#### 4. EFFECTS OF ACID PRECIPITATION ON AQUATIC ECOSYSTEMS

The first Québec studies on the aquatic impact of acid deposition date to the early 1980s, after it was demonstrated that highly acidic precipitation fell over the southwestern portion of the province, a region that is also highly sensitive to acidification (Bobée et al. 1982).

Two major phases in the study of aquatic ecosystems marked the 1980s. Studies conducted in the first half of the decade focused on delineating acid-sensitive areas and areas receiving a high level of acid precipitation. This same period served to appreciate the effects of acidification, explore the neutralizing potential of liming, analyze seasonal variations in surface water quality, and develop forecast models. As previously mentioned, the period 1980-1985 also coincided with the implementation of a Québec government policy aimed at reducing domestic sulphur dioxide emissions.

From 1986-1990, the focal point of studies was the biological and physicochemical components of the Québec Lake Survey (Réseau spatial de surveillance de l'acidité des lacs du Québec-RESSALQ). The physicochemical component of the RESSALQ consisted in quantifying the quality of a number of lakes in southern Québec and then extrapolating the results to all lakes in this territory (Dupont 1993). Studies conducted since 1990 have been increasingly aimed at determining the impact of current and proposed emission reductions.

#### 4.1 Current Situation

#### 4.1.1 Surface water quality

Figure 11 illustrates the spatial distribution of surface water sensitivity based on total alkalinity. Sensitivity is high at 40  $\mu$ eq/L or less, moderate at 40-100  $\mu$ eq/L, and low at over 200  $\mu$ eq/L.

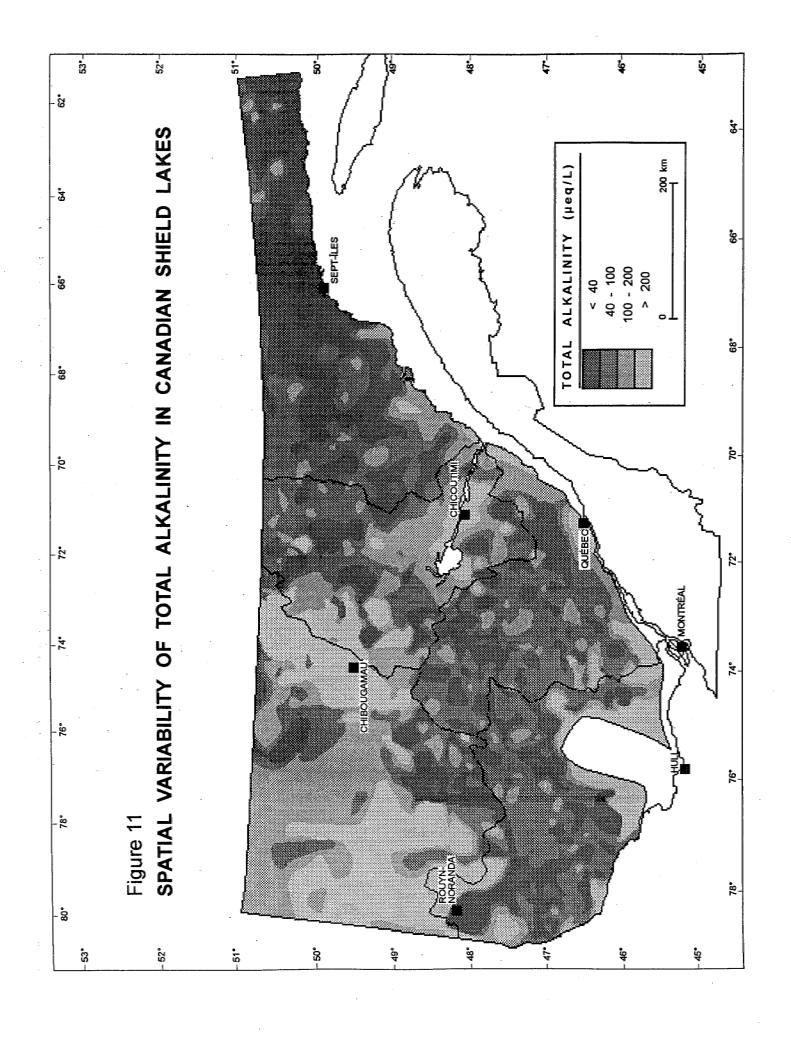
Generally speaking, the landscapes in the Canadian Shield (area north of the St. Lawrence River) have the lowest capacity for neutralizing acid deposition because of their particular geology and geomorphology (Shilts et al. 1981). Most of the rock in the Shield is carbonate-poor granite and gneiss. The shallow, poorly developed soils share the same mineralogical characteristics.

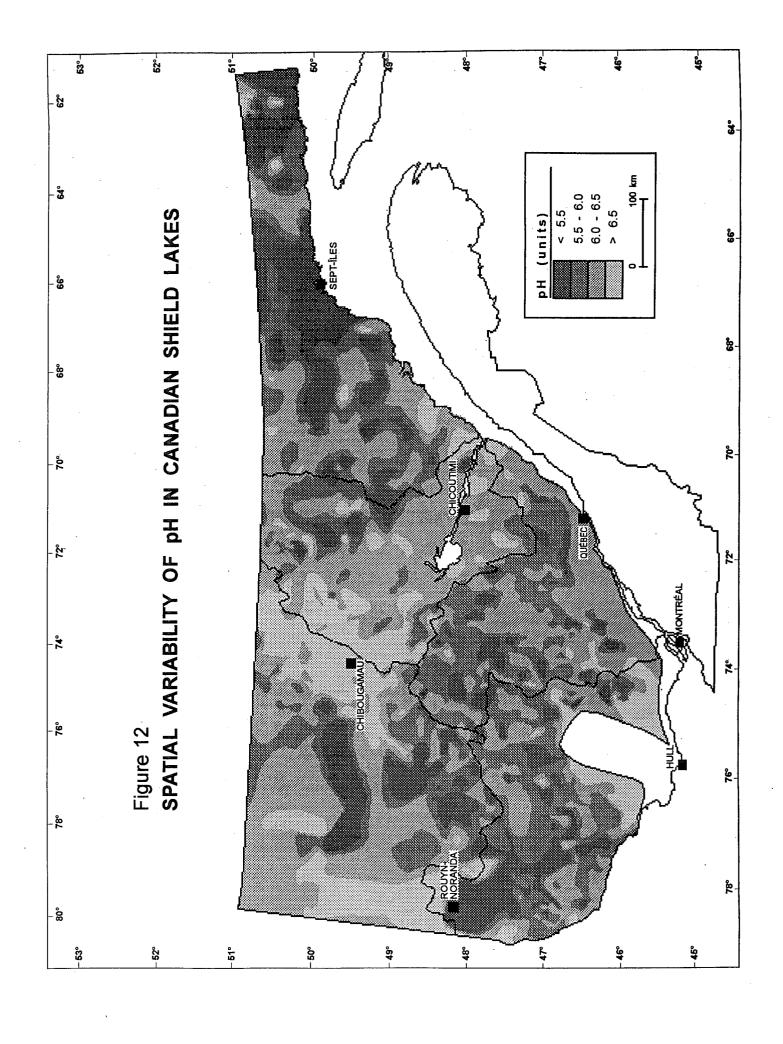
Surface waters are also highly sensitive to acidification at high altitudes (Parc des Laurentides wildlife sanctuary, North Shore). The south shore of the St. Lawrence River, Anticosti Island, the area immediately surrounding Lake Saint-Jean, the area north of Ottawa-Hull and certain sectors of northwestern Québec, on the other hand, are less sensitive to acidification due to natural buffering materials in the soil and watersheds (Dupont 1993).

