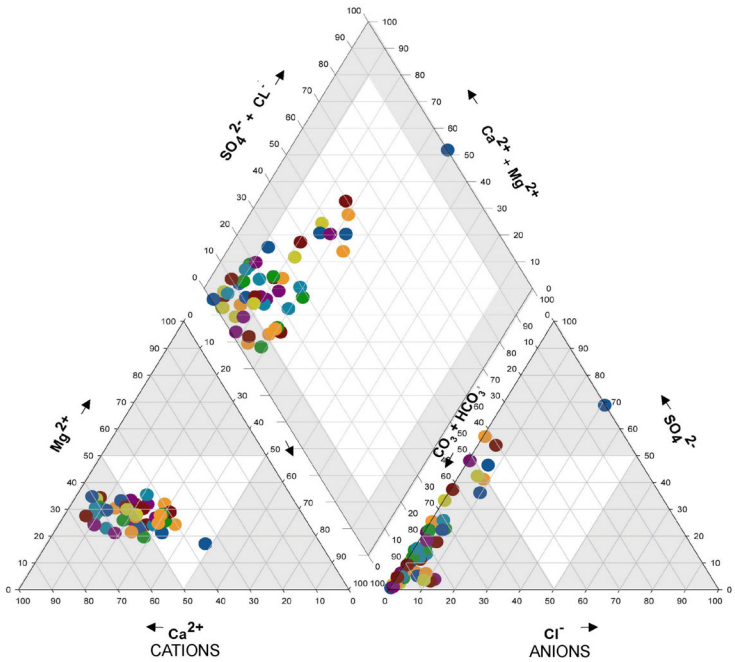


Table 6.6-2 RAMP study lakes having exceptional chemical characteristics (2004 data).

Lake	Region	pH	ANC µeq/L	DOC	Critical Load Exceedance
168 (A21)	Stony Mountains	4.91	Non-detect	16.8	Yes
169 (A24)	Stony Mountains	4.87	Non-detect	37.3	Yes
287 (25)	Stony Mountains	5.13	40	20.1	Yes
448 (L29) Clayton L.	Birch Mountains	4.27	Non-detect	13.04	Yes
447 (L28)	Birch Mountains	5.54	38	30.9	Yes
444 (L25) Legend	Birch Mountains	6.89	176	13.04	No
270	N-E of Fort McMurray	8.28	1348	58.5	No
271	N-E of Fort McMurray	9.44	1282	53.6	No
436 Kearle	N-E of Fort McMurray	8.04	1548	25.2	No

6.6.1.2 Role of Humic Materials in the Acid-Base Status of the RAMP Lakes

The RAMP lakes, having a relatively high median DOC concentration of 23.8 mg/L, can by conventional definition be considered as humic (Forsius 1992, Driscoll *et al*. 1989, Kahl *et al*. 1989; Kortelainen *et al*. 1989). Organic acids comprise a large portion of this dissolved organic carbon and can play a significant role in the acid-base status of these lakes. One of the recommendations of the RAMP Scientific Peer Review Committee was to establish this role. The role of the organic acid component of the DOC was first examined in the 2003 report and has been further examined in the 2004 report. The following aspects of the organic acid-base role of the organic acids were studied:

- The weak organic acid concentrations in the lakes;
- The strong acid component of the organic acids in the lakes, and
- The ANC or buffering attributable to organic acids in these lakes.

In these calculations of organic acidity, the Gran alkalinity was used as an estimate of ANC rather than the total alkalinity normally reported by the laboratory. The Gran alkalinity gives a more accurate estimate of ANC because it actually determines the equivalence point of the titration. The Gran alkalinity is equivalent to the ANC attributable to the combination of bicarbonate alkalinity and weak organic anions. The total alkalinity is titrated to pH 4.5 regardless of the equivalence point and may overestimate or underestimate the true ANC.

6.6.2 Determination of Organic Acid Concentrations and Charge Densities

As described in Section 3.6.7, the free organic acid concentrations of each lake [A^-] for each lake were calculated by anion deficit. The measurements of A- were then used to calibrate the model of Oliver *et al*. (1983), which relates A- in an exponential relationship to DOC and pH. The concentrations of free organic anions at the sample pH of each lake [A^-] are expressed in µeq/L. The organic anion concentration is often divided by the DOC in units of µeq A^- /mg C to yield the charge density which represents the number of dissociated carboxyl groups per mg of DOC at the pH of the sample.

Table 6.6-3 presents a summary of the calculations of A^-, and the charge density by anion deficit. The values of A^- and charge density are presented for 2003, 2004 and for the mean concentrations of the relevant parameters used in the calculations over the three to six years of monitoring. The results for each individual lake are presented in Appendix I. The results for 2004 appear to have greater scatter than those in 2003. This scatter was apparent in all the calculations and appears related to analytical errors especially in the determination of dissolved inorganic carbon. The calculations of A^- and charge density, based on the mean concentrations are probably the most reliable estimates of these parameters.

Table 6.6-3 Summary of calculations of free organic acids and charge densities for 50 RAMP lakes.

(See Appendix I for complete list)

Parameter	Units	2003 Range (Median)	2004 Range (Median)	Mean Range (Median)	Literature (Appendix I)
Free organic anions [A-]	µeq/L	107- 649 (246)	83 - 666 (224)	101 - 658 (249)	-
Charge density	µeq/mg DOC	6.0 - 20.7 (11.2)	3.0 - 15.6 (8.9)	5.5 - 15.9 (11.3)	2.2 - 13.4 (10)

For the mean case, concentrations of free organic anions ranged from 101 to 658 µeq/L with a median value of 249 µeq/L. The charge density, ranged from 5.5 to 15.9 µeq/mg C with a median of 11.3 µeq/mg C. This median value fits well within the range of values reported in the literature, which are listed in Appendix I.

