Impaired Waters Restoration Plan
For Acid Rain Lakes (NYS Forest Preserve)
Adirondack Region, New York

and Proposed
Total Maximum Daily Load (TMDL)
for pH/Acid Rain Impacts

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New York State
Department of Environmental Conservation
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Preface

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The focus of this Impaired Waters Restoration Plan/Total Maximum Daily Load (TMDL) is to address impairment to uses due to acid rain (atmospheric deposition) in a number of lakes in the Adirondack Region. This impairment to uses resulted in the inclusion of these waters in the 1998 (and subsequent) NYS Section 303(d) List of Impaired Waters. Section 303(d) listed waters require the development of a total maximum daily load (TMDL) or other appropriate strategy to achieve water quality standards and restore uses, such as aquatic life support.

About 400 waters are included on the New York State Section 303(d) List because of impairment to aquatic life support attributed to acid rain. The majority of these lakes were added to the list in 1998 and were based on chemistry and biologic data from the mid-1980s or prior. The focus of this restoration strategy/TMDL is limited to those affected lake waters that fall within New York State Adirondack Forest Preserve lands. The reason for limiting the universe of waters to be covered is due to the applicable water quality standards for these waters. The applicable pH standard for most waters outside the Forest Preserve lands is "not less than 6.5." While this is a scientifically derived standard based on the support of aquatic life, it might not be a realistic standard for all waters of the Adirondacks, where natural limitations such as limited acid neutralizing capacity (ANC), soil characteristics, geology and hydrology and other considerations suggest some of these waters may have never attained a pH of 6.5. Even so, acid rain may still restrict aquatic life support in these waters.

The ultimate goal for all waters would be that they achieve all water quality standards for classified waters and support a full and diverse aquatic community. However, State water quality standards such as the pH standard of 6.5 have not been applied to waters within the Forest Preserve because of the alternative protection provided in Article 14 of the New York State Constitution. If State standards were applied, a TMDL would have to demonstrate that prescribed loading reductions could meet this standard. The lack of specific, numeric water quality standards for Forest Preserve Waters allows for some flexibility in developing interim TMDL endpoints. Such variability, as well as the expectation that TMDL loading capacity and allocation scheme will need to be revised as additional information is collected, opens the door to developing a "phased" TMDL

Recent USEPA (2006) guidance clarifying the application of phased TMDLs recommends that:

> "...the use of the term "phased TMDLs" be limited to TMDLs that need to be established despite significant uncertainty and where the State expects that the loading capacity and allocation scheme will need to be revised in the near future as additional information is collected. For example, such significant uncertainty may arise because the State is using a surrogate to interpret a narrative standard, or because there is little information regarding the loading capacity of a complex system such as an estuary and it is difficult to predict how the a water body will react to the planned load reductions."

Regarding the complexity of the system, the nature of the loading sources responsible for this impairment to New York State waters also complicates the loading reduction strategy called for in this restoration plan. Because significant sources lie outside New York State borders any effective loading reduction strategy must include national (regional) reduction efforts. Beyond any initial reductions – and in keeping with the phased TMDL approach – additional reductions are likely to be needed to attain water quality standards and restore uses of at least some of these waters. However the complexity of the transport, deposition, in-water effects and appropriate natural limitations – factors that vary somewhat across the range of 143 target waters – suggest that an incremental/phased approach is appropriate.

Another important aspect of this restoration strategy/TMDL is the associated monitoring plan. EPA recommends that phased TMDLs include monitoring plans to determine if load reductions in fact lead to attainment of water quality standards. The complexity of this particular water quality problem also supports the need for monitoring. But other aspects such as the remote location of many of these waterbodies, the fact that many of them were originally listed as impaired based on data that are now 20-30 (or more) years old and the clear potential that a fair portion of these waterbodies might never achieve full compliance with the existing numeric state water quality standards also highlight the importance of the monitoring component.

While retaining a minimum pH of 6.5 as the ultimate goal for these waters, this phased TMDL uses a hierarchy of interim aquatic life support thresholds. As the emission of acid rain precursors are reduced regionally, monitoring data will be used to assess pH recovery and aquatic life support, and to refine simulation models to see what additional reductions would be necessary to achieve further recovery and a higher level of aquatic life support. This iterative adaptive management cycle is an appropriate strategy to deal with the complexities of restoring these acid rain waters.

Additional note: Although atmospheric deposition is the primary source of mercury loading to many of these same lakes, this TMDL does not address mercury or mercury-related water quality issues.

Impaired Waters Restoration Plan for Acid Rain Lakes (NYS Forest Preserve) and Proposed TMDL for pH/Acid Rain Impacts

1.0 Introduction

The 1998 (and subsequent) New York State Clean Water Act (CWA) Section 303(d) List of Impaired Waters identified a number of lakes (and some streams) in the Adirondack Mountain Region of the state as having designated uses (aquatic life support) impaired by low pH and associated impacts. The listing is based on monitoring data collected by the NYSDEC Division of Fish Wildlife and Marine Resources (DFWMR) and the Adirondack Lakes Survey Corporation (ALSC) during the 1970s and thru 1986. The ALSC found that region-wide, the source of lower pH was predominantly mineral acidity derived from atmospheric deposition. A portion of the low pH lakes contained naturally occurring organic acids derived from their watersheds. This document outlines an Impaired Waters Restoration Strategy/Total Maximum Daily Load (TMDL) for a subset of these lakes; specifically those acid rain-impaired lakes that lie within the New York State Forest Preserve lands. This restoration strategy relies on statewide, regional and national efforts to reduce atmospheric emissions and, in turn, reduce loadings of the acid-producing contaminants sulfur and nitrogen oxides (SO_x, NO_x).

The phased TMDL approach recognizes the significant uncertainty in attaining standards in these waters and relies on an iterative re-evaluation and revision to loading and allocation schemes.

The strategy proposed here is that of a phased TMDL. This approach recognizes the significant uncertainty in attaining standards in these waters – the complexity of the pollutant loading calculations, the lack of recent water quality data and the limits of available models to determine current and projected conditions for many of these waters – and relies on an iterative re-evaluation and revision to loading and allocation schemes. Upon the Federal implementation of initial planned reductions (see Appendix 17.3), these waters will be monitored and re-evaluated to determine how the waterbodies react to the reductions and assess the potential for further recovery by individual waterbodies. Modeling tools will also be refined to reflect additional information that is collected. If uses/standards are not being supported/met, the restoration strategy/TMDL will be revised and the need for appropriate additional reduction measures and other actions to achieve additional recovery (where feasible) will be identified.

Acid Rain Lakes/Streams in NYS Forest Preserve, Adirondack Region, New York	
Waterbody and Segment ID:	Multiple segments, see *Appendix 17.1* for complete list.
Drainage Basin/Sub-basin: Hydrologic Unit Code:	Multiple Basins (Black River, Saint Lawrence River, Lake Champlain, Upper Hudson and Mohawk River Basins). Multiple HUCs
Applicable Stream Standard:	These waters *"are to be maintained in their natural condition."*
Section 303(d) Listing:	These waters are included on the 2006 List (Part 2a and Appendix A), these waters first appeared on the 1998 List.

2.0 Background

In accordance with Section 305(b) of the Federal Clean Water Act (CWA) (33 U.S.C. 1315(B)), New York State is required biennially to prepare and submit to the United States Environmental Protection Agency (USEPA) a report addressing the overall water quality of the State's waters. This report is commonly referred to as the 305(b) Report or the Water Quality Report. New York State updates the water quality information used to satisfy Section 305(b) on a continuing, five-year rotating basin approach through its Waterbody Inventory/Priority Waterbodies List Assessment Program.

In accordance with Section 303(d) of the CWA, the State is also required to prepare and submit to USEPA a biennial report that identifies waters that do not meet or are not expected to meet surface water quality standards and/or do not support appropriate uses after implementation of technology-based effluent limitations or other required controls. This report is commonly referred to as the Section 303(d) List. Waterbodies included on the list are considered to not support appropriate uses due to impairments that require the development of a total maximum daily load (TMDL) or other appropriate strategy to achieve water quality standards and restore uses.

A TMDL represents the assimilative or loading capacity of a waterbody, taking into consideration point and nonpoint sources of pollutants of concern, natural background and surface water withdrawals. These loading capacity calculations quantify the amount of a pollutant a water body can assimilate without violating a state's water quality standards and allocates that load capacity to known point sources in the form of wasteload allocations (WLAs), nonpoint sources in the form of load allocations (LAs), and a margin of safety (MOS). In short, a TMDL is developed to identify all the contributors to surface water quality impacts and set load reductions for pollutants of concern needed to meet water quality standards.

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EPA guidance (Sutfin, 2002) describes the statutory and regulatory requirements for approvable TMDLs, as well as additional information generally needed for USEPA to determine if a submitted TMDL fulfills the legal requirements for approval under Section 303(d) and EPA regulations. New York State believes that this TMDL report adequately addresses the following items in the May 20, 2002 guideline document:

1. Identification of waterbody, pollutant of concern, pollutant sources and priority ranking
2. Description of applicable water quality standards and numeric water quality target(s)
3. Loading Capacity
4. Load allocations (LAs)
5. Wasteload allocations (WLAs)
6. Margin of Safety
7. Seasonal Variation
8. Monitoring Plan to track TMDL effectiveness.
9. Implementation (although a specific Implementation Plan is not required)
10. Reasonable Assurances
11. Public Participation

3.0 Description of Waterbody, Watershed, Pollutant, Sources, Priority Ranking

3.1 Waterbodies and Watershed

The New York State CWA Section 303(d) List of Impaired Water Requiring a TMDL includes 400 waterbodies where the impairment is the result of atmospheric deposition (acid rain). Of these, 143 lakes are located within designated Adirondack Forest Preserve (FP) lands. The focus of this TMDL plan is limited to these Forest Preserve waters due to the specific protections from other sources of pollution afforded these waters and the unique water quality standards that apply to them. A list of these waterbodies is presented in Appendix 17.1. The other acid rain waterbodies outside the Forest Preserve will be addressed in a separate future restoration strategy/TMDL.

The lakes that are the focus of this restoration plan lie in the Adirondack Region of New York State. This region includes portions of a number of larger drainage basins, most of which contain some of the 143 acid rain-impacted lakes of the Forest Preserve lands. The locations of the affected Forest Preserve watersheds in the Adirondacks region are shown in Figure 1. The lakes are distributed widely throughout the region in a number of different major drainage basins. These waterbodies are generally remote and subject to no local sources of impact.

3.2 Pollutants

Acid rain refers to the deposition of sulfuric/nitric acids onto watersheds and ultimately into streams and lakes. Dilute sulfuric and nitric acids are formed when oxides of sulfur (SO_x) and nitrogen (NO_x) react with water in the atmosphere. The specific water quality concern in these waterbodies is not with the sulfuric/nitric acids or SO_x and NO_x levels in the waters, but rather with lowered pH levels and elevated aluminum concentrations that are the result of the atmospheric deposition. Research in the Adirondack Region has shown that lake water acidity also results in higher mercury levels in fish. A recent report summarizing 1990 to 2000 data states that the mean pH of precipitation in New York State is 4.3 (USEPA 2003). Without sufficient buffering capacity of soils in the surrounding watershed, lower pH in a waterbody will occur. In addition to the effect of lower pH, acid waters also react with naturally occurring aluminum in the watershed to increase aluminum concentrations, potentially in excess of water quality standards. Aluminum concentrations above standards are toxic to certain native fish species.

3.3 Sources

Due to the remote location and the general prohibition of discharges to waters within the Forest Preserve, the primary (in fact, the lone significant) source of impairment to these waters is atmospheric deposition. SO_x and NO_x can be transported long distances by atmospheric circulation patterns before landing on the surface of the watershed. The primary source of SO_x emissions is coal-burning power plants, while other sources include petroleum refining and combustion, and metal smelting (NEIWPCC 2004). The combustion of fossil fuels, chiefly by automobiles and electric power plants, is the primary source of NO_x in the atmosphere (NEIWPCC 2004).

While naturally occurring watershed conditions can influence water quality in these lakes, impacts from atmospheric deposition due to anthropogenic sources is the focus of current efforts. Many of these specific sources lie outside the borders of New York State. Because of this (and other factors) this restoration plan is somewhat atypical from more traditional TMDLs. In fact, this situation was recognized when these waters were first included on the New York State Section 303(d) List back in 1998:

> The extensive studies which have been conducted on the "acid rain" waterbodies have shown that the water quality problem and resulting aquatic life impairment is not the result of wastewater discharges subject to control under the Clean Water Act. Therefore, a TMDL analysis in the classical sense may not be appropriate. Since the problem and its solution is a national issue requiring implementation under the Clean Air Act, the Department is requesting that USEPA take the lead in developing the TMDL for all states that are affected by this water quality problem.

The 1998 List also noted that:

> ...Efforts are underway on a national level to reduce pollutant emissions required by the Clean Air Act. New York and other northeast states have taken legal action against EPA to accelerate implementation of controls, particularly in the Midwest. Monitoring of these waters will be continued to assess changes in water quality resulting from implementation of the Clean Air Act. These changes are expected to occur only slowly over the time.

3.4 Priority Ranking

The NYSDEC includes these Forest Preserve lakes on the Section 303(d) List on the part of the List designated as *Part 2a - Multiple Segment/Categorical Impaired Waterbodies Segments (atmospheric deposition)*. It is noted that these waters might be addressed by a pollutant/source-specific TMDL.