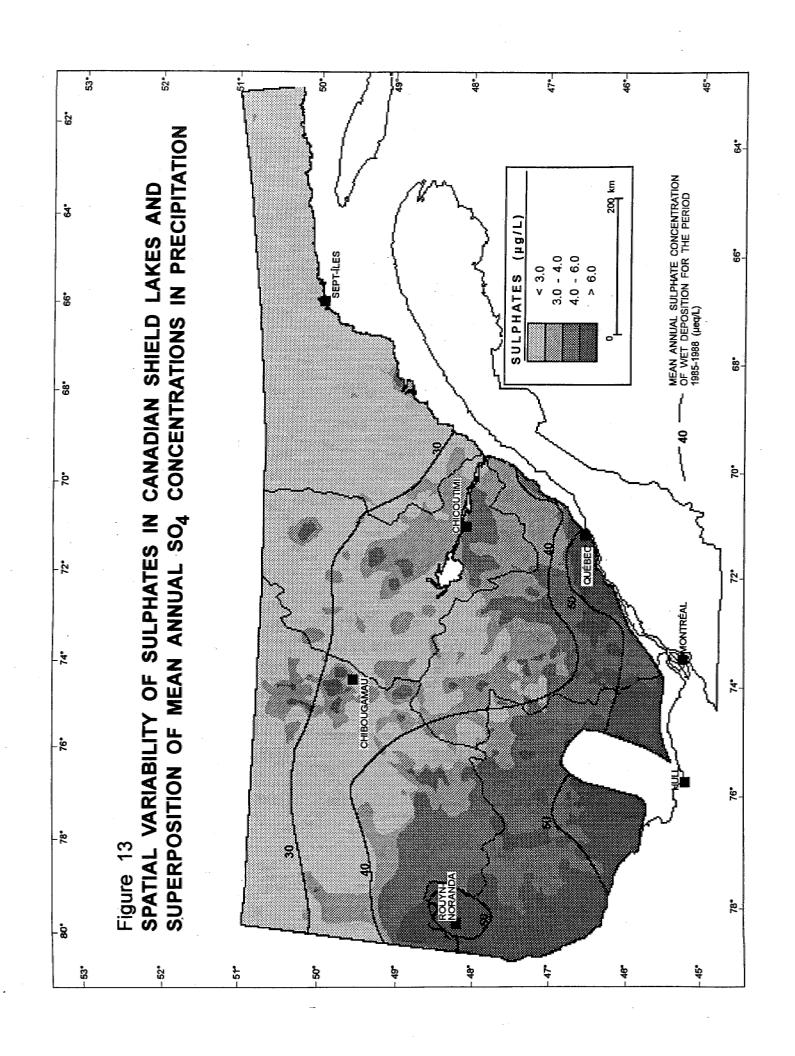
Nearly all acidic lakes (pH  $\leq$  5.5) in Québec are found in the Canadian Shield, where both soil and surface waters are highly sensitive to acid deposition (Figure 12). The majority of these lakes are located east and southeast of Rouyn-Noranda in the Abitibi-Témiscamingue region, near the Parc des Laurentides wildlife sanctuary in the Mauricie region, and on the Mid North Shore. The acidification of most lakes in the Outaouais, Mauricie and Abitibi regions which have been acidified during this century is recent and is associated with high levels of acid deposition, whereas acidic lakes in the North Shore region are almost all naturally occurring (brownwater lakes).

In terms of surface water quality, sulphates are considered a good indicator of the magnitude of acid deposition. A high level of sulphates is often a sign of major acid deposition. While a certain amount of sulphates occurs naturally in watersheds, the concentration is generally low and varies little in the Canadian Shield. The geographical sulphate distribution in surface waters (Figure 13) shows that the highest concentrations occur in southwestern Québec and in the area around Rouyn-Noranda, decreasing towards the north and northeast. This distribution is virtually consistent with the annual spatial distribution of wet sulphate deposition (Figure 3).

Although nitrates are the second largest contributor to wet deposition and although their relative contribution is likely to grow as sulphate levels in precipitation decline, nitrate concentrations in surface waters remain low (20 times lower on average than observed concentrations in precipitation) due to the high rate of assimilation by microorganisms and plants. If worldwide observations are any indication, however, this situation could change. Recent studies provide clear evidence that nitrogen pollutants could end







up playing a major role in surface water acidification. Wright (1991) and Wright and Hauhs (1991), for example, reported that global warming could intensify the acidifying effects of nitrates on surface waters in the boreal forest.

A preliminary report by Jeffries (1995) reveals that several lakes in Canada, particularly several water bodies in Québec, have nearly reached the nitrate saturation threshold, above which acidification may rapidly accelerate. A number of lakes in the Adirondack Mountains have probably already reached this threshold, even though they present very similar characteristics to lakes in the Canadian Shield. A recent American study (EPA 1995) goes further by using the Nitrogen Bounding Study to demonstrate that a large proportion of lakes in the northeastern United States may reach the nitrate saturation threshold within the next 25 to 75 years. The same study indicates that, even if the United States meets its SO<sub>2</sub> emissions reduction goal, the number of acidic lakes could double within the next century. The study recommends cutting emissions by a further 50% in order to at least maintain acidic lakes at 1984 levels.

There are approximately 750 000 lakes of all sizes in Québec. Recent studies (Dupont 1993) conducted in the Canadian Shield south of latitude 51 °N (latitude of Lake Mistassini) show that 6151 (19.3%) of the 31 808 lakes between 0.1 and 20 km² in size were acidic between 1986 and 1990; 16 525 (52%) had a pH value of 6.0 units or under. Below pH 6.0, fish populations start to decline.

The percentage of acidic lakes (pH  $\leq$  5.5) varies from 6.9% to 33% depending on the hydrographic region: North Shore 33%; Outaouais 23%; Abitibi 15.9%; Mauricie 11.8%; Saguenay 6.9%. The same observations are made for lakes with a pH  $\leq$  6: North Shore 66%; Outaouais 62.5%; Mauricie 58.3%; Abitibi 40.1%; Saguenay 29%.

An extrapolation of these figures to the 160 000 lakes over one hectare in size inventoried in the territory south of latitude  $51^{\circ}N$  suggests that a minimum of 29 432 lakes are probably acidic. The combined number of acidic (pH  $\leq$  5.5) and transition lakes (5.5 < pH  $\leq$  6.0) is probably over 81 000.

# 4.1.2 Effects of acidity on aquatic organisms

In terms of biological response to acidification, scientific studies clearly demonstrate that the total number of fish species and other aquatic organisms (plankton, benthos, plants, etc.) declines as acidity increases (Tremblay and Richard 1993). These organisms remain relatively unaffected as long as lakes have a pH over 6.0 units. However, as the pH drops to 5.5, approximately 25% of the most acid-sensitive species, such as minnows and walleye, may be lost. As acidity increases from 5.5 to 5.0, another 50% of fish species disappear. When the pH falls below 5.0, only 25% of acid-tolerant species, such as yellow perch and northern pike, can survive, although they can no longer reproduce.

The adverse effects of acidification therefore include mortality of aquatic organisms and a decline in species richness. Direct and indirect consequences range from a drop in the fish biomass in acidified lakes and depletion of the food chain to increased toxicity from aluminum and other toxic trace metals, reproductive failure, egg and fry mortality, respiratory problems, gill pathologies, a decrease in aquatic organism density, etc. (RMCC 1990; Tremblay and Richard 1993). The disappearance of species also provokes a depletion of the gene pool in fish populations.

Acidification impacts on aquatic vegetation as well. As the pH falls from 6.0 to 5.0 units, vascular plants (macrophytes) are replaced by mosses and algae mats on the lake bottom, accelerating the acidification process.

## 4.2 Reversing Acidification

Surface water acidification can be reversed. Experiments conducted in Sudbury and Coniston, Ontario, demonstrated that cutbacks in emissions of gaseous pollutants lead to an improvement in the quality of surrounding surface water (Dillon et al. 1986; MacIsaac et al. 1986). Field measurements carried out in Ontario and Norway corroborate these results (Wright et al. 1988). However, although it is possible to reverse water chemistry, only partial biological recovery is possible and is much slower (Tremblay and Richard 1993). Species structure may also change following

improvements in surface water quality as certain species disappear and their ecological niches are eventually taken over by new species. Slow biological recovery is explained by the length of time it takes for various aquatic organisms to colonize water bodies. The biological recovery of fish populations may require restocking.

#### 4.3 Liming of Surface Waters

There are two ways to alleviate the effects of surface water acidification: 1) reducing pollution at the source by cutting emissions of gaseous pollutants; and 2) intervening locally by raising the pH of water bodies. MEF has chosen source reduction as the target of its acid precipitation control program, since this is considered the most logical medium and long-term solution.