Model of Oliver et al. (1983)

Examination of the dissociation equations in the Oliver *et al*. (1983) model (Section 3.6.7) indicated that $[A^-]$ is proportional to the DOC content and a non-linear, exponential function of pH. This knowledge was used to fit the calculated values of A^- to an appropriate function of DOC and pH. The data were fitted to an equation of the form:

$$A^- = a \text{ DOC } \exp(b*pH).$$

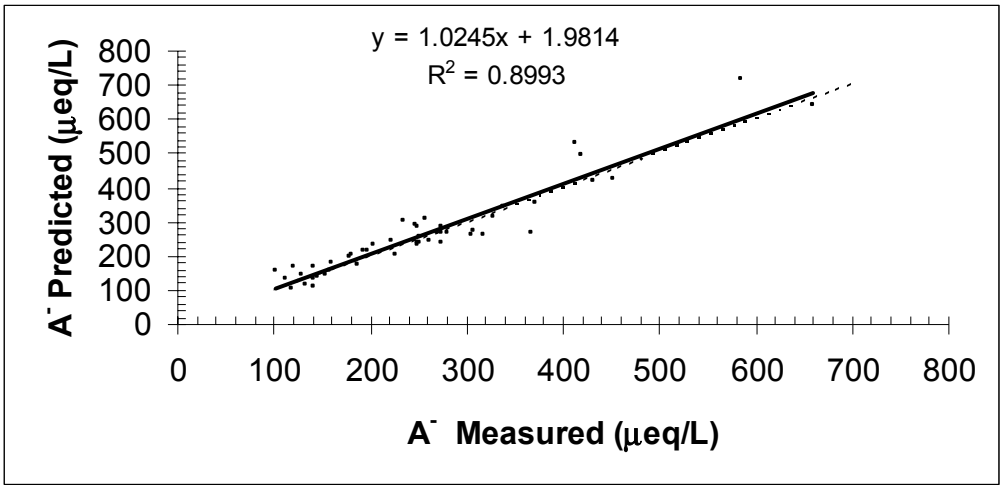
A non-linear regression using SYSTAT 11 was applied to the three cases (2003, 2004, mean concentrations) (Table 6.6-4).

Table 6.6-4 Results of the non-linear regression of A^- on DOC and pH for the 2003, 2004, and mean concentrations.

Constants	Cases 2003	2004	Mean
a	2.52	3.461	3.443
b	0.21	0.145	0.177
R^2 (corrected)	0.88	0.67	0.89

These equations can be used to calculate the organic acid anion concentrations for regional lakes from field measurements of DOC and pH. A plot of the predicted vs. measured values of free organic anions is reproduced in Figure 6.6-3 for the mean case.

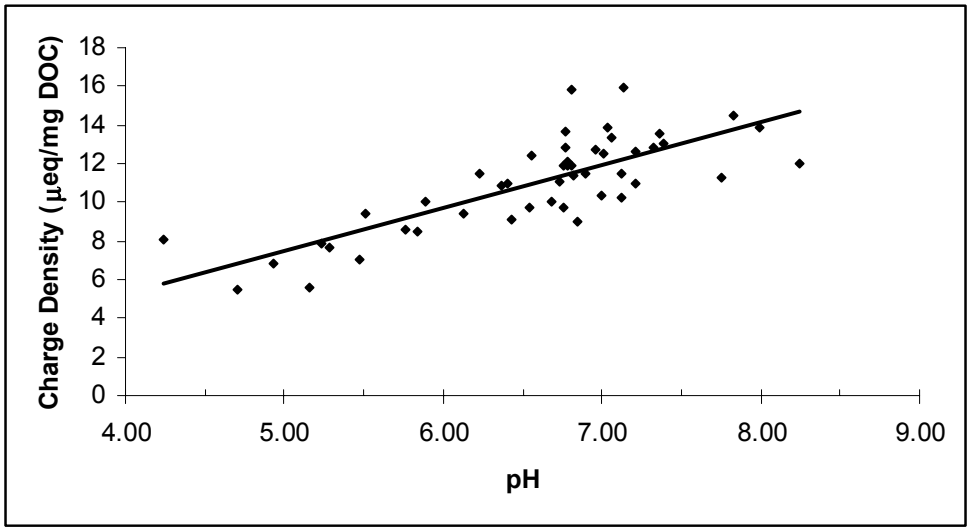
Figure 6.6-3 Organic anion concentrations predicted from derived equation versus the values measured by anion deficit (mean case).



The 1:1 line (broken line) is essentially co-linear with the first line and the slope of the line fitted to the data has a value of 1.025 compared to a theoretical value of 1.0. Most of the scatter occurs at the higher values of A^-, which correspond to lakes having high values of pH (>7.5). At high values of pH, organic groups other than carboxyl (in particular phenolic groups) may play a role in the acid-base dynamics of the lake (Kramer *et al*. 1990).

The derived exponential equation also indicates the strong positive relationship between the charge density (A^-/DOC) and pH, which is represented in Figure 6.6-4.

Figure 6.6-4 Charge density vs. pH of RAMP lakes (mean case).



6.6.3 Calculation of Strong Acid Anions

Early studies on humic lakes assumed that organic acids were all weak acids. Later studies showed that DOC is actually a complex mixture of organic acids dissociating over a wide pH range. A certain fraction of these acids acts as strong acids of low pKa. These strong acids remain dissociated at low pH and reduce the overall ANC of the lake.

Strong acid anions in the RAMP lakes were analyzed by the method suggested by Cantrell *et al*. (1990), Munson and Guerini (1993) and Kortelainen (1993) from the difference between charge balance alkalinity and the Gran alkalinity (Section 3.6.7).