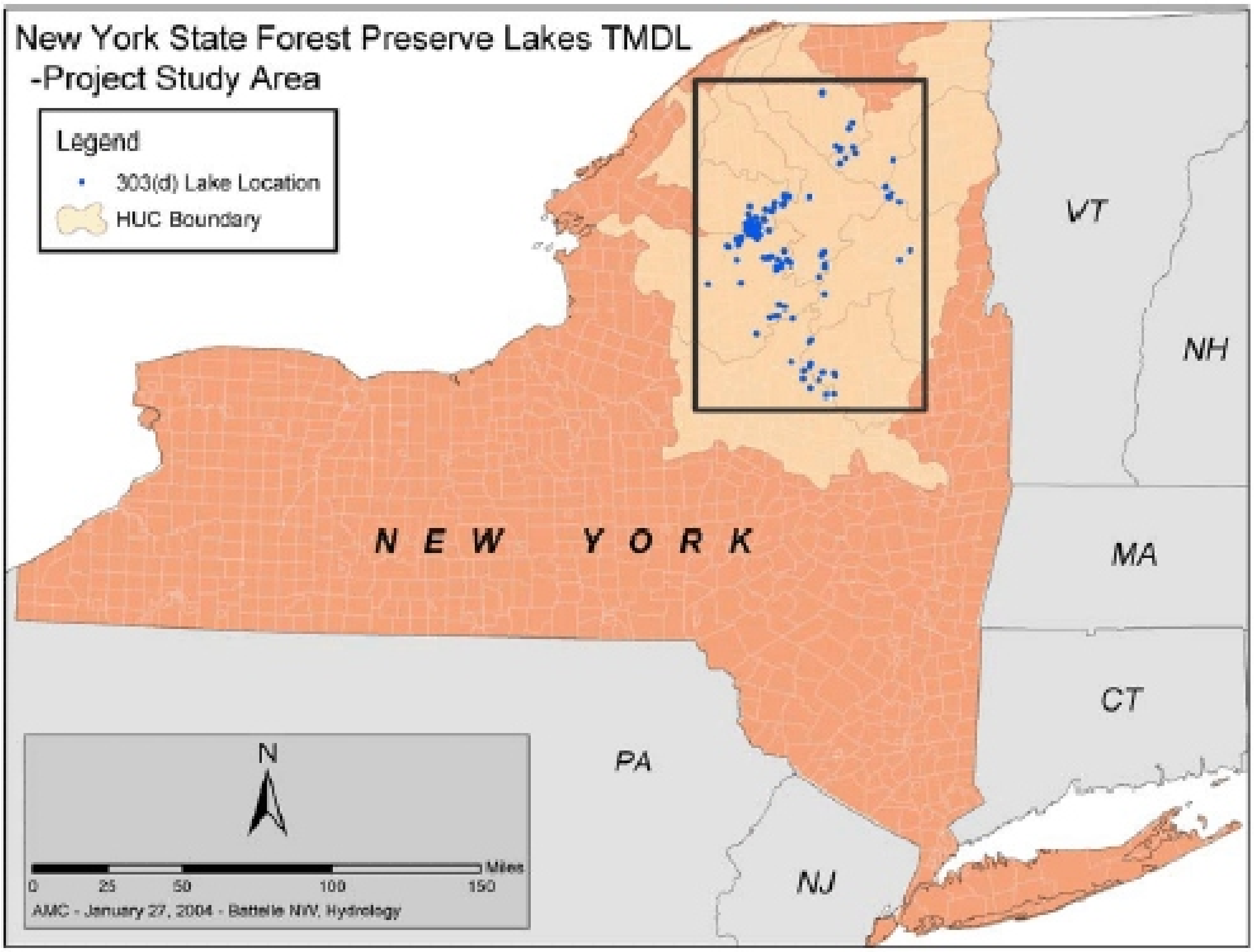

Figure 1 - Acid Rain Impaired Lakes of the Adirondack Forest Preserve Watersheds

Waterbodies on this part of the list that are also in the Forest Preserve are also noted as being *high* priority waters, i.e., waters scheduled for TMDL/restoration strategy development within the next two years.

The identification of priorities for TMDL development is a function of various factors, including severity of problem, availability of monitoring data, local support, availability of funding, applicability/availability of modeling tools, identification of appropriate endpoint (i.e., water quality standards), etc. Additionally, circumstances regarding many of these factors change over time. Consequently USEPA has agreed that states may limit the prioritizing of waters on the list to identification of those waters where TMDL development is a high priority for the next two year period (i.e., until the next Section 303(d) List is published). This flexibility allows states to respond to changing landscape, take advantage of other strategies and approaches, and direct TMDL development to where it will have the greatest benefit.

4.0 Applicable Water Quality Standards and Numeric Targets

New York State has specific numeric water quality standards for pH in classified surface waters of the state. For Class AA, AA-Spcl, A, A-Spcl, B and C waters the pH "shall not be less that 6.5 nor more than 8.5" and for Class D pH "shall not be less that 6.0 nor more than 9.5." New York State also has a specific numeric water quality standard for aluminum for classified surface waters of the state. For Class AA, AA-Spcl, A, A-Spcl, B and C waters, the a water quality standard of 100 µg/l for ionic aluminum applies for the protection of aquatic life (chronic). However, preliminary modeling (Battelle, 2006) found that would be unrealistic to meet these standards in all the acid rain waters of the Adirondacks. In fact, in pre-industrial times, before the development of significant anthropogenic sources of SO_x and NO_x, many of the waters in the region of New York Forest Preserve had pH levels lower than the New York pH standard of 6.5 (Charles et al. 1989).

However, while these standards apply to *classified* waters of the state, waters of the Forest Preserve are not classified. Protection of these waters is regulated by the New York State Constitution, rather than the water quality standards regulations in 6 NYCRR Parts 700-706 cited above. As a result, the possibility of developing a TMDL for these waters – using an endpoint other than 6.5 – was explored.

4.1 Land Classifications

Forest Preserve lands of the Adirondacks are protected by the "forever wild" provisions of Article XIV, §1 of the New York State Constitution, which reads in part as follows: "The lands of the state, now owned or hereafter acquired, constituting the forest preserve as now fixed by law, shall be forever kept as wild forest lands." A reasonable and generally accepted interpretation of the State Constitution language suggests that the waters of the Forest Preserve are to be maintained in their natural condition. It was initially thought that the flexibility provided by this interpretation would allow for the establishment of a TMDL with a pH target of less than 6.5 that would be appropriate for Adirondack lake waters, be reflective of geological limits and character of the Adirondack region, and also be more likely to be attained. However, as outlined below, efforts to establish a single specific numeric criteria for pH and/or aluminum that are known to be reflective of natural limitations for all the 143 waterbodies were not successful. As an alternative to single specific criteria, tiered interim criteria/recovery goals were developed as endpoints for the Forest Preserve acid lakes Phase 1 TMDLs.

4.2 Water Quality Standards

Because protection of the Forest Preserve lands and waters is governed by the language of the State Constitution rather than the parameter-specific numeric water quality standards, it becomes necessary to establish numeric water quality targets for these Phase 1 TMDLs. These targets would be used to determine whether or not recovery has been attained and appropriate uses are protected.

Four potential substances/measurements were considered as numeric targets corresponding to the natural condition of these waters: pH, dissolved reactive Al, acid neutralizing capacity (ANC), and the Acid Stress Index (ASI). Of these, pH and Al were determined to be the most appropriate for use in the development of acid rain TMDLs in the Adirondacks Region. A summary of aluminum chemistry can be found in Neville et al, 1988.

The ANC was discounted because it is not linearly related to pH or Al^{3+} or toxicity, and hence, is not an optimum toxicity indicator. However, although there is no state water quality standard for ANC, this measure can provide a qualitative sense regarding margin of safety in that it represents the buffering capacity remaining in the system. The ASI incorporates aluminum, hydrogen and calcium and ranges from no acid stress to total mortality (Baker et al. 1990a). However ASI is only representative of individual species and therefore is not as suitable as pH or Al for describing lake condition. In the Adirondack Park waters, Baker et al. (1990b) found that pH alone was as good or occasionally a better indicator of water toxicity to fish than composite indexes, such as the ASI.

Having decided on the use of pH and/or aluminum as appropriate indicator parameters, attention then turned to determining appropriate numeric criteria for these parameters. However, efforts to establish single specific numeric criteria for pH and/or aluminum that are known to be reflective of natural limitations of all the 143 waterbodies were not successful. The variation in the characteristics affecting water chemistry and aquatic life support in these waters (lake area, lake volume, watershed area, soil type, soil depth, groundwater flow, retention time, etc.) were too great for single values to be reached.

After considerable consultation and deliberation with DFWMR staff, it was determined that the existing state water quality standards for pH (never below 6.5) and Aluminum (never above 100 µg/l, ionic) in classified waters are also are the most appropriate criteria for describing thresholds for adverse ecological impacts. However, as an alternative to single specific criteria, a hierarchy of interim recovery goals were proposed for the Forest Preserve acid lakes TMDL. These criteria were derived from estimates of toxicity thresholds for pH levels and concentrations of inorganic monomeric aluminum (Al_{IM}) that, although less stringent than existing standards for classified waters, would signal recovery in lakes affected by acid precipitation. For example, one such hierarchal goal would be the attainment of conditions which would allow for the maintenance of populations of acid tolerant fish, of which brook trout (*Salvelinus fontinalis*) is an appropriate representative.

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It can be argued that historically many Adirondack Forest Preserve lakes had naturally low pH values, did not ever achieve year round values exceeding 6.5, and were never inhabited by highly diverse fish assemblages. However it would be grossly inaccurate to assume that the existing state water quality standards for pH have no applicability to the majority of the Forest Preserve lakes. A report of 1812 lakes included in the EMAP survey of the Adirondack Region of New York State found that while 41% (743 lakes) are chronically acidic or sensitive to episodic acidification, of these acid-sensitive lakes only 17% (126) were dominated by naturally occurring organic anions and were therefore assumed to be naturally acidic lakes (Driscoll, 2001). Statistically, then, it would be reasonable to assume that of the 143 lakes singled out for attention in this Restoration Strategy/TMDL, less than 25 would be likely to be naturally acidic lakes. (Sinnott, 2005)

Clearly if a single set of criteria are to be broadly applied to a large number of lakes, then these criteria must be adequately protective of all lakes. Rather than proposing less stringent criteria as ultimate targets, these targets should be adequate to restore water quality and appropriate aquatic life support in all the Forest Preserve lakes. As reductions are implemented and resulting improvements measured, it is appropriate to evaluate individual lakes to determine if, on a case-by-case basis, less stringent criteria might represent the “natural condition” of particular lake. When there is evidence supporting an exception to the more protective statewide criteria ($pH > 6.5$; $Al_{IM} < 1.0$ µm/l), Use Attainability Analyses (UAAs) can be conducted for those lakes where the statewide criteria are unlikely to be attained due to natural acidity. However it is important to stress that such naturally acid lakes must be individually identified, and that the ecosystems of all lakes cannot be assumed to be less supportive of aquatic life until proven otherwise.

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While a pH of never below 6.5 and Aluminum of never above 100 µg/l (ionic) are the ultimate goals for these lakes, it is understood that the achievement of the ultimate goals is an iterative process and that some lakes, due to natural limitations, may not be capable of achieving this goal. Therefore, the following narrative-based tiered interim criteria/recovery goals will be used to establish Phase 1 TMDLs.

4.3 Interim Criteria

Over the past 20 years, the ecological impacts of acid precipitation have been studied extensively and within the Adirondack Region, long-term monitoring and analysis has identified chemical trends in 52 lakes since 1992. Biological investigations related to acidification recovery are also underway. This study has produced criteria indicating thresholds of ecological impairment. Such criteria are useful in identifying lakes that are in the process of recovery.

Table 1 outlines a hierarchy of interim recovery goals for the acid lakes phased TMDL. The first of these recovery goal/criteria (Full Recovery) reflects conditions that would meet existing New York State water quality standards for classified waters of the state. Lakes meeting this goal would support aquatic ecosystems that reflect abundant and diverse aquatic life consistent with unimpacted lakes within the Adirondack Ecological Zone. As discussed above, it is appropriate to consider this tier to be the ultimate goal for all the acid rain lakes, at least initially.

Table 1 - Interim Recovery Goals for Acid Rain Lakes

Tier	**Chemical Criteria**	**Biological Criteria**	**Basis**
Full Recovery	pH: summertime instantaneous values never below 6.5; (snowmelt[1] season pH values consistently greater than 6.0) Aluminum: Al (ionic) < 100 ug/L	Full aquatic biological communities consistent with unimpacted lakes within the Adirondack Ecological Zone.	New York State water quality standards.
Tier 1 - Interim	pH: for snowmelt season pH$_{(10\ D)}$[2] $\geq$ 6.0; Aluminum: AL$_{IM}$[3]$_{(10\ D)}$ $\geq$ 2.0 umol/L or 54 ug/L	Lakes capable of supporting sensitive Cyprinids and sensitive invertebrates survival.	Driscoll et al, 2001, described these values as "indicators" of recovery
Tier 2 - Interim	pH: 1-day average $\geq$ 4.9; snowmelt season pH$_{(10\ D)}$ $\geq$ 5.4 Aluminum: AL$_{IM\ (10D)}$ not to exceed 4 umoles/L or 108 ug/L[4]	Lakes capable of supporting brook trout survival.	Proposed by Battelle, for the support of brook trout.
Naturally Acidic Lakes	N/A		Acid bogs, certain seepage lakes, etc. Based on wetland vegetation and hydrology these waters are considered to be naturally acidic.

[1] March 1 thru May 31 during which runoff from melting snow occurs; also a critical spawning/hatching period.

[2] (10 D) represents ten day rolling average.

[3] inorganic monomeric aluminum.

[4] The conversion for inorganic monomeric aluminum is based on the molecular weight of aluminum (Snyder, personal common). Concentrations of Al$_{IM}$ in micromoles /L can be converted to micrograms /L by multiplying by the atomic weight for Al, 26.982 (Baldigo and Lawrence, 2000)

The other tiers represent interim Phase 1 criteria/goal toward full recovery. The Tier 1 interim criteria/recovery goal reflects a *Lowest Observed Effects Concentration* (LOEC), whereas the Full Recovery goal correspond to *No Observed Effects Concentration* (NOEC) for acid rain-impaired ecosystems. This tier reflect aquatic ecosystems with abundance and diverse communities, but at levels lower than those consistent with unimpacted waters. Lakes at this tier would be capable of supporting more than acid tolerant species of fish.