Liming provides only a stopgap measure, since the process must be repeated as long as lakes and streams remain acidic (Houde et al. 1989). It consists in applying a chemical alkaline product-usually dissolved calcite--to surface waters in order to gradually increase the pH. While liming can be worthwhile for certain groups, such as controlled zones (ZECs) and private clubs, that are experiencing acidification problems, it is not practical where large numbers of lakes are concerned, such as in Québec. In fact, it is because Québec has close to 750 000 water bodies and nearly one in five is acidic and because liming is not effective for brownwater lakes or lakes with a rapid water renewal time, and is near impossible in remote lakes, that MEF opted for source reduction.

# 4.4 Effects of SO, Emission Cutbacks

Canadian and U.S. efforts to reduce emissions of gaseous pollutants are aimed at achieving and maintaining a sulphate deposition target load of 20 kg/ha/yr. Political authorities chose this particular deposition value as it is seen to be protective of moderately sensitive ecosystems. It also serves as the environmental objective for assessing the success of emission cutbacks. However, we now know that 20 kg/ha/yr in sulphate deposition is too high for the most acid-sensitive ecosystems (Hultberg 1988; RMCC 1990; Dupont 1993). The critical load concept was developed in order to assess the impact of

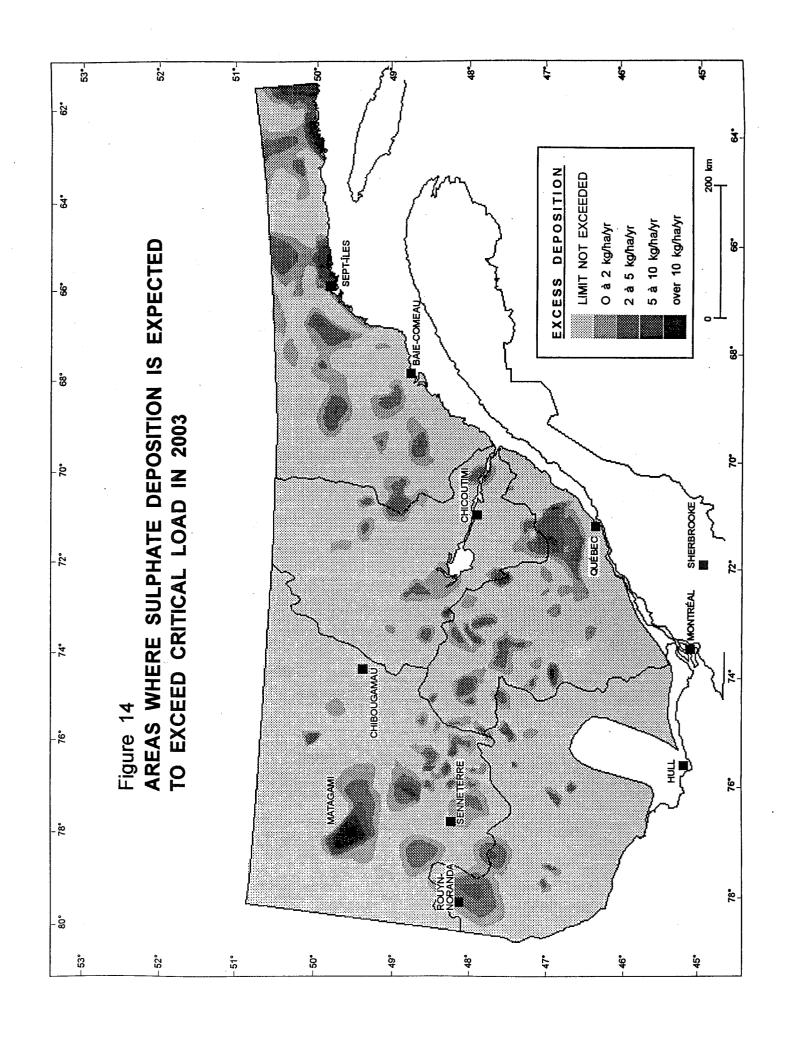
acid deposition and projected emission reductions. The critical load is the highest deposition of sulphates or nitrates that will not cause long-term acidification of surface waters or irreversible damage to aquatic organisms (RMCC 1990).

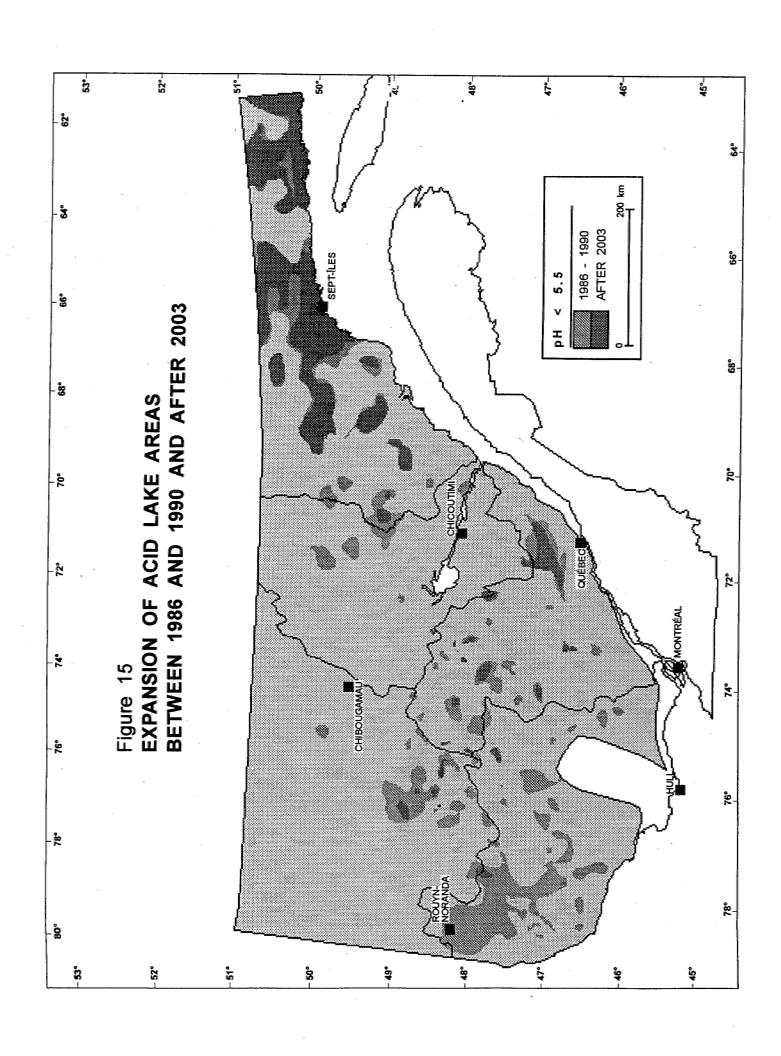
According to Québec studies (Dupont 1993), a large proportion of existing acidic lakes have critical sulphate deposition loads below 20 kg/ha/yr, which implies that a lower deposition target (12-15 kg/ha/yr) is needed in order to protect acid-sensitive ecosystems (Figure 14).

Application of acidification models enables us to predict the probable effects of emission reductions and, by extension, acidic deposition on the acidity of water bodies. According to these models, over 77% of existing acidic lakes in the Outaouais, Mauricie and Abitibi regions can probably be recovered, as acid lake areas may disappear almost entirely in these regions (Figure 15). However, the overall anticipated cutbacks will not be sufficient to reduce annual wet sulphate deposition below the critical load required to maintain non-acid conditions (pH ≥ 6.0). In fact, the lakes in certain parts of the Canadian Shield will either continue to be acidic or have a pH < 6 after 2003 (Figure 15).

It is important to mention that projections made using mathematical models (pollutant transport and acidification models) merely reflect the probable status of acidification in the future; their accuracy cannot be determined, since these models are based on a number of assumptions (Dupont and Grimard 1987). Assessments are based on the Environment Canada acid deposition scenario for 2003. The predicted percentage of acidic lake recovery will be achieved only if the proposed reductions are attained and if nitrates continue to play a minor role in acidification. In addition, projection scenarios are based on a set reduction in U.S. emission rates. In reality, the situation could change if the Trading Emission Program allows the states bordering Canada, whose plants are older than in the southern states, to cut their emissions by less than the 40% reduction goal.