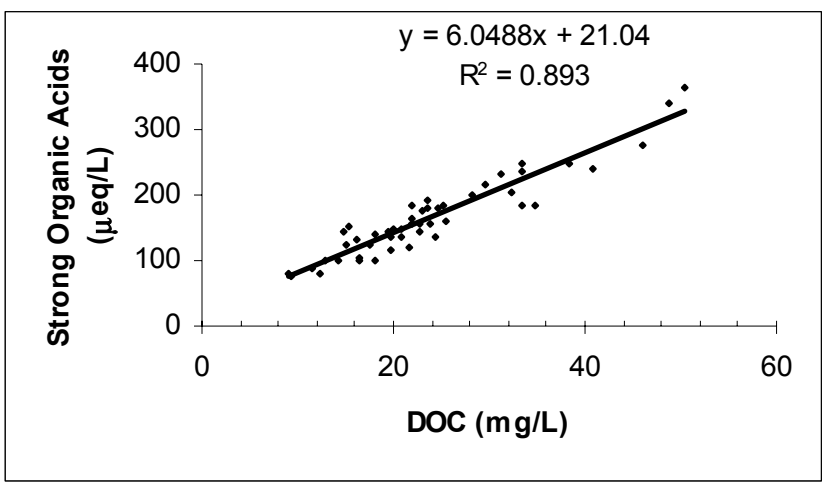
The concentrations of strong organic acids (A^-_{SA}) for each lake are tabulated in Appendix I and, for the mean case, range from 74.6 µeq/L to 363 µeq/L with a median value of 153 µeq/L. Figure 6.6-5 presents the difference between the strong organic acids concentration as a function of DOC. As in the studies cited above, the relationship is linear with a slope of 6.05 µeq/mg DOC. The following relationship applies to the RAMP lakes and can be used to calculate A^-_{SA} from DOC when other data are lacking:

$$A^-_{SA} = 6.05\,[DOC] + 21.04$$

where A^-_{SA}, is expressed in µeq/L and DOC in mg/L.

This equation was applied in Section 6.6.3 in order to modify the Henriksen model in calculations of critical loads of acidity.

Figure 6.6-5 Plot of strong organic acids vs. DOC (mean case).



6.6.4 Calculation of the ANC (Buffering) Attributable to Weak Organic Anions

The ANC or buffering attributable to the weak organic acids (ANC_{org}) was calculated for each lake by the method of Roila *et al*. (1994) as described in Section 3.6.7. The results of these analyses for each lake are presented in Appendix I and are summarized for the 50 lakes in Table 6.6-5. For the mean case, ANC_{org} ranged from 0 µeq/L to 268 µeq/L with a median of 72.6 µeq/L. The ANC_{org} is a strong function of both DOC and pH. The

last column in Table 6.6-5 presents the organic ANC expressed per unit of DOC (ANC_{org}/DOC). This quantity, in effect an "organic buffering density", is frequently calculated in the humic acid literature. For the RAMP lakes, this value ranged from 0.0 µeq/mg C to 7.6 µeq/mg C with a median of 3.6 µeq/mg C. This quantity was plotted against pH in Figure 6.6-6 to show the strong increase of this quantity with pH.

A more comprehensive model to fit the data was determined from the non-linear regression of ANC_{org} on both pH and DOC for the 2003 case:

$$ANC_{org} = 0.00680*DOC \exp(0.8833* pH)$$

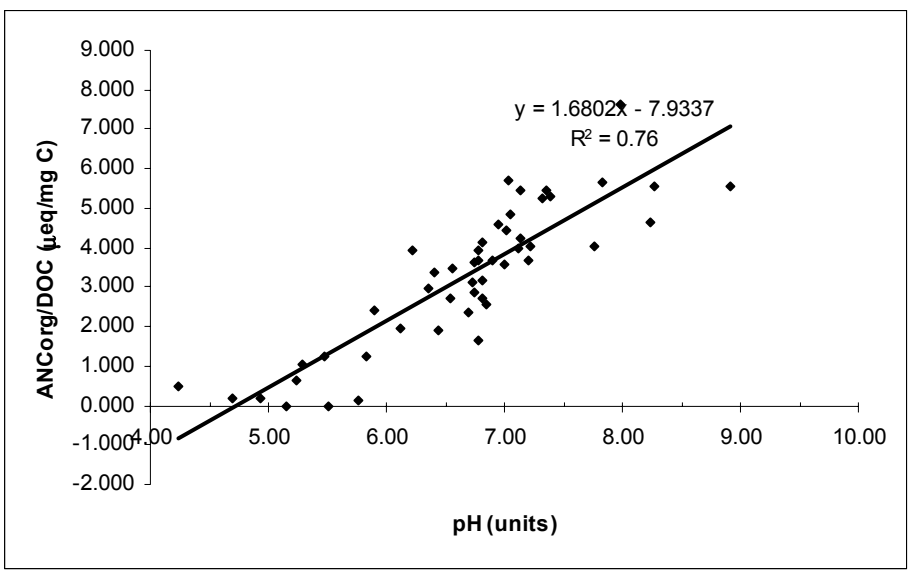
$r^2 = 0.922$, r^2 corrected = 0.831

This model can be used to predict the buffering attributable to weak organic acids from DOC and pH and is applicable to any regional lake. It was applied in Section 6.6.3 in order to modify the Henriksen model in calculations of critical loads of acidity.

Table 6.6-5 Summary of calculations of buffering attributable to weak organic acids (ANC_{org}) and the organic buffering densities for 50 RAMP lakes.

Parameter	Units	2003 Range (Median)	2004 Range (Median)	Mean Case Range (Median)
ANC_{org}	µeq/L	0 – 348 (62.4)	0 - 276 (50.6)	0 - 268 (72.6)
Organic buffering density	µeq/mg DOC	0 – 12.4 (2.9)	0 – 10.7 (2.0)	0 – 7.6 (3.6)