The Tier 2 interim criteria/recovery goal reflects a level of recovery sufficient only to sustain populations of acid-tolerant fish as the only resident, self-reproducing fish species. Brook trout (*Salvelinus fontinalis*) has been suggested as a potential representative acid tolerant species for monitoring and assessment purposes, however, other species, such as the black-nose dace (*Rhinichthys atratulus*) might prove to be more appropriate. These lakes that would also support a less diverse invertebrate assemblage of acid tolerant species.

The last criteria/goals represents Naturally Acidic Lakes. Fish species may not be present in these waters and invertebrates are limited to lower abundances of acid-tolerant species. These lakes are naturally acidic and will not support a healthy population of fish and invertebrates. Note that while such lakes are assumed to exist in the Adirondacks, no specific lakes have been assigned to this category/tier nor has specific criteria for such lakes been developed. Such a designation would need to be carefully evaluated on a case-by-case basis.

In conclusion, it is likely that the natural limitations of each of the 143 waterbodies cause water quality conditions to fall within the range of the four tiers. Modeling efforts to date have been limited in their ability to characterize and assign each of these lakes to one of the four tiered recovery levels at the outset of this process. However this limitation need not stall the implementation of a phased restoration strategy. The initial loading reductions (see Section 9.2) are reflective of the federal and state reduction efforts already identified and being implemented. Ongoing monitoring and assessment, including the refinement of modeling efforts, will continue during the implementation of these emission reduction efforts in order to evaluate the actual recovery and estimate the potential for additional recovery of these lakes. As knowledge is gained regarding the appropriate natural limitations of specific waterbodies, these waters will then be assigned to the appropriate recovery level.

Also note that the Interim Recovery Goals criteria outlined in Table 1 includes corresponding chemical and biological criteria. The advantages of chemical criteria are they are easier to measure and more straightforward basis for a TMDL. However the chemical and biological criteria may not correspond exactly across all lakes. And while chemical criteria has the advantages noted above, biological criteria are generally a better indicator of ecosystem health. Evaluation of recovery in specific lakes will give appropriate weight to both biological and chemical criteria and will recognize that support of a full native aquatic biological community is reflective of waters without impairment to aquatic life uses.

5.0 Water Quality Conditions

New York's Adirondack Park consists of over 6 million acres of forest, lakes, streams and mountains. The area includes the largest wilderness area east of the Mississippi River and is a tremendous natural resource enjoyed by millions of visitors each year. Unfortunately, it is one of the most sensitive regions in the United States to acidic deposition and has been impacted to the extent where significant fish populations have been lost. In the 1990s, EPA reported that 10 % of Adirondack lakes are acidic based on their surveys of 153 waters larger than 10 acres. The ALSC, which included lakes less than 10 acres in their extensive survey of 1469 lakes, found greater impacts: 24% of Adirondack lakes are seriously acidic (pH of less than 5.0 have been recorded). They further found that approximately half of the waters surveyed in the Adirondacks have a mid summer acid neutralizing capacity less than 40 μeq/L and can be classified as sensitive to acidic deposition (Baker, et al, 1990).

Paleoecological studies involving the analysis of sediment cores collected during the 1980s showed that many of the study lakes became acidic only in the last 10-50 years during the time when air pollution and acidic deposition levels were highest. Other studies have similarly documented that fish population declines and losses of entire populations occurred in many lakes within the last 10-50 years.

The list of waters impaired by acid rain/atmospheric deposition that is included in the current Section 303(d) List of Impaired Waters was first developed in the 1998 Section 303(d) List. This list of these waters was established by the Adirondack Lakes Survey Corporation (ALSC) in the mid to late 1980s, and DFWMR studies that go back even farther (1960s and 1970s). The ALSC surveyed approximately 1,400 lakes, representing about one-half of all water bodies in the Adirondacks. Note that the focus of the ALSC work was on Adirondack lakes and does not include impacted, low order streams or impacted waters of the Catskills.

6.0 Desired Endpoint

As discussed in Section 4.0, the protection of the waters of the Forest Preserve are governed by the New York State Constitution as "forever wild" rather than by the specific numeric water quality standards regulations that apply to other classified waters of the state. Initially it was thought that this would allow for the establishing of appropriate – but less stringent and achievable endpoints – for these waters. However as noted above, establishing less stringent common criteria that was adequately protective of all 143 waterbodies was not successful.

As a result the approach taken in this restoration strategy/TMDL has been modified toward that of a phased TMDL. Rather than establishing a traditional TMDL, the objective of which would have been to attain less stringent endpoints, the proposed approach is to strive for the more protective existing pH and Aluminum endpoints that are currently in place for most waters of the state through a phased TMDL. These ultimate endpoints are as follows.

pH	shall not be less that 6.5 (nor more than 8.5).
Aluminum	less than 100 μg/l, measured as ionic aluminum.

However, as a result of natural limitations, some of these 143 waters may never achieve the above ultimate endpoints. The most recent available data and modeling indicate that none of these 143 waters currently meet the less stringent Tier 2 interim criterion/recovery goal, as discussed in Section 4.0 and Table 1. NYSDEC concludes that, due to a long history of human-induced conditions and natural limitations, the initial goal of this TMDL/Recovery Plan should be to establish Phase 1 TMDLs for all 143 waters that meet the Tier 2 interim criterion/recovery goal. These initial endpoints are:

pH	greater than or equal to 5.4, as a 10-day rolling average.

Initial modeling shows that existing planned emission reductions in conjunction with some additional measures (e.g., lime addition) would allow the 143 lakes to reach the above Tier 2 interim criteria/goal. Given the limits of the modeling, the complexity of transport, deposition and in-water effects, the variability of conditions and the uncertainty as to what constitutes the natural condition in each of these lakes, this would seem an appropriate Phase 1 endpoint from which to evaluate progress and consider an appropriate next phase TMDL.

7.0 Source Assessment

The primary and virtually only source of pollutants to these remote waters in undeveloped watersheds is atmospheric deposition. The primary emissions responsible for atmospheric deposition are sulfur dioxide (SO_2) and oxides of nitrogen (NO_x) from the combustion of coal, oil and natural gas. The combustion compounds are transformed into sulfuric and nitric acid and transported downwind before they are deposited.

Sources of emissions responsible for acid rain include many of the conveniences we take for granted everyday. The burning of fossil fuels to supply the electricity we use is a significant source of sulfur dioxide and nitrogen oxides. Another source is the burning of fuels to power cars, trucks, buses and airplanes. Emissions from these common and widespread sources originate virtually everywhere. Some of the emissions originate within New York State; and some component of the pollutant load is from sources worldwide. But the waters of the Northeast and Adirondacks are most affected by sources from Southeast to Midwest United States and Canada.

8.0 Load Capacity

The loading capacity is defined as the greatest amount of loading of a substance that a water can receive without violating water quality standards. In this case, the critical loads would be the amount of sulfuric/nitric acid deposition that result in a lake reaching a specific water quality endpoint. For pollutants that are specifically limited by a water quality standard, the calculation of TMDL loading capacity is straight-forward. However the relationship between SO_x and NO_x emissions and pH in a lake is not only indirect, but nonlinear, interdependent (SO_x and NO_x loading need to be considered in terms of loading pairs) and varies depending upon a host of lake and watershed characteristics. In such complex situations estimates of critical loads are often developed using models. A modeling approach to estimate the response of a variety of lakes to various levels of atmospheric deposition is certainly appropriate in this case.

There are a number of other factors that introduce significant uncertainties into the modeling of lake responses and the calculation of the loading capacity for this TMDL. These considerations, complications and the level of uncertainty inherent in these calculations strongly suggests that the adaptive implementation approach of a phased TMDL is appropriate.

However as discussed previously, there are a number of other factors that introduce significant uncertainties into the modeling of lake responses and the calculation of the loading capacity for this TMDL. These include the lack of current condition baseline data (pH data for most of the lakes are 20 or more years old), the uncertainty in the relationship between sulfuric/nitric acid deposition and the resulting concentrations of pH and aluminum in the lake, and quantification of the availability of acid neutralizing cations in the soil of each lake watershed. There is also some uncertainty regarding the relationship between pH and aluminum concentrations and the resulting level of support and diversity of aquatic life. And as noted above, the ability to model ecological limitations for 143 waterbodies with varying characteristics has proven to be a challenge. And while the ultimate stated goal of this TMDL/Restoration Strategy is full compliance with existing water quality standards for pH and aluminum, recognition that attaining these standards may, in fact, be unrealistic for some of these waters also needs to be taken into consideration. These considerations, complications and the level of uncertainty inherent in these calculations strongly suggests that the adaptive implementation approach of a phased TMDL is appropriate.

The adaptive implementation approach applied here uses the model to estimate what impact defined loading reductions – in this case, those that are planned or already in place (such as the Clear Air Interstate Rule, or CAIR) – will have on water quality. As these reductions are implemented, monitoring of the waters conducted and the models refined, the question of what additional loading reductions would be necessary to meet appropriate goals can be considered with more confidence.

9.0 Pollutant Allocation

Typically a TMDL allocates the Load Capacity among Waste Load Allocation (WLA) or point sources, Load Allocation (LA) or nonpoint sources, and a Margin of Safety (MOS). Given the limitations of the model, some consideration was given to delaying the identification of the TMDL pollutant allocation until after additional data were collected and the model could be further refined. However recent USEPA guidance entitled "Clarification Regarding "Phased" Total Maximum Daily Loads" discussed this specific issue. The guidance recommends that the phased approach is appropriate for "TMDLs that for scheduling reasons need to be established despite significant data uncertainty and where the State believes that the use of additional data...would likely increase the accuracy of the TMDL load calculation and merit the development of a second phase TMDL" (USEPA, 2006).

Using what is acknowledged to be both limited but also the best available modeling information, a pollutant allocation was developed for an initial phase TMDL. A modeling framework was used to provide estimates of pH and aluminum concentrations after the implementation of the CAIR reductions. In summary, the approach included: delineation of lake subwatersheds; classification of subwatersheds based on soil and vegetation types; application of a watershed hydrology model for runoff and groundwater flow; and the application of an enhanced version of the PHREEQC geochemical model to simulate lake chemistry (Battelle 2006, included as Appendix 17.4). However the modeling showed that even after full implementation of the CAIR reductions the desired interim TMDL endpoint is not achieved. Therefore the TMDL uses the addition of $CaCO_3$ (lime) as a buffer in order to reach the interim endpoint (Battelle 2006, included as Appendix 17.5).

The specific components of the pollutant allocation are discussed below and outlined in the *Acid Rain Adirondack Forest Preserve Lakes TMDL* Table in Appendix 17.2.

9.1 Waste Load Allocation

As discussed previously, these lakes are remote waters that are regulated by the New York State Constitution as being "forever wild." Consequently, there are no point sources of significant acidity loading in these watersheds now or expected in the future. Therefore, a wasteload allocation of zero is allotted to point sources to these waterbodies. This allocation is reflected in the WLA column of the TMDL Table in Appendix 17.2.

9.2 Load Allocation

Load allocations have been developed by using models to simulate each of the lakes under specific deposition loads. The modeling approach reflects varying characteristics in each of the lakes that affect water chemistry and aquatic life support such as lake area, lake volume, watershed area, soil type, soil depth, groundwater flow, retention time, etc. Limited calibration of the hydrological components of the model (i.e., quick or surface runoff, shallow and deep groundwater recharge proportions) was conducted using four (4) of the 143 lakes for which data were available. The model was then used to simulate lake responses to loading conditions that represent an estimate of atmospheric deposition reduction after full implementation of the federal Clean Air Interstate Rule (CAIR). The TMDL Table shows for each lake the estimated LA for SO_x and NO_x (specifically SO_4, NO_3 and NH_4) in kg/d based on the CAIR reductions.

The modeling revealed that only one of the 143 lakes (Monument Lake) would meet the initial phase interim recovery pH goal of 5.4. Because a TMDL needs to demonstrate that targets (even initial phase interim targets) can be met, the TMDL Table also includes a column that shows the amount of CaCO3 (lime) that would need to be added to the lake to meet the target pH. It is acknowledged that the liming of these lakes is not the best option or even a practical option for many of the lakes. Such an approach does not address the underlying source of the problem, is only a short-term fix and would result in significant disruption in what is designated a wilderness area. Post-implementation monitoring, model refinements, identification of "natural conditions" in these lakes and future reductions to meet the ultimate water quality criteria is expected to reduce and/or eliminate the need for liming to meet goals in these lakes. However in order to satisfy requirements of a TMDL, these liming calculations are included as a possible option to meet the interim goal.

9.3 Margin of Safety

A margin of safety (MOS) is typically included in TMDL calculations in order to compensate for the uncertainty in the calculation and/or effectiveness of load reductions in achieving water quality restoration goals. This MOS can be either explicit, i.e., expressed in the TMDL as loadings set aside specifically for the MOS, or implicit, i.e., incorporated into the TMDL through conservative assumptions in the analysis. In this TMDL the MOS is expressed implicitly by assigning LAs that reflect meeting a pH of 5.5, rather than the initial phase interim target of 5.4.

A common criticism of TMDLs is the relatively arbitrary nature of the MOS. However as discussed previously, the uncertainty involved in the modeling and loading calculations for this TMDL are quite significant and it would be difficult to identify a MOS sufficient to reasonably assure that restoration goals would be met. Because of such uncertainty this phased TMDL relies on adaptive implementation and monitoring to directly track progress toward restoration. While identification of an MOS is required, the iterative nature of this phased TMDL and the emphasis on a monitoring component to track the restoration of these waters and support model refinements provide additional assurance that water quality goals will eventually be achieved.