The proposed reductions will enable the recovery of 64% of the 29 432 acidic lakes (pH < 5.5) surveyed in the territory under study and, in





particular, 86% of lakes acidified since the turn of the century (Dupont 1993). Of the estimated 29 432 acidic lakes in southern Québec, nearly 10 300 were already naturally acidic prior to industrialization due primarily to the presence of organic matter in surface waters. That leaves just over 19 100 "acidified" lakes. If the reduction target is achieved, approximately 16 300 of these lakes can be recovered, while additional cutbacks will be needed to ensure the recovery of the remaining 2700 lakes acidified since the beginning of the century. It should be noted that these 2700 lakes are concentrated mainly in southern Québec, near areas exploited for recreational tourism. Emission reductions should raise the pH to over 6.0 in nearly 50% of the 81 000 lakes located south of latitude 51°N that currently have a pH below this value. The pH will be raised by over 0.5 to 1.0 units in most cases. However, in the North Shore region, emission cutbacks will have only a minor impact on the recovery of acidic lakes, since most of these lakes are naturally acidic.

The improved quality of precipitation in western Québec is beginning to have positive effects on surface water quality. Environment Canada's LRTAP network (Bouchard 1992) and Phase II of MEF's NORANDA project (Dupont 1992) have both measured a decrease in sulphate levels in surface waters in western Québec. Between 1982 and 1991, sulphate reductions in lakes surveyed under the NORANDA project increased in percentage with the proximity to Rouyn-Noranda, reaching as high as nearly 50% in some cases. Since these reductions are still very recent, only a slight increase in alkalinity has been detected in this area.

# 5. EFFECTS OF ACID PRECIPITATION ON FOREST ECOSYSTEMS

As just mentioned, many lakes in Québec have undergone marked acidification only in recent decades. These lakes are primarily fed by their watershed and the local soils play a causal role in the chemical composition of surface waters. As a result, certain soil properties have been modified by acid precipitation, and these modifications influence nutrient availability and forest health. Acid precipitation therefore has a direct effect on forest cover and an indirect effect through soil.

#### 5.1 Forests

Measuring air pollutants in forests is of crucial importance in assessing the real impacts of acid deposition on forest ecosystems. To this end, Québec's atmospheric monitoring network for agriculture and forested areas (REMPAFAQ), which consists of twenty or so stations throughout Québec's agricultural and forest lands (Figure 2), regularly monitors atmospheric and climatic conditions. At the Lake Clair watershed station (Duchesnay), established in 1987, an intensive study is being conducted to determine the impact of the main environmental stresses, including acid precipitation, on two types of forested ecosystems: a yellow birch-sugar maple stand and a red spruce-balsam fir stand. Below are some of the results obtained to date.

### 5.1.1 Acidity

Since 1988, the average pH of precipitation collected over the forest canopy has remained constant at close to 4.5 (Table 4), or 23 times more acidic than clean rain (pH 5.6) in equilibrium with atmospheric CO<sub>2</sub>. The results of incident precipitation analyses confirm the direct relationship between the acidity of precipitation and the respective SO<sub>4</sub> and NO<sub>3</sub> concentrations (Figure 16). Thus, the higher the sulphate and nitrate concentrations, the more acid the precipitation.

As acid precipitation falls through the trees, it undergoes major chemical transformations and becomes more or less acid, depending on the cover type (Table 4). For the two forest ecosystems under study (yellow birch-sugar maple stand and red spruce-balsam fir stand), water that filters through the foliage (throughfall) and is collected beneath the canopy is less acid than

incident precipitation, due to the leaching of basic cations. During the summer months, however, the sugar maple stand, where throughfall is 2.6 times less acid than incident precipitation, has a greater neutralizing capacity than the balsam fir stand. Furthermore, water chemistry can be greatly modified as precipitation trickles down tree trunks (stemflow). In the sugar maple stand, stemflow is 19 times less acid than incident precipitation and 12 times less acid than beneath the canopy. By comparison, in the balsam fir stand, stemflow is 2.2 times more acid than incident precipitation and 43 times more acid than in the sugar maple stand.

Acidity is highest beneath the organic horizon, where it has remained relatively stable since 1988. The balsam fir stand is again more acidic than the sugar maple stand, likely due to greater production of organic acids.

These results demonstrate beyond a shadow of a doubt that forested ecosystems are active filters whose capacity to neutralize acid precipitation varies in accordance with the species making up the stand.

#### 5.1.2 Sulphates

Between 1988 and 1994, the sulphate concentration in incident precipitation fell by 20% (Table 4), probably due to a reduction in sulphur emissions in Québec, Ontario and, to a lesser extent, the United States. In summer,  $SO_4$  is the dominant anion, whereas in winter,  $NO_3$  predominates.

Despite a major decline in the sulphate concentration in precipitation, mean annual deposition in the Lake Clair watershed (Duchesnay) remains high, having decreased only slightly, primarily as a result of major variations in the amount of rainfall (Table 5). The mean annual wet deposition for the period under study (1988-1994) was 27.7 kg/ha, peaking at of 35.1 kg/ha in 1990 and dropping to a minimum of 24.4 kg/ha in 1991.

As with acidity, soluble SO<sub>4</sub> concentrations in rain water change as the water penetrates the forest ecosystem. At all levels studied (beneath the canopy, stemflow, organic horizon), concen-

Change in precipitation acidity and sulphate and nitrate concentrations in water and soil solution of two forest ecosystems

TABLE 4.

		L	G.M.	+ .+ r	10.1		
		Winter	W.V.	400	2.19	2.38	
	Nitrates (mg/L)	Total	2.18 1.66	12.5	1.74	1.79	
		Sumer	1.51		1.46	1.37	
		Winter	2.43 5.38	185	1.56	1.96	
	Sulphates (mg/L)	Total	2.62		1.97 2.12	2.16	
	i i	Sumer	2.78	22.23	2.23 2.60	2.30	
		Winter <sup>3</sup>	4.08 4.22 4.19	4.26	4.32 4.36	4.23	
	₹	Mean	44.4 25.33	4.27	4.29	4.25	
NCIDENT.	*	Summer	4.42	4.18	4.28 4.28	4.26	
INCI			1988 1989 1990	1991 1992	1993 1994	Mean	

stand	Fin-	22.22 22.23 22.23 22.23 27.23	2.45
Ť.	Mean	2.09 1.58 1.59 1.41 1.59	1.60
Balsam	Sum-	1.0 2.0 2.0 2.0 2.0 2.0 2.0 3.0 3.0 3.0 3.0 3.0 3.0 3.0 3.0 3.0 3	0.94
-	Vin- ter	25.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.	2.77
Maple stand	Mean	24.25.25 26.26 26.	1.93
X	Sum- mer	25.0 25.0 25.0 25.0 25.0 25.0 25.0 25.0	1.34
stand	Win- ter	2.58 2.58 2.58 2.58	3.28
Balsam fir s	Mean	23.56 23.56 23.56 25.83 36 36 36 36 36 36 36 36 36 36 36 36 36	3.40
Bals	Sum- mer	2.3.3.88 2.03.488 2.05.68	3.49
72	Win- ter	7.5.2.5. 7.6.32.24 7.6.32.24	2.03
Maple stand	Mean	2.55 2.39 2.37 2.37 2.37	2.64
*	Sun- mer	22.25 22.85 32.85 32.85 32.85 32.85	3.07
stand	Vinter	44444444444444444444444444444444444444	4.23
Balsam fir s	Mean	44444 4423 4433 4433 4433 4433 4433 443	4.30
Bal	Sum- mer	444444 4242 4413 4413 4413 4413 4413 441	4.37
70	Winter	4.27 4.27 7.27 7.38 7.37	4.25
Maple stand	Mean	44,44 44,44	4.45
Ĭ	Summer	4,4,4,4,4,5,6,5,6,5,6,5,6,5,6,5,6,5,6,5,	79.4
: 6 7		1988 1989 1990 1992 1993 1994	Mean