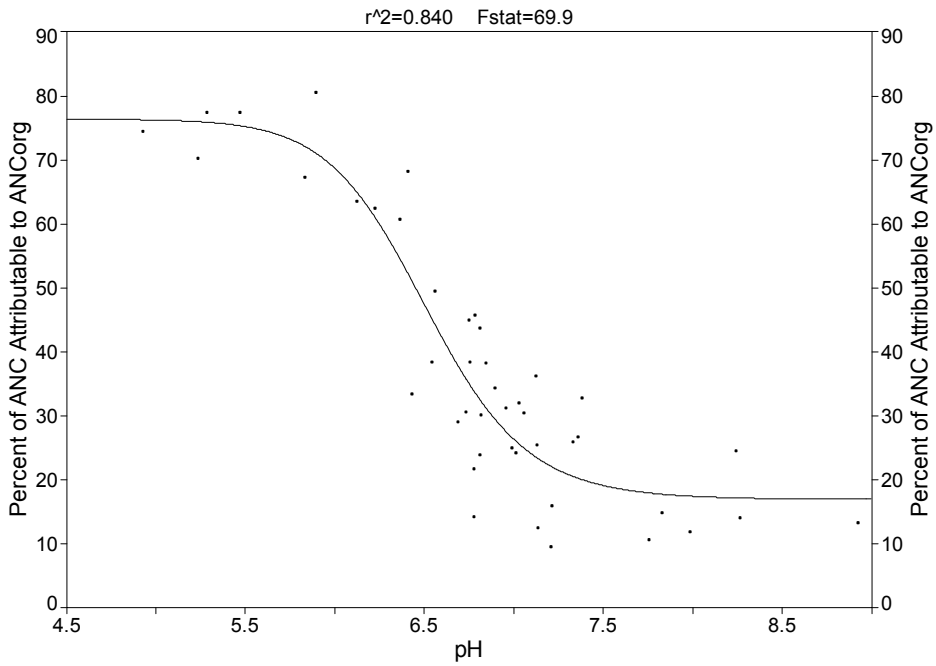
Figure 6.6-6 Organic buffering density versus pH in RAMP lakes (mean case).



Appendix I also presents the proportion of the total ANC or total buffering (expressed as Gran alkalinity) in each lake attributable to weak organic acids. For the mean case, this proportion ranged from 9.7% to 80.5% with a median of 31.2%. The relation between the percent ANC attributable to ANC_{org} and pH is a logistic dose-response curve (Figure 6.6-7) that accounts for about 84% of the variability of the data. At low values of

pH, the proportion of the buffering attributable to ANC_{org} is high, in excess of 80%, but the absolute value of ANC_{org} is low (less than 20 μeq/L). At high values of pH, the proportion of the total buffering attributable to ANC_{org} is small, although the absolute value of the ANC_{org} is high (greater than 200 μeq/L).

Figure 6.6-7 Percent organic buffering as a function of pH for RAMP lakes (mean case).



6.6.5 Comparison of Critical Loads of Acidity to Potential Acid Input

6.6.5.1 Calculations of Critical Loads of Acidity for RAMP Lakes

The critical load of acidity (CL) is the primary measurement endpoint for the ASL component. While other parameters such as Gran alkalinity, base cation contents and nitrates are also significant measurement endpoints, there are as yet insufficient data on most of the lakes to determine trends in these parameters that might indicate acidification (see Section 6.6.4). The critical load is defined as the highest level of acidic deposition that will not cause chemical changes leading to long-term harmful effects to the lake. The critical load, a property solely of the lake and its drainage basin, is a measure of the lake's sensitivity to acidification and can be compared to rates of acidic deposition. The smaller the critical load, the more sensitive a lake is to acidic deposition.

Critical loads of acidity were calculated for each lake for the years 1999 to 2004 using the unmodified Henriksen steady state water chemistry model. For the 2004 data, the Henriksen model was also calculated using the modifications described in Section 3.6.7 to account for the contribution of weak acids (ANC_{org}) which increase the ANC in each lake and the contribution of strong organic acids (A^-_{SA}) which decrease the ANC of each lake. These modifications to the original Henriksen model incorporate Equations 1 and 2 derived in Section 6.6.2 and are also being adopted by the NSMWG. The critical loads of acidity for each RAMP lake are presented in Table 6.6-6.

Table 6.6-6 Calculation of critical loads of acidity to RAMP lakes. 2004-modified is the critical load for 2004 modified for organic buffering and strong organic acids. PAI is the modeled Potential Acid Input.

NOx-SOx GIS No.	Original RAMP Designation	Field pH 2004	DOC 2004 (mg/L)	Gross Catchment Area (Km^2)	Runoff (m^3/s)	Critical Load (keq/ha/y)							Difference Between Methods	PAI keq/ha/y
						1999	2000	2001	2002	2003	2004	2004-modified		
168	A21	4.57	16.79	10.40	0.0404	0.131	0.112	0.126	0.083	0.079	0.055	-0.087	-0.142	0.131
169	A24	4.78	37.27	7.80	0.0264	0.036	0.030	0.035	0.054	0.069	0.040	-0.205	-0.245	0.122
170	A26	5.12	14.83	3.40	0.001	0.025	0.005	0.005	0.006	0.007	0.005	-0.004	-0.009	0.196
167	A29	5.43	14.84	4.50	0.0131	0.057	0.077	0.090	0.068	0.070	0.089	-0.002	-0.091	0.095
166	A86	6.72	21.60	197.00	0.2639	0.069	0.070		0.080	0.087	0.098	0.057	-0.041	0.073
287	25 (287)	5.09	20.12	7.77	0.0223				0.039	0.056	0.044	-0.075	-0.118	0.152
289	27 (289)	6.48	11.88	7.05	0.0216				0.086	0.100	0.101	0.035	-0.066	0.112
290	28 (290)	5.75	19.06	3.24	0.0124				0.146	0.229	0.132	-0.008	-0.139	0.141
342	82 (342)	6.75	25.21	6.10	0.0139				0.225	0.206	0.196	0.119	-0.077	0.075
354	94 (354)	7.22	22.14	8.53	0.0162				0.365	0.270	0.252	0.213	-0.040	0.113
165	A42	7.12	46.16	588.00	1.1136	0.374	0.270	0.241	0.338	0.311	0.414	0.336	-0.078	0.075
171	A47	6.48	19.00	1,254.00	1.8707	0.035	0.111	0.086	0.154	0.128	0.123	0.077	-0.045	0.075
172	A59	4.93	35.27	2,245.00	8.5666	0.297	0.240	0.201	0.254	0.243	0.262	0.002	-0.260	0.075
223	P94 (223)	7.30	50.40	0.70	0.0019				1.196	1.104	1.148	1.054	-0.093	0.331
225	P96 (225)	7.06	34.65	1.26	0.0034				0.799	0.649	0.761	0.667	-0.094	0.126
226	P97 (226)	6.48	29.97	1.80	0.0057				0.438	0.481	0.406	0.266	-0.140	0.209
227	P98 (227)	7.33	32.54	1.92	0.007				1.058	1.024	1.003	0.917	-0.085	0.166
267	1 (267)	7.94	23.01	34.50	0.1182				1.084	1.005	0.980	0.995	0.015	0.109
452	L4	6.06	20.71	20.61	0.092	0.328	0.319	0.280	0.285	0.273	0.242	0.078	-0.164	0.236
470	L7	6.59	30.77	21.53	0.101	0.445	0.515	0.495	0.414	0.429	0.343	0.141	-0.202	0.579
471	L8	7.13	20.41	10.56	0.045	0.753	0.704	0.742	0.638	0.713	0.620	0.527	-0.093	0.538
400	L39	7.17	25.88	19.23	0.0501	0.369	0.242	0.225	0.215	0.211	0.209	0.144	-0.065	0.069
268	E15 (L15b, 268)	7.36	32.27	25.04	0.0809		0.726	0.732	0.644	0.544	0.472	0.400	-0.071	0.319
182	P23 (182)	9.54	20.09	7.33	0.0296				0.394	1.142	1.405	2.017	0.613	0.132
185	P27 (185)	5.17	34.20	4.04	0.0172				0.291	0.267	0.182	-0.095	-0.276	0.188
209	P7 (209)	6.20	19.39	1.93	0.0072				0.293	0.335	0.238	0.112	-0.126	0.236
270	4 (270)	8.61	58.53	18.08	0.0411				1.353	1.207	1.104	1.408	0.304	0.269
271	6 (271)	9.62	53.63	22.04	0.0485				1.290	1.043	0.930	1.931	1.001	0.193
418	Kearl L.	8.00	25.15	71.14	0.169					1.270	1.270	1.290	0.020	0.816