10.0 Seasonal Variation

Like margin of safety, seasonal variation should be considered in TMDL calculations in order to assure that standards are met during all anticipated conditions. It has been observed that levels of pH drop during the spring freshet in response to the rapid influx of low-pH water that has had no opportunity to interact with the deeper soil horizons. Figure 2 shows the magnitude of seasonal and inter-annual pH variability for West Pond in the Adirondacks. West Pond is part of the ALSC Long Term Monitoring program; monthly pH values are shown for 1992-2000 demonstrating interannual variability. Changes in climate patterns (e.g., El Niño) and forest maturation can influence the hydrologic response and, in turn, the chemical response of the lake.

Seasonal variation is a direct result of the relative inflows to waterbodies. The flows for each of the compartments from each of the major lake contributing watershed classes are shown in Figure 3. These hydrographs show flow from the thin till, thick till and direct runoff classes. Thin-soil and deep-soil hydrographs contain shallow groundwater outflow, deep groundwater outflow, and quick (surface) runoff components. The direct runoff land class includes rocky areas and upstream water bodies, and consists only of quick runoff. Seasonal peaks associated with early winter rainfall and spring freshet can be clearly seen.

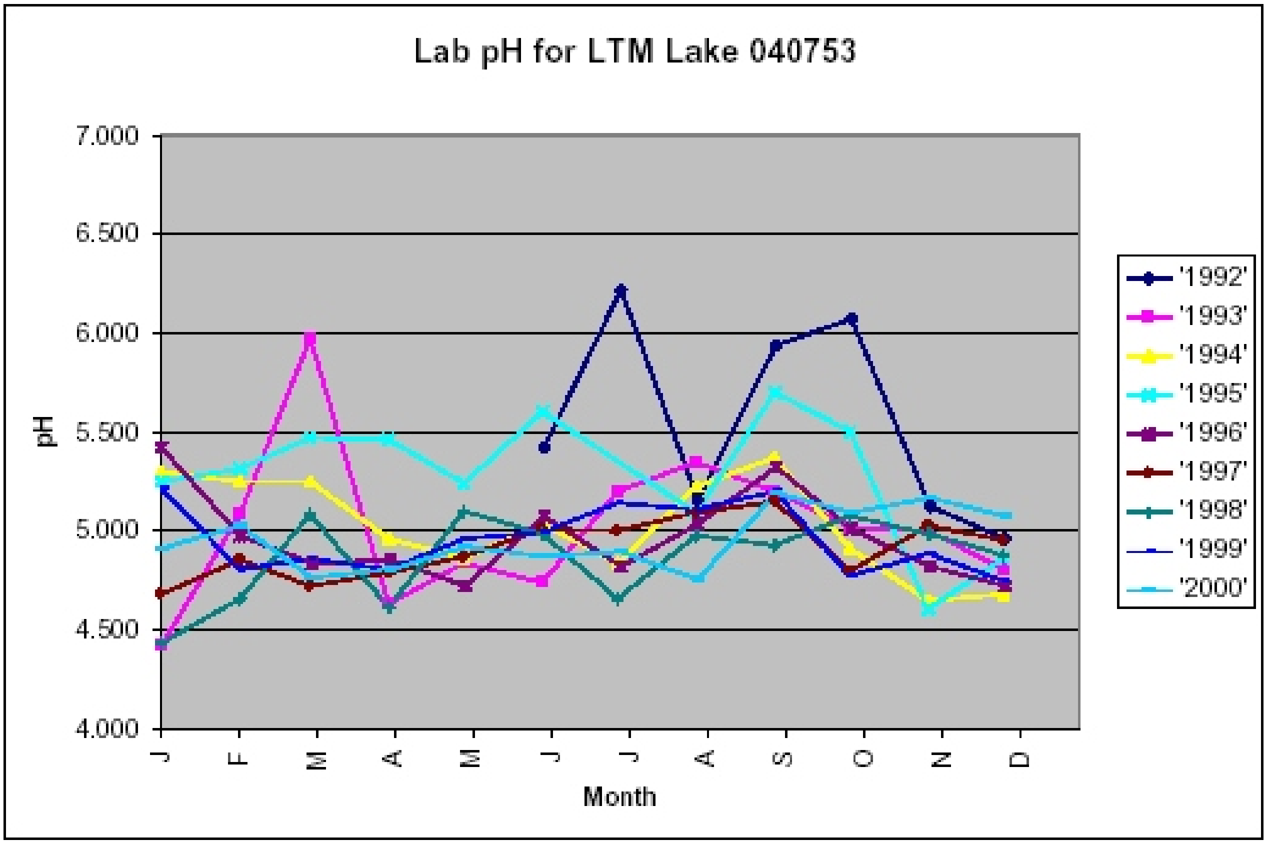
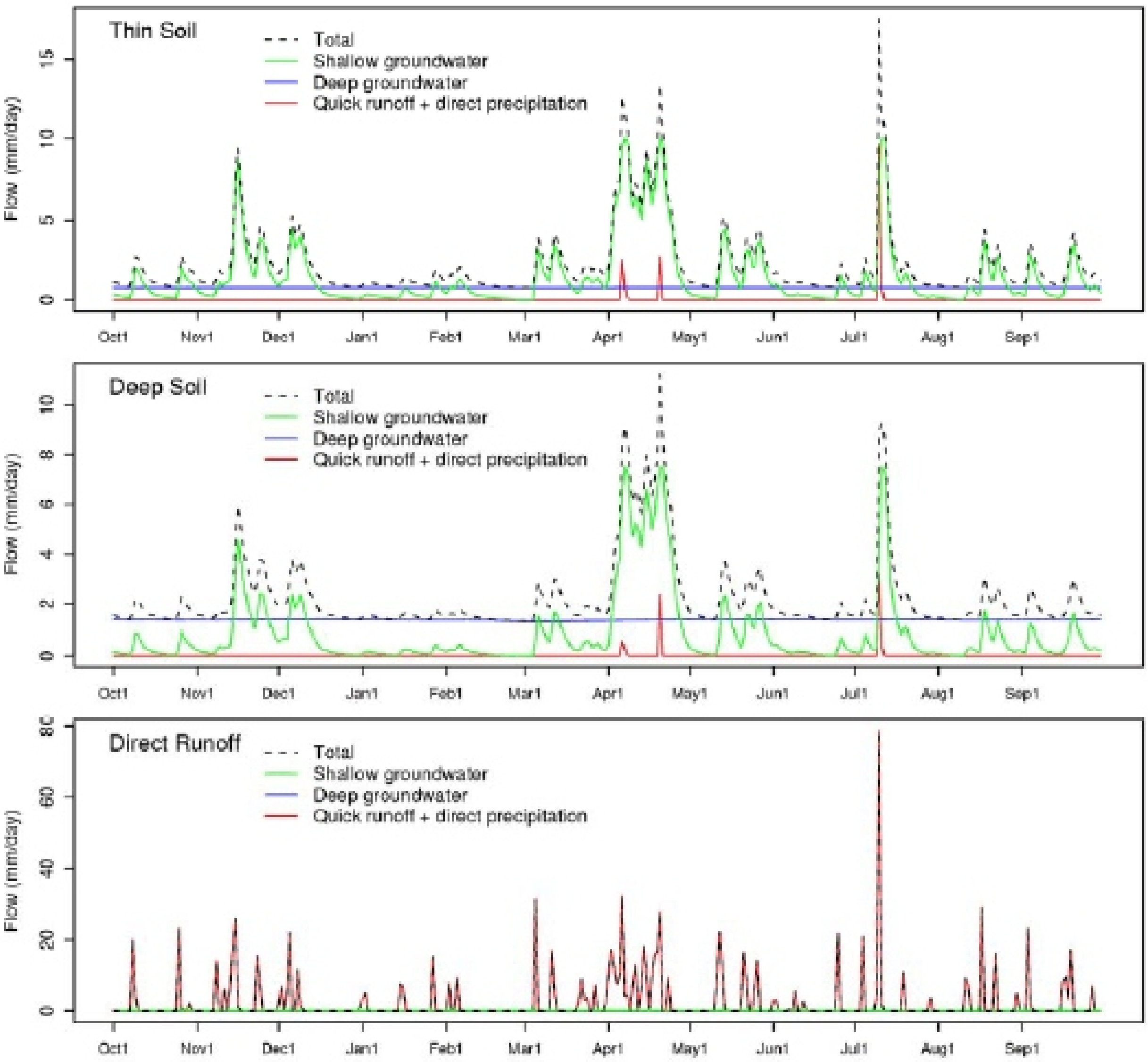


Figure 2 - West Pond, Long-term pH Monitoring Results



Thin Soil

Deep Soil

Direct Runoff

Figure 3 - Typical annual flow patterns for various lake contributing watersheds

In order to account for critical conditions, the pH target of 5.5 (including the MOS), is expressed as a daily minimum average to be met during the period, March 1 - May 31, when lake pH concentrations are expected to be most impacted by winter rainfall and spring freshet. From an ecological perspective, this time period is significant because brook trout hatching occurs and larval forms transform into juvenile fish. Spawning and hatching of other cool water fish (e.g. walleye, northern pike, pickerel, white suckers, etc.,) is also likely to occur.

The design of the monitoring component to support the restoration of these waters will take into account the seasonal variation during spring freshet to better insure that water quality standards and restoration goals are met under all conditions.

11.0 Reasonable Assurances

EPA guidance calls for reasonable assurances when TMDLs are developed for waters impaired by both point and nonpoint sources. In such cases waste load allocations for point sources are dependent on assumptions about nonpoint source load reductions. Therefore it is necessary to provide reasonable assurance that the assumed reduction of nonpoint sources will occur in order for the TMDL to be approved.

However in waters impaired solely by nonpoint sources, reasonable assurances regarding load reductions are not required in order for a TMDL to be approved. It is obviously preferred that TMDLs include some reasonable assurances. But in this case it is difficult for New York State to assure that reductions of loadings well outside its borders will be achieved. Reductions in SO_x and NO_x will be achieved through the implementation of the Federal CAIR program. While NYSDEC will assure that New York State's CAIR reductions are achieved, the state must look to USEPA to insure that other states meet their CAIR reduction obligations.

Going beyond CAIR, NYSDEC intends to insure additional reductions achieved through the implementation of the New York State Acid Deposition Reduction Program (ADRP). The ADRP requires certain electric generators in the State to reduce emissions of SO_x and NO_x to 50 percent below Phase 2 levels of the federal acid rain program in order to protect sensitive areas of the state, including the Adirondack and Catskill mountains.

Additionally, the adaptive/iterative nature of this phased TMDL approach also influences the discussion of reasonable assurance. As noted above the emphasis on a monitoring component to measure actual water quality conditions, track the restoration of these waters and support model refinements provide additional assurance that water quality goals will eventually be achieved.

12.0 Monitoring Plan

As discussed in considerable detail above, the lack of recent data for these lakes, the complexity of the atmospheric, hydrologic and biogeological processes involved in lake acidification, and the limitations inherent in attempting to model conditions in 143 lakes cause considerable uncertainty in the TMDL calculation. As a result, the proposed approach to addressing impairments to these waters by atmospheric deposition is through a phased TMDL. This phased restoration strategy/TMDL initially relies on emission reductions already in place and continued monitoring and assessment of the Section 303(d) Listed waters to determine current conditions (as many are listed based on twenty-plus year old data) and track progress toward restoration. The results of this monitoring and assessment effort are used to identify if further reductions (or additional time for implemented reductions to take full effect) are necessary to meet water quality restoration goals.

This iterative adaptive implementation approach is consistent with the findings of the National Research Council Committee to Assess the Scientific Basis of the Total Maximum Daily Load Approach to Water Pollution Reduction (2001). The Committee recommends an iterative process by which waterbodies previously placed on the 303(d) list are in some cases returned to a "preliminary list" for further assessment. This recommendation of re-assessment has particular utility in the case of these Adirondack Forest Preserve lakes for a couple reasons. As has been pointed out, the most recent monitoring data are twenty or more years old and may not reflect changes (improvements) resulting from reductions over the past two decades. Additionally, although the ultimate goal for these waterbodies is the full compliance with existing water quality standards for classified waters, the nature of the regulatory environment for these waters – specifically, the Constitutional "Forever Wild" clause – suggests that periodic re-assessment of individual waterbodies is appropriate to determine what is an achievable level of restoration.

An appropriate adaptive implementation program for Adirondack Forest Preserve lakes would be two-pronged and iterative, because while the general causes (sulfuric/nitric acid deposition) and effects (increased acidity and mobilized metals and fish extirpations) are well-established trends in these lakes taken as a set, the history, and therefore the potential of every individual lake is not known. Therefore, an adaptive implementation program suited to the state of knowledge and goals would 1) move toward attainment of the water quality standards using initial load reductions based on requirements (federal/regional and statewide) that are currently in place, and 2) move toward the resolution of specific uncertainties regarding other individual lakes and the biogeochemical processes affecting acidity in waterbodies of the Adirondacks region as a whole. The adaptive implementation program would include the following four components, to be conducted concurrently and revisited as necessary when new information is generated:

1. Implement Loading (Emission) Reduction

Initial reductions of SO_x and NO_x emissions and sulfuric/nitric acid loads to Adirondack watersheds are based on requirements that are already in place. These include those included in federal regulation (including the Clean Air Act Amendments and Clean Air Interstate Rule (CAIR)) and state/local measures such as the recently adopted New York State Acid Deposition Reduction Program (ADRP).

2. Monitoring

Water quality monitoring and the development/refining of modeling capabilities (where appropriate) will be conducted to determine current baseline and track progress toward restoration in individual waterbodies. The balance between the monitoring and modeling efforts will depend upon available resources and technical limitations in the modeling.