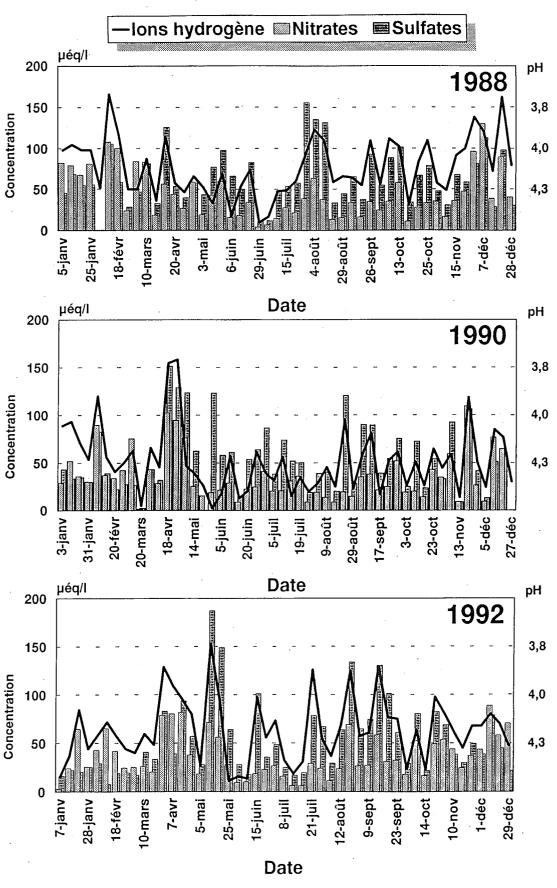
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	33.33	3.91
	33.83	3.91
		1
	5.43	5.54
	5,43 5,65 5,65 5,63	5,54
STEMFLOW	1988 1989 1991 1992 1993	- Hean

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	2.28 2.75 2.76 2.28 2.28	2.92
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	4444 468 469 468 468 468 468 468	4.8%
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NOZ	4.05 4.05 4.02 4.02 4.01	4.10
ORGANIC HORIZON		an
ORG,	1988 1989 1990 1992 1993	Mean

Lake Clair watershed (Duchesnay)
May 1 to October 31
2 Danuary 1 to April 30; November 1 to December 31
4 Wet deposition only

Figure 16 Relationship between acidity of incident precipitation and nitrate and sulphate concentrations



Bassin du lac Clair (Duchesnay)

trations were higher than those measured in incident precipitation, while mean concentrations in the balsam fir stand were significantly higher than in the sugar maple stand (Table 4). However, there appears to be almost no sulphur cycle within trees, which means that the sulphur contained in vegetation could not have been made available and leached to contribute to the noted increase in concentration. Consequently, the increased SO<sub>4</sub> concentration beneath the canopy and in stemflow is probably attributable mainly to the interception and subsequent evaporation of precipitation by the trees, as well as to dry deposition which accumulated on the leaves and trunks and was subsequently solubilized by rain water. In fact, depending on the region and stand type (softwood or hardwood), dry deposition can contribute from 25% to 50% of the total deposition. However, standard monitoring techniques do not yet allow us to quantify the extent of dry deposition in forests with sufficient accu-

The level of soluble SO4 in the organic horizon differed for the two forest ecosystems under study. While SO<sub>4</sub> concentrations were much higher in the balsam fir stand, less sulphates percolated through the humus layer, mainly as a result of greater interception of precipitation due to tree architecture (cone shape offering greater surface contact). During the summer months, only 50% to 60% of sulphate deposition collected beneath the canopy percolated through the organic horizon. It is highly possible that excess deposition stuck to the organic matter and might accumulate there over the years. Little is known about what happens to sulphur in its various forms in forest ecosystems; current research should provide some answers.

# 5.1.3 Nitrates

Apart from a notable decline (24%) between 1988 and 1989, there has been very little decrease in the NO<sub>3</sub> concentration in incident precipitation in the Lake Clair watershed since 1988. In fact, NO<sub>3</sub> concentrations have remained relatively stable since 1990, both in the winter and summer months. The lowest concentration was recorded in summer 1989 and the highest, in winter 1988 (Table 4). In 1994, 23.4 kg/ha of wet nitrate deposition fell on the watershed; this

is 0.5 kg/ha more than the mean load for the sampling period (1988-1994).

Unlike sulphates,  $NO_3$  concentrations decrease beneath the canopy in comparison to incident precipitation, especially in summer. A greater decrease was recorded in the balsam fir stand than in the sugar maple stand. One possible explanation for this is that part of the nitrates in precipitation are absorbed by the foliage. Tree architecture would again explain the differences observed in the two ecosystems.

An even greater drop in the nitrate concentration was observed in stemflow. In the sugar maple stand, nitrate levels were 60% lower in stemflow than beneath the canopy; in the balsam fir stand, a 99% decline was noted. This marked decrease is probably largely attributable to the presence of numerous epiphytes on tree bark in the balsam fir stand which absorb soluble nitrates during rain episodes. This high absorption capacity, coupled with the low stemflow, results in negligible annual nitrate input in soil.

Soluble nitrate concentrations in the organic horizon also differed in the two forest ecosystems under study. During summer, given the negligible stemflow, any NO<sub>3</sub> input to the soil comes exclusively from throughfall. The balsam fir stand receives 60% of the total NO, that falls on the sugar maple stand during summer, with as little as 2% percolation through the organic horizon. To better understand this phenomenon, the processes that take place within the organic horizon must be taken into consideration. Thus, the low amounts of NO<sub>3</sub> observed in the balsam fir stand would seem to indicate significantly less nitrogen mineralization than in the sugar maple stand. It is also possible that nitrogen is absorbed much faster by balsam fir, given the low nitrogen availability in this ecosystem. Additional studies are needed to shed more light on this matter.

Change in precipitation acidity and annual sulphate and nitrate deposition in two forest ecosystems TABLE 5.

INCIDENT4

itati( Totol	(IIII) L6				Sulphates (kg/ha)	k (kg/ha)			,		Nit	Nitrates (kg/ha)	g/ha)	=	
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	٠.		9.6		33	٠		15.2		10.5		23		7.	
	- 5				4 K	4 M		- 2		- L		2.2 4.6		<u>-</u> 0	~ ~
434 559 240 502	82		19.5		28.2	i vi w		7.7		12.8		:0:X		12.2	. ~ 4
1 281 526	9		17.4		27.7	.7		10.3		10.4		22.9		12.5	2
		i													
Balsam fir stand	m fir stand	Š		Map	Maple stand		Balsan	Balsam fir stand	<u> </u>	Maç	Maple stand		Bals	Balsam fir stand	g g
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515	919		404 404 403	17.3	25.3	8.0	19.9	32.1	12.2	2.0	9.9	10.6	0.4	14.6	ထ်ဝ
492 673 1 161 454 597 1 041	1 161		88777	20.5	28.7. 28.7. 28.7.	. 2.6.	20.5 16.0	33.1 26.9	19.6	0.0 4.0 5.0	50.5 52.3 53.9	-0.0	. 00 0 1 10 4	14.0 14.0	55
466 593 1 050 457		45.		20.3	29.8	9.5	20.7	35.7	15.0	8.8	21.7	12.9	5.6	16.8	11.2

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STEMFLOW	1988 1989 1990 1992 1993	Mean

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	0.29 0.26 0.21 0.17 0.35	0.24
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	9.6 12.4 7.8 7.7 7.7	9.8
		,
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	6.4 6.5 12.9 11.3	10.0
	15.4 11.9 10.7 10.6 7.7	12.3
	15.4 11.9 11.1 10.7 12.7	12.3
		-
,	136 135 226 333 216 216	206
	136 135 226 333 216 217	206
		•
	333 333 326 322 352 352	336
RIZON	333 333 356 324 322 352 352	336
ORGANIC HORIZON	1988 1989 1990 1992 1993	Mean

1 Lake Clair watershed (Duchesnay)
2 May 1 to October 31
3 May 1 to April 30; November 1 to December 31
4 Wet deposition only

## 5.1.4 Leaching

When it rains, dry deposition which has accumulated on foliage and deposition carried in incident precipitation interact to cause the leaching of basic cations that are important nutrients for trees (e.g. K, Ca, Mg) (Table 4). Research conducted at the Lake Clair watershed, discussed at greater length in Laflamme et al. (1990), showed a significant correlation between basic cation leaching and acid deposition-related sulphates. and a negative correlation between basic cation leaching and the amount of precipitation collected beneath the canopy. K was shown to be subject to the greatest leaching, followed by Ca and Mg; the annual nutrient losses through leaching amount to 13.9, 3.0 and 0.7 kg/ha/yr respectively. Combined with other pressures, such as biotic (e.g. insects, diseases, etc.) and abiotic (e.g. climatic fluxes, drought) factors, and depending on their magnitude and duration, the leaching of nutrients which are essential to tree growth may cause additional stress and thus contribute to or magnify existing nutrient imbalances within the ecosystem.