Table 6.6-6 (cont'd.)

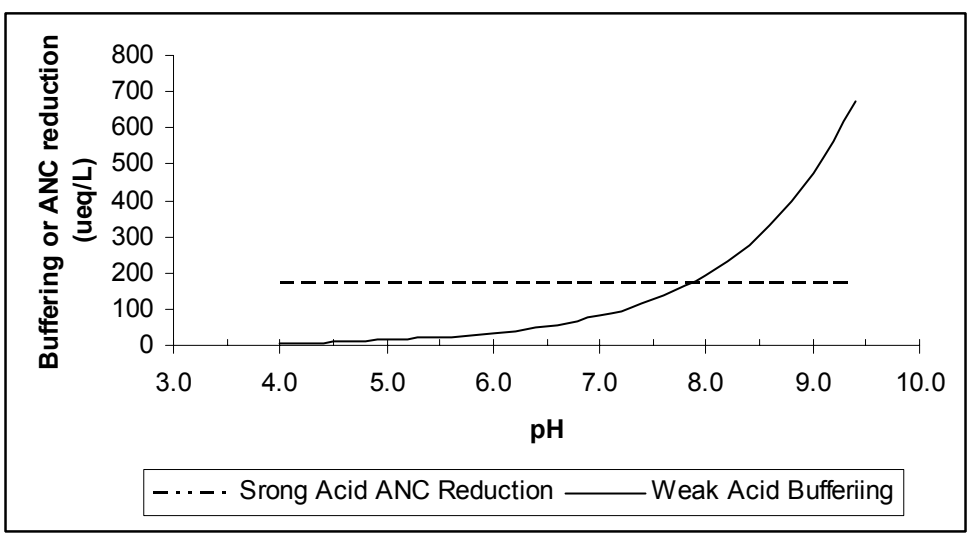
NOx-SOx GIS No.	Original RAMP Designation	Field pH 2004	DOC 2004 (mg/L)	Gross Catchment Area (Km^2)	Runoff (m^3/s)	Critical Load (keq/ha/y) 1999	2000	2001	2002	2003	2004	2004-modified	Difference Between Methods	PAI keq/ha/y
436	L18	7.14	13.71	223.99	0.325	0.245	0.247	0.253	0.254	0.257	0.250	0.226	-0.024	0.054
442	L23	6.95	19.38	23.44	0.043	0.124	0.119	0.118	0.124	0.111	0.110	0.065	-0.045	0.069
444	L25	6.87	13.04	93.10	0.1765	0.134	0.140	0.148	0.119	0.125	0.136	0.099	-0.037	0.054
447	L28	5.46	30.87	19.00	0.0448	0.122	0.104	0.115	0.112	0.103	0.137	0.002	-0.135	0.040
448	L29	4.03	13.55	13.05	0.033	0.005		0.028		0.004	0.006	-0.073	-0.080	0.086
454	L46	6.44	22.90	57.20	0.169	0.748	0.579	0.495	0.484	0.475	0.470	0.365	-0.106	0.067
455	L47	6.66	36.62	49.21	0.1016	0.439	0.361	0.345	0.340	0.301	1.414	1.314	-0.100	0.040
457	L49	6.66	26.71	31.11	0.0666	0.380	0.391	0.341	0.368	0.333	0.362	0.283	-0.079	0.040
464	L60	8.14	23.32	60.21	0.163	0.411	0.486	0.486	0.478	0.472	0.460	0.501	0.041	0.040
175	P13 (175)	9.45	52.21	4.27	0.012				1.248	1.146	1.120	2.149	1.029	0.132
199	P49 (199)	6.46	21.20	0.84	0.0044				0.362	0.352	0.412	0.237	-0.175	0.153
473	A301	7.37	24.20	NA	NA	NA	NA	NA	NA	NA				
118	L107	7.41	22.48	12.20	0.0092		0.130	0.137	0.129	0.125	0.126	0.114	-0.012	0.007
84	L109	6.94	30.17	115.80	0.3537	0.490	0.515	0.508	0.479	0.466	0.446	0.341	-0.105	0.014
88	O-10	6.93	34.86	5.10	0.0118	0.350	0.289	0.256	0.250	0.245	0.228	0.138	-0.090	0.014
90	R1	7.18	33.40	24.30	0.0788	0.370	0.386	0.396	0.381	0.374	0.375	0.279	-0.096	0.014
146	E52	7.16	24.74	17.60	0.0439	0.398	0.409	0.429	0.437	0.421	0.411	0.351	-0.060	0.027
152	E59	6.94	15.90	30.10	0.0124	0.033	0.029	0.032	0.032	0.033	0.035	0.026	-0.009	0.027
89	E68	6.65	21.52	54.10	0.1576		0.436	0.424	0.339	0.352	0.315	0.223	-0.091	0.027
91	O-1	6.84	28.17	3.30	0.001	0.016	0.015	0.014	0.015	0.016	0.019	0.009	-0.011	0.027
97	O-2	6.42	26.69	9.30	0.0029	0.033	0.034	0.034	0.031	0.030	0.029	0.017	-0.013	0.027
Minimum											0.005	-0.205	-0.276	
Maximum											1.414	2.149	1.029	
Median											0.252	0.144	-0.079	