3. Assess Recovery

Results of monitoring and modeling of individual waterbodies will be evaluated to determine chemical and biological recovery based on Proposed Tiered Recovery Goals. Proposed Tiered Recovery Goals are discussed in more detail in Section 4.0.

4. Consider Further Potential Recovery

The assessment of individual lakes will determine if other factors might limit the attainment of ultimate recovery goals and whether it is appropriate to establish that "natural conditions" for some individual waters are less than those outlined in the full recovery goal.

An adaptive implementation or phased TMDL allows load allocation policies and monitoring programs to be developed consistent with the current level of scientific support and with the reasonable expectation that ongoing monitoring and modeling concurrent with load reductions will reduce uncertainty and correspondingly improve management recommendations. The National Resource Council (NRC) Committee has recommended an adaptive implementation approach in its 2001 examination of the scientific basis of the TMDL program conducted by request of the U.S. Congress. Although this NRC report did not explicitly address the challenges of atmospheric deposition, it did address the science needed by states to comply with TMDL program requirements and its general conclusions concerning the proper role of the scientific method in implementing TMDL programs are applicable.

The strength of an adaptive management approach lies in the balance between caution and scientific probing. Unnecessary societal costs that provide little or no environmental benefit, are limited by a cautious approach and scientific investigations to probe uncertainty and improve our understanding.

The strength of an adaptive management approach lies in the balance between caution and scientific probing. Unnecessary societal costs that provide little or no environmental benefit, are limited by a cautious approach and scientific investigations to probe uncertainty and improve our understanding. Uncertainty is an inevitable consequence of several elements of environmental problem-solving: in this case, the complex and nonlinear interplay of atmospheric, watershed, and chemical processes; the abstraction of reality provided by models; and the lack of current baseline data for assessing and applying models to many of these waterbodies. The inevitability of uncertainty requires an implementation strategy that properly balances caution with application of the results of continuing investigation and monitoring. Adaptive implementation as defined by the Committee is *"a process of taking actions of limited scope commensurate with available data and information to continuously improve our understanding of a problem and its solutions, while at the same time making progress toward attaining a water quality standard"* (NRC 2001 p.90).

Recent USEPA guidance clarifying phased TMDLs note that the implementation of the TMDL should include a monitoring plan and a scheduled timeframe for the revision of the TMDL. The guidance also recognizes that these elements would not be an intrinsic part of the TMDL, nor would these elements be subject to USEPA approval.

The details of the monitoring plan to support this phased TMDL will be developed separately . The scope of the plan will depend upon available resources and support from USEPA. However in order to make the most of those resources, the plan will also be developed in collaboration with the NYSDEC Division of Air and Division of Fish Wildlife and Marine Resources, both of which have considerable interest and experience in the study of atmospheric deposition. It is anticipated that the monitoring effort would be incorporated into existing monitoring efforts already in place and would begin in 2007.

13.0 Implementation

The first phase of reductions outlined in this restoration strategy/TMDL are based upon federal/regional requirements that are already in place and being implemented. These include the Clean Air Interstate Rule (CAIR) that was put into place in 2005, as well as reductions that were included in the 1990 Clean Air Act Amendments. In addition, other reductions through the state and local measures, such as the New York State Acid Deposition Reduction Program provide additional reductions that are not accounted for in the loading calculations.

A table with projected reductions under CAIR and NYS programs is included as Appendix 17.3.

14.0 Public Participation

14.1. Availability for Comment

Notice of availability of the Draft Impaired Waters Restoration Strategy/TMDL was included in the State Environmental Notice Bulletin on August 16, 2006 as a Region 4, 5, 6 and statewide notice. A 30-day public review period was established for soliciting written comments from stakeholders prior to the finalization and submission of the TMDL for USEPA approval. The public comment period officially ended on September 15, 2006.

Comments were received from The Adirondack Council. These comments addressed various aspects of TMDL which were considered in finalizing the TMDL (see discussion below). In addition, continued Department review and discussion with USEPA resulted in some clarifications and modifications. The Massachusetts Department of Environmental Protection also requested clarification of some of the information in the TMDL.

14.2. Response to Public Comments

Many of these comments submitted by The Adirondack Council (Council) reflect some of the same concerns (interstate sources of loading, natural limitations, lack of recent lake-specific monitoring data, counter-intuitive modeling results requiring some verification) that led NYSDEC to propose a phased-TMDL that relies on an incremental, adaptive management approach to restoring these waters, rather than a more traditional TMDL.

The Council points out that the primary source of pollutants causing acid rain impaired lakes are located outside New York State; and that restoration activities should address these sources rather than be limited to management methods that can be conducted within the state. NYSDEC agrees with this and notes in the *Preface* to the TMDL that "any effective loading reduction strategy must include national (regional) reduction efforts." The fact that sources lie outside New York State and that this TMDL is "atypical from more tradition TMDLs" and that "the problem and solution is a national issue" requiring federal leadership by USEPA is also noted in the discussion of *Sources* (Section 3.3).

The Council commended DEC for stating a goal of restoring lakes to their natural chemistry, but also noted such a goal is problematic, pointing out that natural pH in some lakes may be lower than chemical goals set by the TMDL. While both chemical and biological criteria are outlined in the TMDL, there is concern that the chemical criteria will be used to determine recovery, even though a full native aquatic biological community has been restored. NYSDEC agrees that biological support may be a better indicator of ecosystem health. In the discussion of *Interim Criteria* (Section 4.3) language has been added to the effect that biological indicators could drive the determination of recovery in some lakes.

The Council supports the assertion that increased monitoring in these waters is needed. They also suggest it would be useful and efficient to monitor these waters for impacts from mercury at the same time. NYSDEC agrees that establishing a mercury baseline would be valuable and will consider adding this component to the monitoring effort, dependent upon available resources.

The Council notes that the "modeling done for the TMDL seems to be flawed." This assessment was based on the discrepancy between CAIR and TMDL modeling results and the fact that the TMDL model yielded results with little change in pH. NYSDEC has acknowledged in the TMDL document the limitations of the model information and the need for further refinement of the modeling. The capabilities of the model were the focus of considerable discussion with USEPA during the development of this TMDL. And it was these limitations that contributed to the decision to propose a phased TMDL/adaptive management strategy. It is anticipated that newer monitoring data and future refinements to the model will shed light on the Council's questions concerning the difference between CAIR and TMDL modeling results.

The Council strongly opposes the use of lime ($CaCO_3$) to raise pH in these lakes. They point out it this approach does not address the underlying source of the problem, is only a short-term fix and would result in significant disruption in what is designated a wilderness area. NYSDEC acknowledges and agrees with the concerns expressed by the Council. As noted in the *Load Allocation* (Section 9.2) discussion, the liming calculations are included in order to satisfy requirements for TMDL approval, specifically a demonstration that targets (in this case, initial phase interim targets) could be met. The discussion goes on to acknowledge that:

> ...the liming of these lakes is not the best option or even a practical option for many of the lakes. Such an approach does not address the underlying source of the problem, is only a short-term fix and would result in significant disruption in what is designated a wilderness area. Post-implementation monitoring, model refinements, identification of "natural conditions" in these lakes and future reductions to meet the ultimate water quality criteria is expected to reduce and/or eliminate the need for liming to meet goals in these lakes.

The Council also expressed support for the biological criteria of "full aquatic biological communities consistent with unimpacted lakes within the Adirondack Ecological Zone" that is included in the TMDL They state that such criteria will be more appropriate in determining necessary reductions than criteria that focuses on more popular fishing species.

15.0 Acknowledgments

The authors of this TMDL wish to acknowledge the efforts of the staff of the USEPA Region 2 - New York City and their consultants at Battelle. Considerable thanks and appreciation are also extended to NYSDEC staff in the Division of Air and the Division of Fish Wildlife and Marine Resources.

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17.0 Appendices

Appendices to this report include:

17.1	NYS Section 303(d) Listed Adirondack Forest Preserve Acid Rain Lakes
17.2	Phase 1 Acid Rain TMDL for Adirondack Forest Preserve Lakes
17.3	Air Deposition Changes Due to Planned EPA and State Programs
17.4	New York State Forest Preserve Lakes TMDL Support Document (Battelle, 2006a)
17.5	Support Document for Liming Calculation (Battelle, 2006b)

Appendix 17.1

The 143 water bodies in NYS Forest Preserve that appear on NYS Section 303(d) List for Acid Impairment

Lake Name	Water Index Number WI/PWL ID	NYTME	NYTMN	Major Drainage Basin	Pollutants, with Reference	Use Impairment	LTM Site
ALUMINUM POND	SL-1-P109..P293...P315 0903-0006	538111.2500	4846308.0000	St.Lawrence	pH=5.59 ALSC, 1984	No Fish ALSC, 1984	No
AMPHITHEATER POND	C-15-P114...P131 formerly 1003-0018	550420.8750	4906345.2130	Lk Champlain	-	-	-
ASH POND	SL-25-P309-12-12-P326 formerly 0905-0028	513714.2344	4883127.8572	Oswegatchie/Black	pH=5.01 ALSC, 1984	No Fish ALSC, 1984	No
BALSAM LAKE	H-240-180-78-P909 1203-0007	516850.1562	4830852.5000	Mohawk	pH=4.86 DFW, 1975	No Fish DFW, 1969	No
BARTLETT POND	C-86-3-P338 1001-0027, formerly 1003-0012	578160.1563	4909362.6713	Lk.Champlain	pH=5.48 ALSC, 1984	No Fish ALSC, 1984	No
BEAR POND	SLC-32-P257A-P264...P271 formerly 0902-0007	556782.9687	4916380.7851	St.Lawrence	pH=4.93 DFW, 1982		No
BLACK POND (EAST)	SL-1-P109-162--P233-1-P234 0903-0007	573788.7188	4894360.6890	St.Lawrence	pH=6.32 ALSC, 1984	No Fish ALSC, 1984	No
BLACK POND (WEST)	SL-1-P109-15-P178-1-P179 0903-0027	532826.2500	4888598.0000	St.Lawrence	pH=5.36 ALSC, 1985	No Fish ALSC, 1985	No
BUCK POND	SL-1-P109-4-1-P081 formerly 0903-0037	500176.0937	4879043.0000	St.Lawrence	pH=4.5 DFW, 1975	No Fish DFW, 1975	-
BUCK POND	SL-25-P309..124-P343 0905-0001	532497.7812	4814416.8781	Oswegatchie/Black	pH=4.89 DFW, 1975	No Fish DFW, 1975	No
CARRY POND	H-469...P669 1104-0003	541218.8438	4836689.9800	Upper Hudson	pH=4.92 DFW, 1977	-	Yes
CHUB LAKE	H-369..20..P264 1104-0013, formerly 1104-0004	538220.0626	4789638.0000	Upper Hudson	pH=4.24 DFW, 1979	-	No
CLOCKMILL POND	H-369-20-23-4-P228 1104-0013, formerly 1104-0005	533344.4063	4798004.4333	Upper Hudson	pH=4.02 DFW, 1979	-	No

Lake Name	Water Index Number WI/PWL ID	NYTME	NYTMN	Major Drainage Basin	Pollutants, with Reference	Use Impairment	LTM Site
CONLEY LINE PD	SL-1-P109..133-P202-3-P204 formerly 1003-0003	557872.9375	4913151.0000	St.Lawrence	pH=4.50 DFW, 1976	-	No
COVEY POND	SL-25-132-P373...P374 formerly 0905-0029	505382.6250	4870714.6273	Oswegatchie/Black	pH=4.35 ALSC, 1984	No Fish ALSC, 1984	No
CRACKER POND	SL-25-118...P375 formerly 0905-0005	508821.0937	4875888.0000	Oswegatchie/Black	pH=4.88 ALSC, 1984	No Fish ALSC, 1984	No
CROOKED LAKE	SL-25-132-P373 0905-0006	505075.1563	4871307.5000	Oswegatchie/Black	pH=4.64 DFW, 1975	No Fish DFW, 1968	No
CROPSEY POND	Ont 19- 40-22-P492-1-P480 0801-0039	494455.1563	4862132.5000	Oswegatchie/Black	pH=4.53 ALSC, 1984	No Fish ALSC, 1984	No
CURTIS POND	SL-25-P309-9-2-P313 formerly 0905-0004	519181.0937	4889633.0000	Oswegatchie/Black	pH=4.00 DFW, 1982	-	No
DOG POND	SL-25-P309-9-P316 0905-0004, formerly 0905-0031	522106.0937	4889028.0000	Oswegatchie/Black	pH=5.10 ALSC, 1984	No Fish ALSC, 1984	No
DONUT POND	SL-25-P309-9-5-P315 formerly 0905-0081	520736.0938	4889428.0001	Oswegatchie/Black	pH=4.75 unknown	No Fish ALSC, 1986	No
DOUGLAS POND	SLC-32-20-95-P148 formerly 0902-0012	549703.9063	4915673.4119	St.Lawrence	pH=4.69 unknown	No Fish ALSC, 1985	No
DUCK POND	Ont 19- 40-22-P492 0801-0039, formerly 08010040	493340.1563	4865842.5000	Oswegatchie/Black	pH=4.58 ALSC, 1984	No Fish ALSC, 1984	No
E. BEECHRIDGE POND	SL-25-073-26-44-P203 formerly 0905-0020	501450.1563	4867977.5000	Oswegatchie/Black	pH=4.76 DFW, 1982	No Fish DFW, 1972	No
EAST POND	Ont 19- 60-P676-2-2-P678 0801-0041	495865.1563	4842982.5000	Oswegatchie/Black	pH=4.93 ALSC, 1984	No Fish ALSC, 1984	No
EMERALD LAKE	SL-25-73-26-40..P190 0905-0008	498381.0937	4874293.0000	Oswegatchie/Black	pH=4.71 ALSC, 1984	No Fish ALSC, 1984	No
FERRIS LAKE	H-240-144-38-P777 1201-0003	529946.1250	4794532.0000	Mohawk	pH=4.94 DFW, 1978	-	No