Research conducted on the Lake Clair watershed clearly demonstrates the implication of acid precipitation in nutrient cycles and sulphur and nitrogen dynamics in Québec forests through the atmospheric input of NO<sub>3</sub> and SO<sub>4</sub>. Furthermore, it is important to consider that the impacts of air pollutants are often both extremely subtle and gradual, and have a cumulative effect. Recent studies conducted using a simulation model (Arp 1993) to assess critical NO<sub>3</sub> and SO<sub>4</sub> loads (values over which sustained yield of biomass is no longer possible) in similar ecosystems in the United States (Huntington Forest) and Ontario (Turkey Lake) showed that the critical thresholds for these ecosystems are probably well below current deposition levels at the Duchesnay forest station and in other regions of Québec. It is therefore crucial that Québec continue conducting research in this area in order to better appreciate the exact impacts of acid precipitation and find concrete solutions as soon as possible.

# 5.2 Indirect Effects on Forest Ecosystems Through Soil

In forest ecosystems, the natural soil-vegetation cycle of basic elements maintains the chemical

composition of the soil solution in equilibrium with pedologic input and drainage losses. Acid precipitation increases mobile anion input (SO<sub>4</sub><sup>2</sup>, NO<sub>3</sub>) in forest ecosystems, and if the soil is unable to immobilize these anions, the latter alter the soil balance and carry acid cations such as Al3+ and essential basic cations such as Ca2+, Mg2+ and K+ with them in drainage water. Studies conducted on watersheds that receive acid precipitation show a significant loss of cations in relation to atmospheric input. Measurements taken at the Lake Clair watershed indicate that Al3+ and Ca2+ migration is primarily accompanied by SO2 migration, which testifies to the major impact these anions have on the soil chemical balance (Table 4).

Accelerated leaching of cations in the soil causes changes in the availability of certain basic elements and exacerbates cation imbalances on the soil exchange complex. Soil cation imbalances in turn hinder the assimilation of essential nutrients. Research conducted in sugar maple stands in the Québec Appalachians showed that foliar deficiencies are associated with a Ca2+/Mg2+ and K<sup>+</sup>/Mg<sup>2+</sup> imbalance, and an imbalance between Ca2+ and the soil exchangeable acidity (Quimet and Camiré 1995). Foliar deficiencies in sugar maple stands are that much more severe given that Ca/Mg, K/Mg and Ca/Al cation exchange ratios decrease in the mineral soil layer. Similarly, the increase in nitrate input can cause a nutritional disequilibrium in sugar maple stands, creating additional demand on the soil for mineral cations. In southern Québec, a decline among maples is often characterized by a high N/K ratio in leaves.

#### 5.3 Forest Decline and Dieback

Acid precipitation influences soil chemistry and there is growing agreement among North American and European scientific communities that soil imbalances caused by acidification are largely responsible for forest declines and associated nutrient deficiencies. Aerial surveys conducted between 1985 and 1987 showed that half of the 2.12 million hectares of sugar maple stands inventoried showed signs of decline (Figures 17a and b). Based on the extent and the non-specific nature of decline and dieback (they can

attack all tree species in the maple stand), it is safe to say that large-scale stresses within the territory are the primary contributing factors.

Characteristic signs of decline and dieback include nutrient stress (Bernier and Brazeau 1988a, 1988b and 1988c) and declines in growth rate (Ouimet and Fortin 1922) (Figure 18). The results of forest fertilizer trials and the known relationships between soil cation imbalances and foliar deficiencies strongly suggest that modifications in soil chemistry as a result of acid precipitation are one of the main causes of forest declines in Québec.

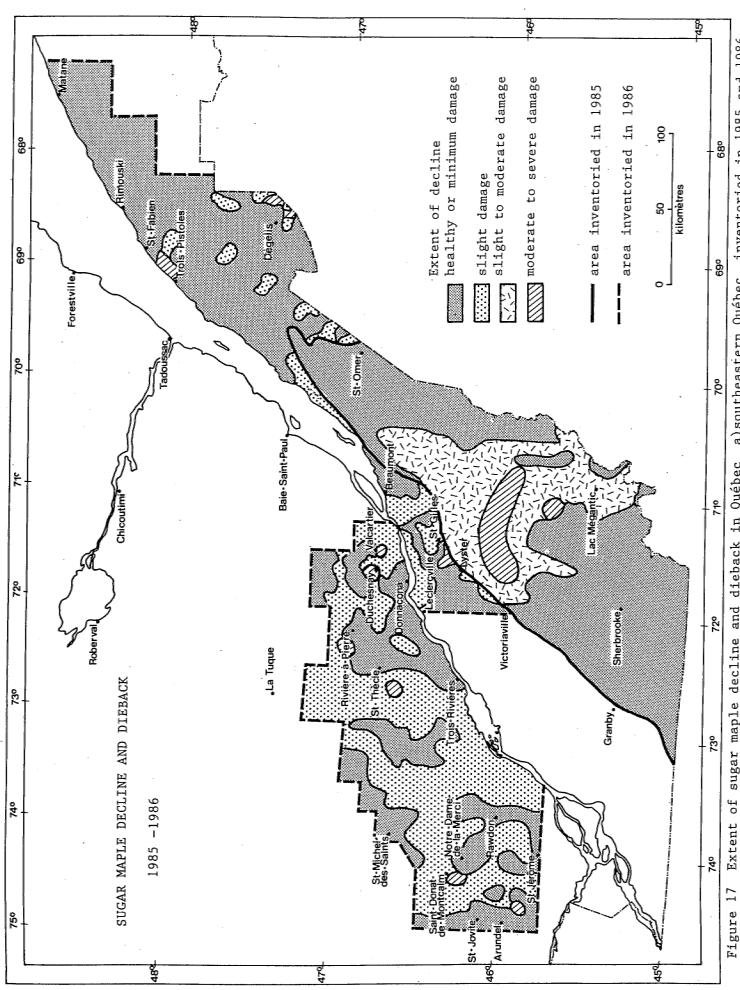
## 5.4 Attempts to Curb Decline and Dieback

Various experiments have been conducted in Québec to mitigate the damages caused by the decline of sugar maple stands. Fertilization and stand tending are the two principal measures currently being implemented to improve tree nutrient status and heighten resistance to environmental stresses.

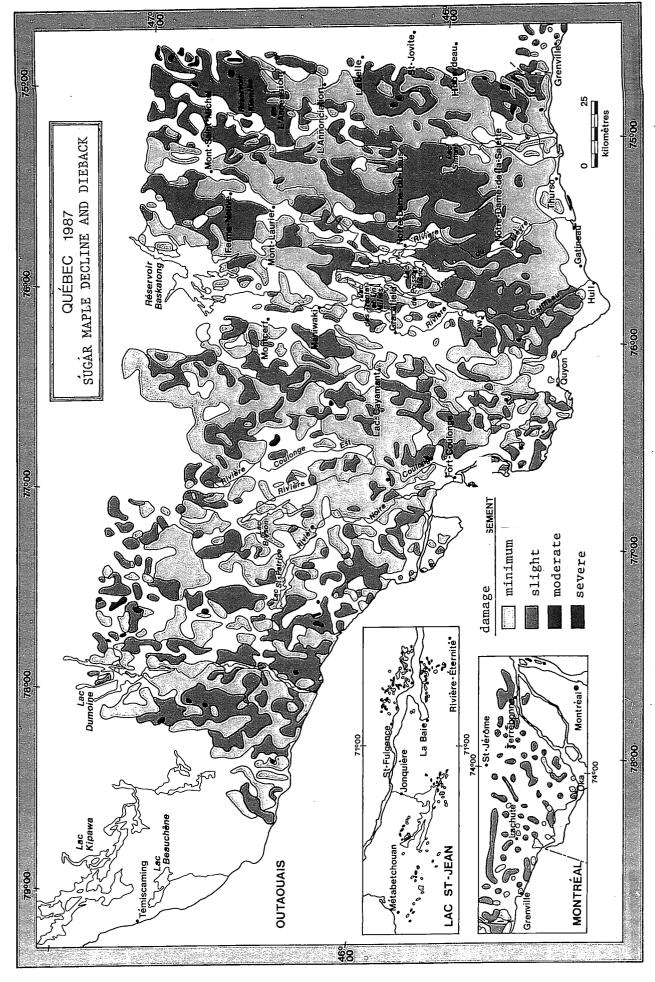
The addition of nutrients limiting maple growth and metabolism through fertilization is generally effective in correcting the observed mineral deficiencies in declining forests and in restoring vigour to the trees (Hüttl 1989; Nys 1989; Ouimet and Fortin 1992). Ouimet and Fortin (1992), for example, succeeded in decreasing the N/K ratio in leaves and increasing the annual radial increment by 50% through fertilization.