Using the unmodified Henriksen equation, critical loads in 2004 ranged from to 0.005 keq H^+/ha/y (Lake 170; A26) to 1.414 keq H^+/ha/y (Lake 455; L47). The median critical load over all the lakes in 2004 was 0.252 keq H^+/ha/y. As noted in 2003, lakes located in the upland regions (the Birch Mountains, the Muskeg River Uplands, the Caribou Mountains and the Stony Mountains) or in the Canadian Shield are the most sensitive by the critical load criterion. These areas are generally "lowlands" (despite their relatively high elevation) with extensive networks of fens and bogs. The Canadian Shield lakes are soft water lakes located on granitic bedrock. For example, Lake 170 (A26), having the lowest mean CL over the five years of the RAMP program (0.009 keq H^+ /ha/y), is located in the Stony Mountains. Clayton Lake (44; L29) with a mean CL of 0.011 keq H^+/ha/y is located in the Birch Mountains. Lake 91 (O-1) with a mean CL of 0.016 keq H^+/ha/y is located in the Caribou Mountains. In general, the ponds (designated with a P) had relatively high CLs and were not particularly sensitive to acidification by this criterion (Table 6.6-6).

Application of the modified model to the 2004 data altered the values of the CL considerably (Table 6.6-6). Most values of the CL decreased relative to those calculated with the previous model. Negative critical loads were observed in 8 lakes. Overall, the median value of the CL for 2004 decreased by 0.108 keq/ha/y (0.252 vs. 1.44 keq/ha/y). The significant decrease in critical load implies that these lakes are much more sensitive to acidification than was previously anticipated.

While there was a general decrease in critical loads with the modified model, the critical loads of a small number of lakes actually increased, especially in lakes having a high pH (e.g., 270, 271, Kearle Lake and L60). The reason why some critical loads decreased while other increased is explained in Figure 6.6-8 showing the separate effects of the terms for weak organic acids and strong organic acids within the model as a function of pH.

Figure 6.6-8 The effects of buffering and ANC reduction in the modified Henriksen model as a function of pH. A median DOC concentration of 24.5 was assumed.



At low pH, the linear term in the model, representing the reduction in ANC from strong acids, is dominant over the exponential term, representing the increase in ANC from weak organic acids (buffering). Under these conditions, the overall ANC of a lake (and its critical load) are reduced. At pH 7.8 and greater, the exponential term, representing the increased buffering attributable to weak organic acids is dominant over the effects of the strong organic acids. ANC (and the critical load) increase monotonically with pH. For a given DOC, lakes having high pH, therefore, will display an increase in critical load.

6.6.5.2 Comparisons of the Critical Loads of Acidity to Potential Acid Input

The lake-specific critical loads of acidity were compared to the modelled potential acid input (PAI) at each lake location attributable to both natural and anthropogenic causes (Table 6.6-6). The PAI corresponds to the nitrates and sulphates in dry and wet deposition minus the neutralizing effects of base cations. Values of the PAI at each lake were those modelled for the OPTI-Canada Inc. Long Lake Project Environmental Impact Assessment in 2002 under a cumulative effects scenario and are identical to values used in the NSMWG mapping report (WRS 2004). Exceedances of the critical load by the PAI indicate a potential for acidification for a particular lake under the modelling scenario. Exceeded lakes are identified in Table 6.6-6 and their locations are indicated in Figure 6.6-9.

In 2004, using the unmodified Henriksen model, 11 of the 50 currently monitored lakes (22%) had critical load exceedances. Table 6.6-7 summarizes their key chemical characteristics. As expected, these lakes are of low pH, low conductivity, low ANC and low base cation concentrations. The bicarbonate buffering capacity in these lakes is severely reduced. The DOC is also high in most of these lakes. Clayton Lake in the Birch Mountains and Lakes 168 and 169 in the Stony Mountains stand out as having no ANC at all and the lowest base cation concentrations of all the lakes. Most of the exceeded lakes are quite small (1-2 km^2 in area).

The modified critical load model gave a different picture not only of lake sensitivity but of the risks of acidification to the RAMP lakes. A total of 20 lakes (40%) were exceeded by the PAI, an increase of 9 lakes over the unmodified model. The chemical characteristics of the nine additional lakes are also summarized in Table 6.6-7. These lakes were generally higher in pH and ANC than the 11 lakes exceeded under the unmodified model. The organic terms in the model were sufficient to lower the critical loads of these lakes to the point where an exceedance by the PAI was observed.

6.6.5.3 Implications of the New Values of Critical Load for the RAMP Lakes

The decrease in the critical loads with the modified model and the increase in the rate of exceedance of the critical load imply that the RAMP lakes are more sensitive to acidification than anticipated. By the critical load criterion, many (40%) of the RAMP lakes are "at risk" to acidification even under background levels of deposition.