Lake Name	Water Index Number WI/PWL ID	NYTME	NYTMN	Major Drainage Basin	Pollutants, with Reference	Use Impairment	LTM Site
FIFTH CREEK POND	Ont 19- 57-10-3-P635 0801-0075, formerly 0801-0042	493615.1563	4854172.5000	Oswegatchie/Black	pH=4.13 DFW, 1979	-	No
FLORENCE POND	Ont 19- 60-5-P664-P664a formerly 0801-0067	478169.5938	4842230.0184	Oswegatchie/Black	pH=5.20 ALSC, 1984	No Fish ALSC, 1984	No
GAL POND	SL-25-133-1-P376 formerly 0905-0009	508466.0938	4876833.0000	Oswegatchie/Black	pH=5.09 ALSC, 1984	No Fish ALSC, 1984	No
GOOSENECK LAKE	Ont 19-P1007-10-3-P1010 formerly 0801-0043	511682.3594	4824063.2880	Oswegatchie/Black	pH=4.24 ALSC, 1984	No Fish ALSC, 1984	No
GRASS POND	SLC-32-P171 formerly 0902-0002	539992.6250	4944965.4959	St.Lawrence	pH=4.61 ALSC, 1984	1977 No Fish ALSC, 1984	Yes
GRASSY POND	SL-25-131-P362 formerly 0905-0033	511926.7344	4881026.2814	Oswegatchie/Black	pH=4.81 ALSC, 1984	No Fish ALSC, 1984	No
HAWK POND	Ont 19- 40-P493-6-1-P504 0801-0044	503255.1563	4867117.5000	Oswegatchie/Black	pH=4.65 ALSC, 1984	No Fish ALSC, 1984	No
HIGH POND	SL-1-P109-11...P172 0903-0025	513076.0937	4880923.0000	St.Lawrence	pH=5.48 ALSC, 1984	No Fish ALSC, 1984	No
HOLMES LAKE	H-369-P127-46-12-P168-1-P168 1104-0006	546160.0625	4782053.0000	Upper Hudson	pH=4.25 DFW, 1979	-	No
INDIAN LAKE	Ont 19- 81-58-5-P852 0801-0002	519695.1562	4829037.5000	Oswegatchie/Black	pH=4.89 ALSC, 1984	No Fish ALSC, 1984	Yes
INDIAN MOUNTAIN P	SL-25-P309-12-1-2-P325 0906-0037	514450.8594	4885828.2523	Oswegatchie/Black	pH=4.87 ALSC, 1984	No Fish ALSC, 1984	No
JOCK POND	Ont 19- 40-P493-32-16-P583 0801-0077, formerly 0801-0045	511334.9376	4855322.4275	Oswegatchie/Black	pH=4.78 ALSC, 1984	1975 No Fish ALSC, 1984	No
KITFOX POND	SLC-32-20-95-96-P142 formerly 0902-0003	549470.5313	4914983.3578	St.Lawrence	pH=4.92 DFW, 1982	-	No
LAKE COLDEN	H-543-15-P706 1104-0007	581729.0625	4886158.0000	Upper Hudson	pH=4.70 BWR, 1983	-	No

Lake Name	Water Index Number WI/PWL ID	NYTME	NYTMN	Major Drainage Basin	Pollutants, with Reference	Use Impairment	LTM Site
LITTLE CROOKED LK	SL-25-132-3...P372 formerly 0905-0010	504640.1563	4872362.5000	Oswegatchie/Black	pH=4.62 ALSC, 1984	No Fish ALSC, 1984	No
LITTLE ECHO POND	??? formerly 1003-0006	551268.1563	4906029.2793	Lk.Champlain	pH=4.10 DFW, 1976	No Fish DFW, 1976	Yes
LITTLE FISH POND	SL-25-P309-11-P319-P320 formerly 0905-0082	518176.0938	4884788.0000	Oswegatchie/Black	pH=5.33 source unknown	No Fish ALSC, 1986	No
LITTLE LONG POND	SLC-32-20-95-P141 0902-0004	549211.5001	4915502.0001	St.Lawrence	pH=4.70 DFW, 1982	-	No
LITTLE METCALF LK	H-240-180-P799-19-P768 1201-0227, formerly 1203-0009	522536.2500	4791248.7442	Mohawk	pH=4.81 DFW, 1975	No Fish DFW, 1975	No
LITTLE NORTH WHEY	??? formerly 1003-0007	549227.5938	4907234.1403	Lk.Champlain	pH=4.43 ALSC, 1984	No Fish ALSC, 1984	No
LONE DUCK POND	SL-25-126-4-P350 formerly 0905-0088	501996.0938	4875928.0000	Oswegatchie/Black	pH=5.32 source unknown	No Fish ALSC, 1986	No
LONG POND (03-170)	SLC-32-P170 0902-0005	539956.5000	4944307.0000	St.Lawrence	pH=4.67 DFW, 1980	-	No
LONG POND (07-755)	H-240-144-28-P750-2-P755 1201-0007	533411.1250	4785217.0000	Mohawk	pH=4.70 DFW, 1978	-	No
LOST POND	SL-1-P109.. 162-P235-1-P237 formerly 0903-0009	577189.2500	4890323.0000	St.Lawrence	pH=4.67 ALSC, 1984	No Fish ALSC, 1984	Yes
LOWER CHAIN POND	SL-1-P109.. 172-P293-13-8-P326 formerly 0903-0010	515080.2501	4850187.9915	St.Lawrence	pH=4.57 ALSC, 1984	No Fish ALSC, 1984	No
LOWER HELMS POND	SL-1-P109.. 172-P293...P298 formerly 0903-0024	540898.0312	4858419.3242	St.Lawrence	pH=7.08 source unknown	No Fish ALSC, 1985	No
LOWER LILYPAD PD.	Ont 19- 40-P493-32-P584-3-P587 0801-0077, formerly 0801-0048	510540.1563	4855682.5000	Oswegatchie/Black	pH=4.67 ALSC, 1984	No Fish ALSC, 1984	No
LOWER LOOMIS PD.	H-369-20-31-P256 1104-0013, formerly 1104-0010	539995.0625	4793703.0000	Upper Hudson	pH=4.60 DFW, 1975	No Fish DFW, 1961	No

Lake Name	Water Index Number WI/PWL ID	NYTME	NYTMN	Major Drainage Basin	Pollutants, with Reference	Use Impairment	LTM Site
LOWER MOSHIER PD.	Ont 19- 40-22-P489 0801-0049	494181.1250	4864591.2000	Oswegatchie/Black	pH=4.96 DFW, 1982	-	No
LOWER RILEY POND	SL-25-126-7-1-P354 0905-0088, formerly 0905-0011	502136.0938	4872358.0000	Oswegatchie/Black	pH=4.30 DFW, 1977	-	No
LOWER SOUTH POND	SL-25-73-26-43-P198 0905-0012	499246.0938	4870068.0000	Oswegatchie/Black	pH=4.60 ALSC, 1984	No Fish ALSC, 1984	No
LOWER WALLFACE PD	H-508...P718 1104-0007, formerly 1004-0004	575758.9375	4888426.6655	Upper Hudson	pH=4.86 DFW, 1975	No Fish DFW, 1975	No
MARION POND	H-391-P374...P398 formerly 1104-0020	587194.0625	4859333.0000	Upper Hudson	pH=4.80 DFW, 1978	-	No
MECO LAKE	H-369-20-23-P234-3-P235-2-P276 1104-0013, formerly 1104-0011	546714.9687	4792431.1739	Upper Hudson	pH=4.70 DFW, 1975	No Fish DFW, 1969	No
MERRIAM LAKE	Ont 19- 81-18-17-P752-4-P756 formerly 0801-0050	512400.1562	4856077.5000	Oswegatchie/Black	pH=4.61 ALSC, 1984	1975 No Fish ALSC, 1984	No
MIDDLE CHAIN POND	SL1-P109.. 172-P293-13-8-P327 0903-0211, formerly 0903-0011	515035.1406	4850316.2534	St.Lawrence	pH=4.65 ALSC, 1984	No Fish ALSC, 1984	No
MIDDLE LOOMIS PD.	H-369-20-31-P257 1104-0013, formerly 1104-0012	540385.0625	4793958.0000	Upper Hudson	pH=4.64 DFW, 1975	No Fish DFW, 1961	No
MIDDLE NOTCH POND	SLC-29-22-…P045 formerly, formerly 0902-0015	565352.2812	4933776.5042	St.Lawrence	pH=5.77 ALSC, 1985	No Fish ALSC, 1985	-
MIDDLE SOUTH POND	SL-25-73-26-43-P199 0905-0012, formerly 0905-0013	498526.0938	4870818.0001	Oswegatchie/Black	pH=4.72 ALSC, 1984	No Fish ALSC, 1984	No
MONUMENT LAKE	Ont - 19-P1007-10-3-P1011..P1012 0801-0080, formerly 0801-0051	514239.9063	4824892.4586	Oswegatchie/Black	pH=4.47 ALSC, 1984	No Fish ALSC, 1984	No
MOUNTAIN LAKE	Ont 19- 81-58-12-P855 0801-0052	516115.1562	4825082.5000	Oswegatchie/Black	pH=4.38 ALSC, 1984	No Fish ALSC, 1984	No
MUIR POND	SL-25...126-5-P351 0905-0088, formerly 0905-0041	500956.0938	4875938.0000	Oswegatchie/Black	pH=4.43 ALSC, 1984	No Fish ALSC, 1984	No

Lake Name	Water Index Number WI/PWL ID	NYTME	NYTMN	Major Drainage Basin	Pollutants, with Reference	Use Impairment	LTM Site
N. BEECHRIDGE POND	SL-25-073-26-44-P201 formerly 0905-0019	500541.0938	4868348.0001	Oswegatchie/Black	pH=4.89 DFW, 1982	No Fish DFW, 1972	No
OSWEGO POND	Ont 19- 40-P493-32-P584-1-P585 801-0077, formerly 0801-0053	508070.1563	4855457.5000	Oswegatchie/Black	pH=4.87 BWR, 1984	-	No
OTTER POND	SL-25-118-1-P340 0905-0193, formerly 0905-0014	500796.0938	4883513.0000	Oswegatchie/Black	pH=4.76 DFW, 1979	-	No
PELCHER POND	SL-1-P109.. 172-P293-13...P325 0903-0002	523066.2500	4852693.0001	St.Lawrence	pH=4.57 DFW, 1979	-	No
PINE POND	SL-1-P109.. 172-P293-4...P309 formerly 0903-0022	539546.2500	4856683.0001	St.Lawrence	pH=4.77 source unknown	No Fish ALSC, 1985	No
POOR LAKE	H-240-180-91-2-P919 1203-0003	523851.1563	4823357.0000	Mohawk	pH=4.35 DFW, 1978	-	No
POTTER POND	SL-1-P109.. 172-P293-4...P305 formerly 0903-0012	541403.2500	4851682.3831	St.Lawrence	pH=4.92 ALSC, 1984	No Fish ALSC, 1984	No
REDLOUSE LAKE	H-240-144-34-P771 1201-0008	529491.1250	4790352.0000	Mohawk	pH=4.90 DFW, 1980	-	No
ROCK LAKE	SL-25-73-26-40-5-P189 0905-0015	498811.0937	4873228.0001	Oswegatchie/Black	pH=4.92 BWR, 1984	-	No
ROCK LAKE (05-229)	H-369..20-P229 formerly 1104-0013	544505.0625	4787133.0000	Upper Hudson	pH=4.97 ALSC, 1984	No Fish ALSC, 1984	No
ROCK LAKE (05-275)	H-369-20-48-P275 1104-0013, formerly 1104-0014	547190.0313	4790485.8026	Upper Hudson	pH=4.65 DFW, 1978	-	No
ROUND POND	O-19-88-P907 0801-0407, formerly 1104-0078	488504.5938	4827167.0899	Oswegatchie/Black	-	-	No
RUSSIAN LAKE	Ont 19- 81-18-17-P752-8-P774 0801-0006	515895.1562	4854537.5000	Oswegatchie/Black	pH=4.67 BWR, 1984	No Fish DFW, 1962	No
SALMON LAKE	Ont 19- 40-P493-7-P517 0801-0054	504865.1563	4865637.5000	Oswegatchie/Black	pH=5.00 DFW, 1982	-	No

Lake Name	Water Index Number WI/PWL ID	NYTME	NYTMN	Major Drainage Basin	Pollutants, with Reference	Use Impairment	LTM Site
SAND LAKE	SL-25-73-26-40-P191 0905-0016	499381.0937	4873198.0000	Oswegatchie/Black	pH=4.83 BWR, 1984	-	No
SAND LAKE	H-369..P225 1104-0015	534573.6563	4800351.4636	Upper Hudson	-	-	-
SILVER LAKE	H-369..20-43-P270 1104-0016	546295.0625	4793743.0000	Upper Hudson	pH=4.92 DFW, 1975	No Fish DFW, 1969	No
SITZ POND	SL-25-73-26-40...P192 0905-0008, formerly 0905-0017	500186.0937	4871238.0000	Oswegatchie/Black	pH=4.61 ALSC, 1984	No Fish ALSC, 1984	No
SLENDER POND	SL-25-131-P363 formerly 0905-0074	511991.0938	4880613.0000	St.Lawrence	pH=5.20 ALSC, 1985	No Fish ALSC, 1985	-
SOUTH POND	Ont 19- 81-18-17-P752..P772 0801-0057	509934.7500	4854881.8541	Oswegatchie/Black	pH=4.69 ALSC, 1984	No Fish ALSC, 1984	No
STEWART LAKE	H-240-144-13-P717-2-1-P730 1201-0009	542154.5313	4781635.4815	Mohawk	pH=4.25 DFW, 1979	-	No
STONEY POND	SL-1-P241-27-P260-6-P264 0903-0189, formerly1104-0018	582024.0625	4853958.0000	Upper Hudson	pH=4.70 DFW, 1977	-	No
STREETER FISHPOND	SL-25-126-P352...P353 formerly 0905-0067	502136.0938	4873573.0000	Oswegatchie/Black	pH=4.77 DFW, 1981	No Fish ALSC, 1985	No
SUNSHINE POND	Ont 19- 40-22-3-P487 0801-0039, formerly 0801-0058	495900.1563	4865222.5001	Oswegatchie/Black	pH=4.69 ALSC, 1984	No Fish ALSC, 1984	No
T-LAKE	H-240-180-74-21-P862 1203-0004	533796.1250	4811267.0000	Mohawk	pH=4.82 DFW, 1975		No
TOAD POND	SL-25-132-P369 formerly 0905-0046	505321.0938	4873998.0001	Oswegatchie/Black	pH=4.67 ALSC, 1984	No Fish ALSC, 1984	No
TOAD POND	SLC-32-81-P238-2-P244 0902-0008	554261.6250	4924887.5445	St.Lawrence	pH=4.46 ALSC, 1984	No Fish ALSC, 1984	No
TROUT LAKE	H-369..20-P260 1104-0013, formerly 1104-0019	523501.1563	4799182.0000	Upper Hudson	pH=4.76 DFW, 1979	-	No