The operational fertilization program carried out between 1989 and 1992 enabled nearly 2000 Québec producers to treat their sugar maple stands and help control dieback. This large-scale operation appears to have been successful: a follow-up shows that the application of fertilizer reduced the percentage of trees showing signs of active decline and dieback (Ouimet 1991) and continues to benefit the trees four years later.

Studies suggest that the productivity and stability of forest ecosystems can be improved by planting a variety of species (mixed stands), each with its own ecological niche and the capacity to enhance soil fertility. However, this is relatively uncharted territory and further research is needed to find suitable solutions.



Extent of sugar maple decline and dieback in Québec a)southeastern Québec, inventoried in 1985 and 1986



Extent of sugar maple decline and dieback in Québec b) southwestern Québec, inventoried in 1987 Figure 17

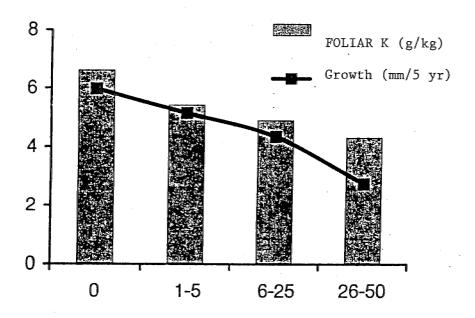


Figure 18. Relationship between rate of decline, tree nutrient status in terms of potassium and radial increment in sugar maples in southeastern Québec for the past five years

#### 6. OTHER IMPACTS

#### 6.1 Human Health Effects

Acid precipitation can affect human health both directly and indirectly. The direct responses, which are primarily related to respiratory health, are caused by atmospheric acids and their precursors (NO<sub>2</sub> and SO<sub>2</sub>). Acid precipitation can also affect human health in an indirect way through acidic deposition to the soil and alterations in the biophysical environment. The most common example is the acidification of surface waters and the subsequent mobilization of heavy metals, which can increase exposure to these toxic substances through drinking water and fish. However, in the opinion of the U.S. Environmental Protection Agency (EPA), such indirect effects currently do not represent major implications for human health (NAPAP 1990). The EPA considers the direct effects to be of far greater concern (NAPAP 1993).

It is difficult to separate the direct health effects associated with acid precipitation from the effects of airborne pollutants as a whole. Several studies have demonstrated that conventional and toxic airborne pollutants can synergistically interact to produce human health responses.

Studies of human health responses to acid precipitation should be limited to pollutants emitted by major fuel-burning sources, that is, SO<sub>2</sub>, nitrogen oxides and suspended particulates, which are compounded by their products (sulphuric acid and ammonium compounds). Ozone and photochemical smog, although they interact substantially with nitrogen oxides, are not considered part of the acid precipitation problem.

Sulphur dioxide, nitrogen oxides and hydrocarbons released through combustion react to form acid aerosols (diameter  $< 1 \mu m$ ), including sulphuric acid ( $H_2SO_4$ ) and ammonium bisulphate ( $NH_4HSO_4$ ). Some of these chemical forms are either partially or completely neutralized and contribute little to total aerosol acidity.

Exposure to acid aerosols in fine particle form is critical, since these particles can be inhaled and accumulate on the surfaces of the lower respiratory tract.

Three principal means are used to assess the human health effects of acid precipitation: human volunteer studies, animal experiments and epidemiological studies of exposed human populations (NAPAP 1993).

Human volunteer studies, in which individuals are exposed to similar aerosol acidity concentrations as those found in ambient air, have demonstrated the potential for acute and chronic responses. Asthmatics show acute responses (bronchial constriction) to acid aerosol exposure: acid aerosols depress the respiratory tract's immune response system, increasing individual susceptibility to infection. Acid aerosols primarily attack the respiratory tract by slowing mucociliary clearance (Folinsbee 1992).

Animal experiments have shown that chronic exposure to low aerosol acidity concentrations can cause permanent damage to the respiratory tract. For example, rabbits exposed to low aerosol acidity concentrations on a daily basis showed chronic bronchitis-like changes, whereas a single exposure to the same dose generally produced only passing, and reversible, alterations in clearance (American Thoracic Society 1991).

There is evidence that, for several types of health responses, such as lung function and lung and tracheobronchial mucociliary clearance, the potential toxicity of acid aerosols is related more to the level of acidity (pH) than to the level of sulphates, with H<sub>2</sub>SO<sub>4</sub> being the most toxic, followed by ammonium bisulphate (NH<sub>4</sub>HSO<sub>4</sub>) and ammonium sulphate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (Schlesinger et al. 1990).

Epidemiological studies conducted in relation to acute pollution episodes in the 1950s and 1960s showed significant associations between particle concentrations and mortality rates; during these episodes, a constituent element of suspended particulates was sulphuric acid, believed to be the causative agent (Folinsbee 1992). In southern Ontario, Bates and Sitzo (1989) found positive associations between hospital admissions and elevated levels of sulphates in the air. Ambient acid concentrations also produced symptoms of chronic bronchitis in children (Raizenne et al.

1989). A Québec study (Delfino et al. 1994) of the Montréal region showed that between 1984 and 1988, hospital admissions in July and August for respiratory conditions other than asthma were 9.6% higher on days where sulphate concentrations exceeded 8.1  $\mu$ g/m³ during the 4 days prior to admission.

The sparsity of data on ambient aerosol acidity concentrations precludes an accurate characterization of exposure (NAPAP 1993).

Québec's air pollution monitoring network measures ambient sulphate levels at 41 sites. However, given that the acid levels associated with acidic aerosols produce greater responses than sulphate levels, ambient H<sup>+</sup> should also be measured, as this will make it possible to study the spatial and temporal variability of aerosol acidity and sulphate concentration in Québec. Currently, the wide variability in the relationships between the two parameters would appear to preclude extrapolating the pH value of aerosols to sulphate concentrations (Lipfert and Wyzga 1993).

The EPA currently considers that not enough data exists on the effects of acid aerosols to establish dose-response functions that would enable us to quantify human health risks with sufficient accuracy (NAPAP 1993).

#### 6.2 Materials

Acid precipitation and air pollutants in general can cause all kinds of damage to materials. Acidic pollution leads to the deterioration not only of building limestones, but also of other materials such as certain metals, paints and plastics (Canada/U.S. Agreement 1992). Of greatest concern is the degradation of historic buildings and monuments. This problem has become so serious in Europe that the EUROCARE program was created to devise and implement measures to prevent environmental damage to cultural resources. As well, several studies on the degradation of historic monuments are being conducted in the United States. Canadian studies in this area were conducted at the École polytechnique in Montréal. To date, no provincial or federal government study has been conducted in Québec.

#### a) metals

The decline in rates of metal corrosion in recent decades has been consistent with the decline in atmospheric SO<sub>2</sub> levels.

In the past few years, research has enabled us to better appreciate the relative contribution of pollutants to metal corrosion; research under NAPAP (1992), for example, showed that acid deposition (dry and wet) is responsible for between 31% and 78% of the disintegration of galvanized steel and copper. It also showed that the corrosion rate increases with exposure; for example, galvanized steel corrodes at a rate of  $0.6 \, \mu \text{m/yr}$  in unpolluted areas, rising to  $1.5 \, \mu \text{m/yr}$  in urban areas.

Spence and McHenry (1994) calculated the corrosion rate for galvanized steel plates by linking an acid deposition model with an atmospheric corrosion model (SO<sub>2</sub> emissions used were 1985 levels for eastern North America). The corrosion rate was shown to be high in the Montréal area, at 1.48  $\mu$ m/yr, compared with over 0.75 µm/yr for all of southern Québec. The highest value obtained through modelling was in the area south of the Great Lakes, at 2.0  $\mu$ m/yr. The study showed that an overall 50% reduction in all emissions under consideration (U.S. and Canadian) would result in a 30% drop in the corrosion rate in the Montréal area and a minimum 20% decline in the rate for all of southern Québec (south of Québec City and the Abitibi region). According to Spence and Henry's model, approximately two-thirds of corrosion in southern Québec is anthropogenic.