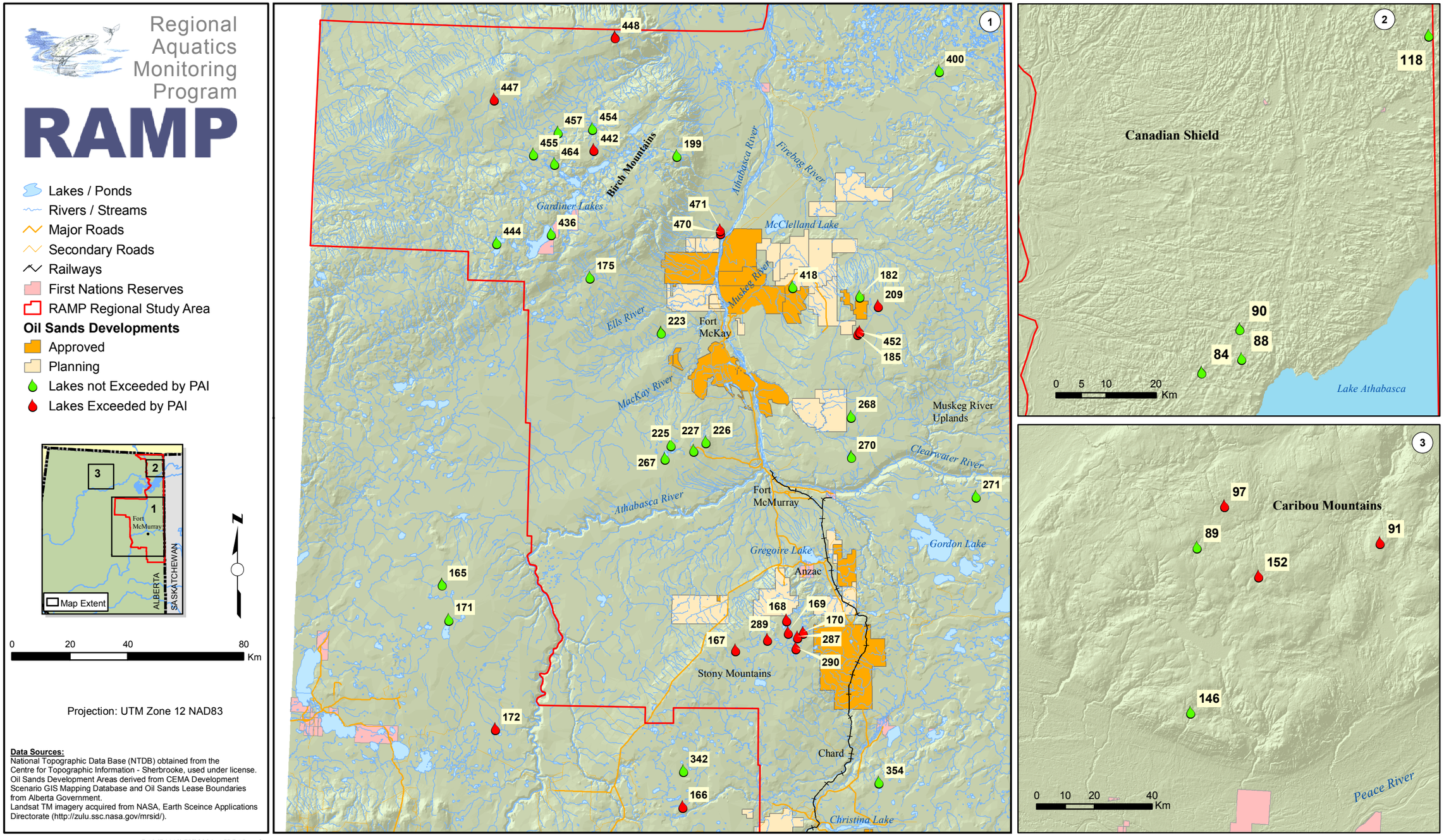
Table 6.6-7 Key chemical parameters in the 11 lakes having critical load exceedances under the unmodified Henriksen model and the additional nine lakes exceeded under the modified model (shaded values).

Lake	Original Name	pH	ANC µeq/L	Cond. µS/cm	DOC mg/L	Lake Area Km^2
168	A21	4.57	0	13.8	16.8	1.38
169	A24	4.78	0	12.5	37.3	1.45
170	A26	5.12	2	14.3	14.8	2.78
167	A29	5.43	18	12.6	14.8	1.05
287	25	5.09	2	12.6	20.1	2.18
289	27	6.48	64	17.2	11.9	1.83
290	28	5.75	26	17.0	19.1	0.544
185	P27	5.17	32	19.3	34.2	3.94
470	L7	6.59	110	25.9	30.8	0.330
448	L29 Clayton	4.03	0	14.7	13.6	0.650
91	O-1	6.84	74	22.3	28.2	0.800
166	A86	6.72	118	28.5	21.6	2.17
172	A59	4.93	22	28.8	35.3	108
452	L4	6.06	66	21.8	20.7	0.610
471	L8	7.13	368	49.2	20.4	0.560
209	P7	6.2	100	22.8	19.4	0.146
442	L23	6.95	150	23.5	19.4	3.44
447	L28	5.46	38	19.5	30.9	1.30
152	E59	6.94	206	32.4	15.9	9.53
97	O-2	6.42	194	32.2	26.7	3.10

This assessment hinges on the ability of the Henriksen model to predict lake sensitivity. The assumptions of the model have been discussed at length in the NSMWG report (WRS 2004) and will not be repeated here in detail. One important assumption of the original Henriksen model, discussed in the 2003 report, was that calcium and magnesium bicarbonates provide the principal source of buffering in each lake. The bicarbonate assumption is implicit in the unmodified model in which the weathering of base cations alone accounts for alkalinity generation in the catchment. Questions have always been posed by stakeholders as to the possibility of organic buffering replacing the bicarbonate buffering in low ANC-low pH lakes. This would imply that low ANC lakes are less sensitive than indicated by the model.

The use of the modified Henriksen model represents an attempt to eliminate the bicarbonate assumption. The new terms in the modified model include both the buffering attributable to weak organic acids and the reduction in ANC attributable to strong organic acids. The output of the model indicates that the combination of low pH and high DOC in most of the RAMP lakes results in a decrease in their critical loads and an increase in their potential sensitivity to acidification. Although this is the first time that an organic correction has been applied to the Henriksen model, the methodologies for calculating the effects of the organic components are entirely consistent with those in the international literature. NSMWG is currently modifying its critical load database of 450 lakes using the same formulations. There is no methodological reason to question the results of the modified model, specifically the decrease in critical loads, without questioning some of the more basic assumptions in the Henriksen model itself (e.g., steady state).