Lake Name	Water Index Number WI/PWL ID	NYTME	NYTMN	Major Drainage Basin	Pollutants, with Reference	Use Impairment	LTM Site
TWELFTH TEE POND	C-15-P114..P184 formerly 1003-0010	552551.1250	4910091.7574	Lk.Champlain	pH=4.75 BWR, 1984	-	No
TWIN LAKE (SOUTH)	H-240-180-74-16-1-P856 1203-0005	532921.1250	4810292.0000	Mohawk	pH=4.64 DFW, 1980	-	No
TWIN PONDS	SL-25-73-26-38-P183-P185 0905-0035, formerly 0905-0059	496381.0938	4866703.0001	Oswegatchie/Black	pH=4.44 source unknown	No Fish ALSC, 1985	No
UNNAMED P #2-133	C-15-P114..P153 formerly 1003-0019	550184.5625	4906375.0937	Lk.Champlain	pH=4.04 ALSC, 1985	No Fish ALSC, 1985	-
UNNAMED P #3-189	SLC-32-52-15-P179A...P189 formerly 0902-0010	556177.5938	4928059.6891	St.Lawrence	pH=4.26 ALSC, 1984	No Fish ALSC, 1984	No
UNNAMED P #4-194	SL-25-073-26-P193-…P194 formerly 0905-0060	497828.1250	4867083.9486	Oswegatchie/Black	pH=4.67 ALSC, 1985	No Fish ALSC, 1985	-
UNNAMED P #4-202	SL-25-73-45-P202 formerly 0905-0048	501274.3281	4870707.2409	Oswegatchie/Black	pH=4.51 ALSC, 1984	No Fish ALSC, 1984	No
UNNAMED P #4-204	SL-25-73-26-P204 formerly 0905-0050	501841.0937	4869448.0000	Oswegatchie/Black	pH=4.49 ALSC, 1984	No Fish ALSC, 1984	No
UNNAMED P #4-205	SL-25-73-47-P205 formerly 0905-0021	502901.0938	4870333.0000	Oswegatchie/Black	pH=4.67 ALSC, 1984	No Fish ALSC, 1984	No
UNNAMED P #4-206	SL-25-73...P206 formerly 0905-0052	502511.3125	4871088.1109	Oswegatchie/Black	pH=4.22 ALSC, 1984	No Fish ALSC, 1984	No
UNNAMED P #4-207	SL-25-73-47-P207 formerly 0905-0053	502429.2032	4870189.2900	Oswegatchie/Black	pH=4.56 ALSC, 1984	No Fish ALSC, 1984	No
UNNAMED P #4-208	SL-25-73-48-P208 formerly 0905-0022	503541.0937	4870053.0000	Oswegatchie/Black	pH=4.48 ALSC, 1984	No Fish ALSC, 1984	No
UNNAMED P #4-209	SLC-32-56-P209 formerly 0905-0055	503096.0938	4870108.0000	St.Lawrence	pH=5.32 ALSC, 1984	No Fish ALSC, 1984	No
UNNAMED P #4-210	SL-25-73-26..P210 formerly 0905-0064	503777.3907	4869640.0755	Oswegatchie/Black	pH=4.62 ALSC, 1985	No Fish ALSC, 1985	-

Lake Name	Water Index Number WI/PWL ID	NYTME	NYTMN	Major Drainage Basin	Pollutants, with Reference	Use Impairment	LTM Site
UNNAMED P #4-212	SL-25-73-26..P212 formerly 0905-0065	504686.3906	4869494.6381	Oswegatchie/Black	pH=4.67 ALSC, 1985	No Fish ALSC, 1985	-
UNNAMED P #4-213	Sl-25-73-26..P213 formerly 0905-0066	504767.1719	4869267.0168	Oswegatchie/Black	pH=4.54 ALSC, 1985	No Fish ALSC, 1985	-
UNNAMED P #4-314	SL-25-P309--9...P314 formerly 0905-0080	520071.0938	4889108.0000	Oswegatchie/Black	pH=4.58 source unknown	No Fish ALSC, 1986	No
UNNAMED P #4-320A	SL-25-P309-11...P320A formerly 0905-0083	518454.3906	4884752.9483	Oswegatchie/Black	pH=5.09 source unknown	No Fish ALSC, 1986	No
UNNAMED P #4-320B	SL-25-P309-11...P320B formerly 0905-0084	519366.0938	4885983.0000	Oswegatchie/Black	pH=4.44 source unknown	No Fish ALSC, 1986	No
UNNAMED P #4-321A	SL-25-P309-11...P321B formerly 0905-0085	518786.0937	4884388.0000	Oswegatchie/Black	pH=5.78 source unknown	No Fish ALSC, 1986	No
UNNAMED P #4-322B	SL-25-P309-11...P322B formerly 0905-0086	518586.0938	4884503.0000	Oswegatchie/Black	pH=5.09 source unknown	No Fish ALSC, 1986	No
UNNAMED P #4-356	SL-25-128-1-P356 formerly 0905-0068	509236.0313	4881941.6005	Oswegatchie/Black	pH=4.77 source unknown	No Fish ALSC, 1985	No
UNNAMED P #4-370	SL-25-132-3-P370 formerly 0906-0004	506036.0938	4873198.0000	Oswegatchie/Black	pH=4.35 source unknown	No Fish ALSC, 1985	No
UNNAMED P #4-371	SL-25-132-6-P371 formerly 0905-0056	506005.1563	4872102.5000	Oswegatchie/Black	pH=4.50 ALSC, 1984	No Fish ALSC, 1984	No
UNNAMED P #4-439	Ont 19- 40-18-2-2-P439 formerly 0801-0086	488587.0469	4862030.0628	Oswegatchie/Black	pH=4.56 ALSC, 1984	No Fish ALSC, 1984	No
UNNAMED P #4-440	Ont 19- 40-18-2-P440 formerly 0801-0087	488415.1562	4861947.5001	Oswegatchie/Black	pH=4.60 ALSC, 1984	No Fish ALSC, 1984	No
UNNAMED P #4-444A	Ont 19- 40-18-7-P444A formerly 0801-0103	488994.6562	4865431.4004	Oswegatchie/Black	pH=4.85 ALSC, 1985	No Fish ALSC, 1985	-
UNNAMED P #4-456	Ont 19- 40-19-P456 formerly 0801-0088	489210.1563	4860992.5001	Oswegatchie/Black	pH=4.75 ALSC, 1984	No Fish ALSC, 1984	No

Lake Name	Water Index Number WI/PWL ID	NYTME	NYTMN	Major Drainage Basin	Pollutants, with Reference	Use Impairment	LTM Site
UNNAMED P #6-119	SL-1-P109-11-2-P119 formerly 0903-0021	535493.4688	4879599.4900	St.Lawrence	pH=4.42 ALSC, 1985	No Fish ALSC, 1985	-
UNNAMED P #6-124	SL-1-P109-11-2-P120..P124 formerly 0903-0019	536801.3751	4880165.3275	St.Lawrence	pH=5.38 ALSC, 1985	No Fish ALSC, 1985	-
UNNAMED P #6-330	SL-1-P109.. 172-P293-13-7...P330 formerly 0903-0015	518110.1562	4852102.5001	St.Lawrence	pH=5.31 ALSC, 1984	No Fish ALSC, 1984	No
UPPER CHAIN POND	SL-1-P109.. 172-P293-13-7...P328 formerly 0903-0016	515190.4844	4850704.7817	St.Lawrence	pH=4.60 ALSC, 1984	No Fish ALSC, 1984	No
UPPER HAYMARSH PD	SL-1-P109.. 172-P293-13...P322 0903-0017	521051.2500	4854003.0000	St.Lawrence	pH=5.88 ALSC, 1984	No Fish ALSC, 1984	No
UPPER NOTCH POND	SLC-29-22…P046 formerly 0902-0014	565291.6250	4933808.5519	St.Lawrence	pH=5.19 ALSC, 1985	No Fish ALSC, 1985	-
UPPER RILEY POND	SL-25-126-7-1-P355 0905-0088, formerly 0905-0023	502801.0938	4872218.0000	Oswegatchie/Black	pH=4.40 DFW, 1977	-	No
UPPER SISTER LAKE	Ont 19- 81-18-17-P752-7-P769 formerly 0801-0008	519145.1563	4859052.5000	Oswegatchie/Black	pH=4.17 DFW, 1977	-	No
UPPER TWIN LAKE	Ont 19-119-P1000 0801-0060	504645.1563	4814747.5000	Oswegatchie/Black	pH=4.33 DFW, 1975	No Fish DFW, 1973	No
UPPER WALLFACE PD	H-P715-5-8-P719 1104-0007, formerly 1004-0005	575529.0625	4888743.0000	Upper Hudson	pH=4.78 BWR, 1983	No Fish DFW, 1975	No
WALKER LAKE	SL-25-73-26...P214 0905-0024	504430.1563	4868517.5000	Oswegatchie/Black	pH=4.77 ALSC, 1984	No Fish ALSC, 1984	No
WASHBOWL POND	SL-25-118...P346 0905-0088, formerly 0905-0087	504106.0938	4877368.0000	Oswegatchie/Black	pH=4.36 source unknown	No Fish ALSC, 1986	No
WEST POND	SL-25-132-1-P364 formerly 0905-0025	507841.0938	4876558.0000	Oswegatchie/Black	pH=4.87 ALSC, 1984	No Fish ALSC, 1984	No
WHITE BIRCH LAKE	H-240-180-74-22-3-P865 1203-0001, formerly 1203-0006	534648.9688	4814149.8031	Mohawk	pH=4.92 DFW, 1975	No Fish DFW, 1975	No

Lake Name	Water Index Number WI/PWL ID	NYTME	NYTMN	Major Drainage Basin	Pollutants, with Reference	Use Impairment	LTM Site
WILDER POND	Ont 19- 40-P493-7-P528-2..P531 0801-0068, formerly 0801-0061	511130.1563	4870302.5000	Oswegatchie/Black	pH=4.92 ALSC, 1984	No Fish ALSC, 1984	No
WILLYS LAKE	SL-25-73-26-49-P211 0905-0026	503635.1562	4868427.5000	Oswegatchie/Black	pH=4.73 ALSC, 1984	No Fish ALSC, 1984	Yes
WITCHOPPLE LAKE	Ont 19- 40-P493-7-P528 0801-0062	506660.1563	4868032.5001	Oswegatchie/Black	pH=4.91 DFW, 1976	-	No
WOLF POND	SL-25-126-P352 0905-0194, formerly 0905-0027	501131.0937	4874763.0000	Oswegatchie/Black	pH=4.67 DFW, 1981	-	No

Notes:
All NYTM coordinates are based on: Projection UTM; Zone 18; Datum NAD83; Units METERS; Spheroid GRS1980.

Current (if applicable) and former WI/PWL ID numbers are indicated for each segment in order to facilitate tracking of waterbodies that have been renumbered, consolidated with other waterbodies into a single assessment unit, and/or are no longer tracked individually.