The role of nitrogen oxides in metal corrosion has not been clearly established. Similarly, studies targeting different shapes and structures show that application of a dose-response function must take into account the significant variation in corrosion rates for different materials and structures.

#### b) painted surfaces

Painted surfaces degrade when exposed to acidic concentrations that are significantly higher than ambient levels and to precipitation with a considerably lower pH than the ambient air. While

sulphur compounds and airborne particles can damage automotive paints, it has been shown that factory-applied paints are extremely resistant to acid deposition.

#### c) stone and masonry

Acid deposition contributes to the decay of stone structures by causing the disintegration and loss of material or surface details (erosion), black crusts which disfigure stone surfaces, and chipping and fractures.

Disintegration and erosion are the most conducive to quantitative measurement. Studies in Germany showed the erosion rate for sandstone to be between 11 and 52  $\mu$ m/m of rain in polluted urban and industrial areas. In the United States (NAPAP 1992), marble apparently erodes at 1/10 to 1/100 that rate. In certain places, anthropogenic acidification accounted approximately 30% of average disintegration, two-thirds of which was attributable to sulphur compounds and the remaining one-third, to nitrogen compounds. A number of factors have to be considered when establishing doseresponse functions: total precipitation, acidity of precipitation, exposure time, surface geometry, co-occurring organic compounds, etc. The formation of black crusts is associated with the SO<sub>2</sub> concentration in the air; studies are presently being conducted in the United States and Europe to better understand how dry deposition to stone occurs.

## d) assessing damage

One area in which information is limited is the assessment of physical damage caused by acid deposition and the service life of materials. More research needs to be conducted into the links between the deposit of contaminants and material maintenance cycles. Currently, there is not enough knowledge to assess the damages associated with acid deposition.

#### 6.3 Agriculture

The following information is taken from Bélanger (1984), whose study was aimed at recommending measures to overcome problems of acid precipitation and ozone pollution experienced in

Québec's agricultural industry. The study focused on soil acidification, the effects of acid precipitation on crop yields and the phytotoxic effects of gaseous pollutants.

As previously mentioned, acidification is the main threat to soil, as it alters soil chemistry and can degrade soil fertility, deplete the soil of available nutrients, cause an increase in elements that are toxic to plants, and slow biological responses. However, a number of sources other than acid deposition can also contribute to soil acidification, including fertilization (nitrogen components), the breathing of soil organisms, the uptake of basic cations through plant roots, etc. Bélanger reports that acidification from nitrogenous fertilizers is between 2 and 10 times greater than from acid deposition. Moreover, the current state of data indicates that all acidifying substances affecting farmland, including nitrogenous fertilizers, cause 10 times more acidity than acid deposition.

Soil acidification and the associated adverse effects can generally be corrected through crop production practices, particularly liming. Regularly limed soils will therefore be relatively unharmed by the deposition of acids. Furthermore, only a fraction of the lime normally applied to farmland is needed to neutralize acid deposition.

Nitrogen and sulphur are important for crop growth. Bélanger (1984) underlines that the atmospheric input of nitrogen compounds (deposition) is negligible and that the amount of sulphur that falls in precipitation is approximately the same as the amount obtained through root uptake. The fertilization value of acid deposition in eastern Canada is apparently over 10 times the lime value needed to neutralize the deposited acids.

Relatively little is known about the direct effects of acid precipitation on crop yield as compared to the phytotoxic effects of gaseous contaminants such as sulphur dioxide and ozone.

#### 7. CONCLUSION

Sulphur dioxide emissions have declined substantially in Québec in the past decade, falling from just over 1 MT in 1980 to less than 400 000 tonnes in 1996. By comparison, from 1980 to 1990, SO<sub>2</sub> emissions decreased 17.6% in the other Canadian provinces and 23% in the provinces east of Saskatchewan, excluding Québec. Ontario, whose emissions contribute to acid deposition in Québec, cut its total SO<sub>2</sub> emissions from 1.8 MT in 1980 to 900 000 tonnes in 1992 and 574 000 tonnes in 1994, for an overall reduction of 68%.

However, Québec continues to receive a high level of acid deposition. Currently, between 11 and 31 kg/ha/yr of wet sulphate deposition and between 7 and 25 kg/ha/yr of wet nitrate deposition fall over southern Québec. From 1990 to 1993, an area of approximately 100 700 km² received an annual sulphate deposition loading greater than 20 kg/ha/yr. The mean annual pH of precipitation is around 4.35 and approximately 68% of weekly precipitation has a pH below 4.6.

During the period 1985-1993, an important decrease in sulphate concentrations in precipitation was observed in southern Québec (0.5-4.0% per year depending on the region). During this same period, the Abitibi region experienced an approximately 20% decline in sulphate concentrations, primarily as a result of Québec's  $SO_2$  emissions reduction policy and the efforts of Noranda Minerals Inc. Finally, the frequency of precipitation posing a threat to aquatic ecosystems (pH < 4.6) has not changed since the early 1980s for Québec as a whole. In other words, weekly precipitation acidic enough to harm aquatic ecosystems was just as frequent in the early 1990s as during the previous decade.

In 2003, sulphate deposition in excess of 12-15kg/ha/yr is expected to still fall over a large portion of southern Québec (south of Lake Saint-Jean and the Abitibi region).

Surface waters in southern Québec, particularly in the Canadian Shield, are highly sensitive to acidification. Nearly one in five lakes in Québec is currently acidic (pH  $\leq$  5.5), while over half of all lakes have a pH below 6.0 (acidic and transition lakes). A large share of the acidified lakes in southwestern Québec are the result of acid deposition since the beginning of the century.

This recent acidification has also had direct and indirect effects on aquatic organisms, such as a decline in species diversity, fish mortality, etc. However, SO<sub>2</sub> emission cutbacks should nevertheless enable the physicochemical recovery of most of the existing acidic lakes. Only partial biological recovery will be possible though, since the gene pool represented by lost species can never be reproduced. Acidification can be reversed in most acidic lakes once annual wet sulphate deposition has dropped to below 12 to 15 kg/ha/yr. Nitrates could end up playing a major role in surface water acidification, since a large proportion of lakes in the northeastern United States are expected to reach the nitrate saturation threshold within the next 25 to 75 years. If this happens, the number of acidic lakes could increase.

decline, With respect to forest research conducted in the Lake Clair watershed (Duchesnay forest station) provides clear evidence of the implications of acid precipitation for nutrient cycles and sulphur and nitrogen dynamics in Québec's forest ecosystems. The effects of air pollutants are often subtle, gradual and cumulative. Recent studies have shown that critical loads for ecosystems similar to those found at the Duchesnay forest station are probably lower than deposition levels currently observed at Duchesnay and in other regions of Québec. The relationships between soil cation imbalances and foliar deficiencies, as well as experimental fertilization, strongly suggest that alterations in soil chemistry as a result of acid precipitation are a major contributing factor in nutrient stresses observed in Québec forests. In other areas, the impact of acid deposition on Québec farmland is apparently negligible.

With respect to human health responses, studies conducted in southern Ontario showed a positive association between hospital admissions and elevated sulphate concentrations in the air. Acidic aerosol concentrations in the ambient air were also correlated with chronic bronchitis-like symptoms in children. However, the current state of data on aerosol acidity concentrations in the air precludes both an accurate characterization of exposure and the establishment of a doseresponse relationship that would enable a quantitative measurement of health risks associated with acid aerosols.

Finally, little is known about the damages caused to buildings, monuments and materials by acid precipitation in Québec.

It is crucial that Québec continue its efforts to control acid precipitation. These efforts must be aimed at sufficiently monitoring the situation (especially as regards projected reductions in the states bordering Canada as provided for in the Canada/United States Air Quality Agreement), assessing the impacts of acid precipitation with greater accuracy, and determining whether the proposed reductions will be sufficient to reverse surface water acidification, all with a view to implementing concrete solutions without delay.

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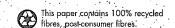
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<del>기계기기</del> 등 없다. 이 사람들은 그 원호 (1985년 등 1985년 )
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<del>으로 보다</del> 다는 경험하는 하는 것 같은 것은 것 같은 것은 것이 없다.
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