Figure 6.6-9 RAMP acid-sensitive lakes with calculated Potential Acid Input exceeding calculated critical loading.



RAMP1110\GIS\2004_ASLPAI.mxd

6.6.6 Detection of Trends in Measurement Endpoints

Central to the RAMP ASL component is the detection of changes in measurement endpoints that would indicate incipient acidification of these lakes. These changes would then be judged by the impact criteria outlined Section 3.6.7 to determine whether a significant impact has occurred. Potential trends in the measurement endpoints were examined using the Mann-Kendall non-parametric test. The ASL database pushes the limits of the Mann-Kendall test to detect trends. In order to detect a trend, the test requires a minimum of four measurements. Thirty-one of the lakes have 5 or six years of sampling. The other 19 lake have three or fewer years of data. With these few years of data, the possibility of reporting a false positive or negative trend in the data may be very high.

Table 6.6-8 presents the S scores (i.e., the Mann-Kendall test statistic) for nine parameters over the 31 lakes. Statistically significant scores are shaded. The PAI is provided in the last column. The results are somewhat confusing and reflect the uncertainty in using this test with so few years of data. The sum of the base cations appears to have decreased significantly in many lakes. This would suggest that acidification of the drainage basin has reached the point in these lakes where the base cations have been depleted in the catchment soils. Overall, these changes in SBC were poorly correlated with parallel changes expected in alkalinity and Gran alkalinity. Linear regressions of the scores of SBC on alkalinity and Gran alkalinity were not significant. However, it is worth noting that at the highest acid deposition rates (PAI > 0.2 keq/ha/y), the changes in the sum of the base cations and the Gran alkalinity were all consistent in direction. Decreases in base cations (negative scores) were associated with parallel decreases in Gran alkalinity. This trend was observed in lakes 452 (L4), 450 (L7), 471 (L8) and 268 (E15). However, the significant changes in pH were all positive, rather than negative. Nitrates, an increasingly important constituent of acid deposition in the region, generally decreased in most lakes with one significant increase in Lake A26. If nitrates are lost from the catchment system and contribute to the acidification of these lakes (nitrogen leakage), they should increase in the lakes rather than decrease. Similarly, total dissolved nitrogen generally decreased in most lakes. Sulphates also largely decreased rather than increased in the RAMP lakes over the six years of monitoring. As mentioned in Section 3.6.7, sulphates are poorly correlated to acid deposition and H^+ in these lake systems because of the presence of neutral sulphates in dry deposition.

This confusing set of results suggests that currently, with so few years of data, it is impossible to detect definitive trends in measurement endpoints that would indicate incipient acidification. The parallel decreases in SBC and Gran alkalinity at the highest rates of acidic deposition suggest that incipient acidification is a possibility but, as yet, the effects are not significant. Further attention, in the form of monitoring, may be warranted for those lakes receiving the highest rates of acidifying substances.

Table 6.6-8 Results of Mann-Kendall trend analysis on assessment and other relevant chemical parameters to detect incipient acidification of RAMP lakes.

The numbers represent the Mann-Kendall statistic, S. Shaded values are statistically significant values of S. Negative values represent overall decreases in the parameter. Positive changes represent overall decreases. The modelled potential acid input is acidic input is provided for comparison.

Lake ID	Original RAMP Designation	pH	Total Alkalinity	Gran Alkalinity	Calcium	Sulphate	Total Dissolved Nitrogen	Nitrates and Nitrites	Dissolved Organic Carbon	Sum Base Cations	Potential Acid Input (keq/Ha/y)
168	A21	5	-4	-3	-11	-9	-9	-9	-7	-13	0.131
169	A24	11	11	-2	7	-9	-3	-7	11	7	0.122
170	A26	-3	-3	6	-3	-9	-3	11	-1	-1	0.196
167	A29	5	1	6	6	-3	-1	-5	3	5	0.095
166	A86	6	6	2	10	4	0	0	6	10	0.073
165	A42	7	11	6	13	-9	2	-5	5	3	0.075
171	A47	7	9	0	7	-1	7	7	3	7	0.075
172	A59	3	1	-8	5	3	5	-3	-5	1	0.075
452	L4	5	3	-6	-7	-7	-1	5	-1	-13	0.236
470	L7	1	-7	-6	-5	-9	-11	-6	7	-9	0.579
471	L8	5	-3	-2	-1	-5	-11	1	3	-9	0.538
400	L39	7	-5	-4	-9	-7	-9	-3	11	-15	0.069
268	E15 (L15b)	2	0	-6	-8	0	-4	-6	0	-8	0.319
436	L18	9	15	10	5	-3	1	-5	7	9	0.054
442	L23	13	11	4	-9	-13	1	-1	3	-11	0.069
444	L25	5	5	0	-3	-5	1	-1	9	-1	0.054
447	L28	13	13	4	-3	-5	-1	-9	13	-1	0.040
448	L29	2	0	-1	-6	-8	-4	-6	-2	0	0.086
454	L46	-3	-11	-6	-11	-9	3	3	3	-15	0.067
455	L47	1	1	2	-3	-9	3	7	9	-5	0.040
457	L49	5	9	0	-5	-7	9	3	11	-7	0.040
464	L60	9	13	8	5	-13	5	1	13	-5	0.040
118	L107	6	2	4	-8	2	0	-4	8	-6	0.007
84	L109	-1	-3	-10	-11	-11	-1	1	11	-11	0.014
88	O-10	7	3	0	5	-8	-5	-5	3	-15	0.014
90	R1	3	1	-2	-3	-9	1	-3	7	-1	0.014
146	E52	11	13	4	3	-9	-2	-9	5	5	0.027
152	E59	11	13	8	5	1	3	-1	7	5	0.027
89	E68	-6	-6	-10	-8	-4	-2	0	-2	-8	0.027
91	O-1/E55	13	11	4	1	-5	-1	-5	5	5	0.027
97	O-2 E67	8	11	0	-13	-13	-3	-1	-1	-11	0.027