Appendix 17.2

Phase 1 Acid Rain TMDL for Adirondack Forest Preserve Lakes

Lake Name	Current pH (modeled)	Total Maximum Daily Load (TMDL)						
		Waste Load Allocation	Load Allocation (in kg/d)			pH w/CAIR Reductions	Amount of $CaCO_3$ to be added (kg/d)	Margin of Safety
			SO_4^{-2}	NO_3^{-1}	NH_4^{+1}			
ALUMINUM POND	5.03	0	8.73	11.13	1.55	5.04	12.38	Implicit
AMPHITH.P#2-131	5.37	0	0.20	0.26	0.04	5.41	0.08	Implicit
ASH POND	5.00	0	2.54	3.23	0.45	5.01	3.67	Implicit
BALSAM LAKE	5.44	0	2.40	3.06	0.43	5.47	0.30	Implicit
BARTLETT POND	4.98	0	2.16	2.75	0.38	4.99	3.03	Implicit
BEAR POND	5.33	0	2.94	3.75	0.52	5.46	0.47	Implicit
BLACK POND EAST	5.22	0	1.79	2.28	0.32	5.25	1.64	Implicit
BLACK POND WEST	5.38	0	4.13	5.26	0.73	5.40	1.77	Implicit
BUCK POND	5.19	0	4.01	5.11	0.71	5.20	4.48	Implicit
BUCK POND	5.14	0	1.10	1.41	0.20	5.16	1.34	Implicit
CARRY POND	5.37	0	0.50	0.64	0.09	5.46	0.08	Implicit
CHUB LAKE	5.41	0	2.24	2.86	0.40	5.44	0.58	Implicit
CLOCKMILL POND	5.38	0	19.48	24.84	3.46	5.41	7.91	Implicit
CONLEY LINE POND	5.00	0	0.82	1.04	0.15	5.01	1.22	Implicit
COVEY POND	5.15	0	0.53	0.67	0.09	5.16	0.64	Implicit
CRACKER POND	5.38	0	3.93	5.01	0.70	5.40	1.67	Implicit
CROOKED LAKE	4.55	0	6.85	8.74	1.22	4.88	3.41	Implicit
CROPSEY POND	4.93	0	2.59	3.30	0.46	4.98	3.49	Implicit
CURTIS POND	5.42	0	2.04	2.60	0.36	5.45	0.45	Implicit
DOG POND	5.38	0	5.51	7.03	0.98	5.41	2.23	Implicit
DONUT POND	5.33	0	2.45	3.12	0.43	5.35	1.48	Implicit
DOUGLAS POND	5.35	0	0.10	0.13	0.02	5.42	0.03	Implicit
DUCK POND	5.39	0	1.27	1.62	0.23	5.43	0.38	Implicit
E.BEECHRIDGE POND	5.39	0	1.51	1.92	0.27	5.46	0.21	Implicit
EAST POND	5.47	0	8.81	11.24	1.57	5.49	0.59	Implicit
EMERALD LAKE	5.31	0	1.70	2.17	0.30	5.35	0.97	Implicit
FERRIS LAKE	5.44	0	5.58	7.12	0.99	5.48	0.38	Implicit
FIFTH CREEK POND	5.39	0	1.47	1.88	0.26	5.46	0.22	Implicit
FLORENCE POND	5.38	0	0.12	0.15	0.02	5.43	0.04	Implicit
GAL POND	4.89	0	34.89	44.49	6.21	4.96	44.00	Implicit
GOOSENECK LAKE	5.21	0	1.78	2.28	0.32	5.22	1.89	Implicit
GRASS POND	5.26	0	1.14	1.45	0.20	5.28	1.04	Implicit
GRASSY POND	5.39	0	0.22	0.28	0.04	5.46	0.03	Implicit
HAWK POND	5.45	0	3.49	4.45	0.62	5.48	0.30	Implicit
HIGH POND	5.33	0	0.60	0.77	0.11	5.42	0.18	Implicit
HOLMES LAKE	5.40	0	2.68	3.42	0.48	5.43	0.86	Implicit
INDIAN LAKE	5.47	0	37.70	48.07	6.70	5.48	2.80	Implicit
INDIAN MOUNTAIN P	5.37	0	0.91	1.16	0.16	5.43	0.24	Implicit
JOCK POND	5.34	0	1.16	1.48	0.21	5.36	0.69	Implicit
KITFOX POND	5.41	0	0.81	1.04	0.14	5.44	0.20	Implicit
LAKE COLDEN	5.38	0	22.73	28.99	4.04	5.39	11.25	Implicit
LITTLE CROOKED LK	5.45	0	2.08	2.65	0.37	5.48	0.16	Implicit
LITTLE ECHO POND	5.23	0	0.32	0.41	0.06	5.27	0.27	Implicit
LITTLE FISH POND	4.89	0	11.36	14.49	2.02	4.95	14.75	Implicit
LITTLE LONG POND	5.40	0	2.89	3.68	0.51	5.45	0.53	Implicit
LITTLE METCALF LK	5.41	0	0.78	1.00	0.14	5.45	0.16	Implicit
LITTLE NORTH WHEY	5.20	0	0.37	0.47	0.07	5.21	0.41	Implicit
LONE DUCK POND	5.23	0	0.80	1.02	0.14	5.26	0.73	Implicit
LONG POND(03-170)	5.42	0	2.47	3.15	0.44	5.47	0.30	Implicit
LONG POND(07-755)	4.99	0	27.26	34.77	4.85	5.01	38.27	Implicit

Phase 1 Acid Rain TMDL for Adirondack Forest Preserve Lakes

Lake Name	Current pH (modeled)	Total Maximum Daily Load (TMDL)						
		Waste Load Allocation	Load Allocation (in kg/d)			pH w/CAIR Reductions	Amount of $CaCO_3$ to be added (kg/d)	Margin of Safety
			SO_4^{-2}	NO_3^{-1}	NH_4^{+1}			
LOST POND	5.39	0	0.61	0.78	0.11	5.44	0.15	Implicit
LOWER CHAIN POND	5.20	0	1.78	2.27	0.32	5.26	1.44	Implicit
LOWER HELMS POND	4.92	0	3.91	4.99	0.70	4.96	5.23	Implicit
LOWER LILYPAD PD.	5.36	0	4.33	5.52	0.77	5.39	2.06	Implicit
LOWER LOOMIS POND	5.20	0	5.25	6.70	0.93	5.22	5.49	Implicit
LOWER MOSHIER PD.	5.02	0	11.19	14.27	1.99	5.05	15.46	Implicit
LOWER RILEY POND	5.21	0	4.31	5.50	0.77	5.24	4.08	Implicit
LOWER SOUTH POND	5.36	0	8.84	11.28	1.57	5.42	2.93	Implicit
LOWER WALLFACE PD	4.97	0	4.87	6.21	0.87	5.00	6.99	Implicit
MARION POND	5.29	0	0.57	0.72	0.10	5.43	0.13	Implicit
MECO LAKE	5.37	0	2.54	3.23	0.45	5.39	1.16	Implicit
MERRIAM LAKE	5.44	0	1.84	2.35	0.33	5.48	0.15	Implicit
MIDDLE CHAIN POND	5.37	0	1.32	1.68	0.23	5.42	0.40	Implicit
MIDDLE LOOMIS PD.	5.26	0	3.02	3.86	0.54	5.27	2.78	Implicit
MIDDLE NOTCH POND	4.96	0	2.87	3.66	0.51	4.97	4.45	Implicit
MIDDLE SOUTH POND	5.42	0	4.03	5.14	0.72	5.47	0.44	Implicit
MONUMENT LAKE	5.30	0	0.81	1.03	0.14	5.45	0.14	Implicit
MOUNTAIN LAKE	5.33	0	0.84	1.07	0.15	5.46	0.13	Implicit
MUIR POND	5.23	0	2.24	2.85	0.40	5.26	1.97	Implicit
N.BEECHRIDGE POND	5.26	0	2.23	2.84	0.40	5.29	1.79	Implicit
OSWEGO POND	5.01	0	6.61	8.43	1.18	5.02	9.35	Implicit
OTTER POND	5.28	0	35.32	45.04	6.28	5.29	29.95	Implicit
PELCHER POND	5.46	0	4.10	5.22	0.73	5.50	0.04	Implicit
PINE POND	5.24	0	2.59	3.30	0.46	5.25	2.59	Implicit
POOR LAKE	5.46	0	3.89	4.96	0.69	5.48	0.34	Implicit
POTTER POND	5.18	0	1.58	2.01	0.28	5.19	1.80	Implicit
REDHOUSE LAKE	5.42	0	2.22	2.83	0.39	5.44	0.57	Implicit
ROCK LAKE	5.44	0	7.30	9.31	1.30	5.47	0.83	Implicit
ROCK LAKE(05-229)	5.25	0	7.41	9.45	1.32	5.29	5.93	Implicit
ROCK LAKE(05-275)	5.38	0	1.27	1.62	0.23	5.43	0.39	Implicit
ROUND POND	5.38	0	0.82	1.05	0.15	5.47	0.10	Implicit
RUSSIAN LAKE	5.45	0	6.10	7.78	1.08	5.47	0.79	Implicit
SALMON LAKE	5.11	0	93.42	119.15	16.62	5.14	110.38	Implicit
SAND LAKE	5.45	0	2.61	3.33	0.47	5.49	0.17	Implicit
SAND LAKE	5.38	0	47.82	60.98	8.50	5.40	20.71	Implicit
SILVER LAKE	5.46	0	9.40	11.99	1.67	5.49	0.41	Implicit
SITZ POND	5.32	0	5.39	6.87	0.96	5.33	3.70	Implicit
SLENDER POND	5.39	0	0.92	1.18	0.16	5.46	0.13	Implicit
SOUTH POND	5.41	0	6.03	7.69	1.07	5.43	1.74	Implicit
STEWART LAKE	5.43	0	2.98	3.80	0.53	5.47	0.32	Implicit
STONEY POND	5.46	0	11.26	14.36	2.00	5.48	1.14	Implicit
STREETER FISHPOND	5.35	0	0.75	0.96	0.13	5.46	0.10	Implicit
SUNSHINE POND	5.45	0	2.08	2.65	0.37	5.48	0.16	Implicit
T LAKE	5.42	0	9.99	12.74	1.78	5.44	2.74	Implicit
TOAD POND	5.45	0	2.61	3.33	0.47	5.49	0.17	Implicit
TOAD POND	5.45	0	2.61	3.33	0.47	5.49	0.17	Implicit
TROUT LAKE	5.47	0	8.41	10.73	1.50	5.50	0.17	Implicit
TWELFTH TEE POND	5.21	0	0.94	1.20	0.17	5.23	0.99	Implicit
TWIN LAKE (SOUTH)	5.40	0	2.11	2.69	0.38	5.44	0.53	Implicit

Phase 1 Acid Rain TMDL for Adirondack Forest Preserve Lakes

Lake Name	Current pH (modeled)	Total Maximum Daily Load (TMDL)						
		Waste Load Allocation	Load Allocation (in kg/d)			pH w/CAIR Reductions	Amount of $CaCO_3$ to be added (kg/d)	Margin of Safety
			SO_4^{-2}	NO_3^{-1}	NH_4^{+1}			
TWIN PONDS	5.43	0	2.10	2.68	0.37	5.48	0.21	Implicit
UNNAMED P #2-133	5.00	0	0.50	0.64	0.09	5.01	0.78	Implicit
UNNAMED P #3-189	4.95	0	0.55	0.70	0.10	4.95	0.72	Implicit
UNNAMED P #4-194	4.85	0	18.00	22.96	3.20	4.95	23.25	Implicit
UNNAMED P #4-202	5.42	0	0.63	0.80	0.11	5.45	0.14	Implicit
UNNAMED P #4-204	4.91	0	51.91	66.20	9.23	4.96	66.36	Implicit
UNNAMED P #4-205	5.38	0	1.13	1.45	0.20	5.46	0.19	Implicit
UNNAMED P #4-206	5.21	0	1.93	2.46	0.34	5.22	2.02	Implicit
UNNAMED P #4-207	5.00	0	12.47	15.91	2.22	5.03	17.51	Implicit
UNNAMED P #4-208	4.91	0	10.81	13.78	1.92	4.98	14.93	Implicit
UNNAMED P #4-209	5.34	0	0.70	0.89	0.12	5.35	0.43	Implicit
UNNAMED P #4-211	4.88	0	8.62	11.00	1.53	4.95	11.26	Implicit
UNNAMED P #4-212	4.96	0	6.13	7.82	1.09	5.00	8.64	Implicit
UNNAMED P #4-213	4.99	0	3.94	5.03	0.70	5.03	5.45	Implicit
UNNAMED P #4-314	5.28	0	4.35	5.55	0.77	5.30	3.67	Implicit
UNNAMED P #4-320A	4.99	0	3.50	4.47	0.62	4.99	5.04	Implicit
UNNAMED P #4-320B	5.33	0	1.25	1.59	0.22	5.36	0.71	Implicit
UNNAMED P #4-321A	5.41	0	1.26	1.60	0.22	5.45	0.23	Implicit
UNNAMED P #4-322B	5.36	0	0.17	0.22	0.03	5.43	0.05	Implicit
UNNAMED P #4-356	5.10	0	1.54	1.97	0.27	5.11	2.07	Implicit
UNNAMED P #4-370	4.94	0	2.21	2.82	0.39	4.95	2.85	Implicit
UNNAMED P #4-371	5.41	0	1.05	1.34	0.19	5.46	0.16	Implicit
UNNAMED P #4-439	5.13	0	1.34	1.71	0.24	5.15	1.70	Implicit
UNNAMED P #4-440	4.83	0	1.84	2.35	0.33	4.93	2.54	Implicit
UNNAMED P #4-444A	5.43	0	0.93	1.18	0.16	5.45	0.19	Implicit
UNNAMED P #6-119	4.97	0	0.64	0.82	0.11	4.98	0.84	Implicit
UNNAMED P #6-124	4.95	0	1.86	2.38	0.33	4.96	2.39	Implicit
UNNAMED P #6-330	5.41	0	0.85	1.08	0.15	5.45	0.17	Implicit
UPPER CHAIN POND	5.34	0	0.31	0.39	0.05	5.37	0.16	Implicit
UPPER HAYMARSH PD	5.21	0	6.71	8.56	1.19	5.23	6.94	Implicit
UPPER NOTCH POND	5.03	0	0.97	1.24	0.17	5.04	1.50	Implicit
UPPER RILEY POND	5.24	0	2.72	3.47	0.48	5.26	2.53	Implicit
UPPER SISTER LAKE	5.17	0	49.09	62.60	8.73	5.19	54.41	Implicit
UPPER TWIN LAKE	5.47	0	27.12	34.59	4.82	5.48	2.80	Implicit
UPPER WALLFACE PD	5.45	0	1.85	2.36	0.33	5.47	0.23	Implicit
WALKER LAKE	5.41	0	2.80	3.57	0.50	5.47	0.37	Implicit
WASHBOWL POND	5.25	0	0.41	0.52	0.07	5.30	0.31	Implicit
WEST POND	4.89	0	28.23	36.01	5.02	4.96	35.75	Implicit
WHITE BIRCH LAKE	5.19	0	2.43	3.10	0.43	5.21	2.55	Implicit
WILDER POND	5.22	0	2.47	3.15	0.44	5.24	2.38	Implicit
WILLYS LAKE	5.44	0	5.42	6.91	0.96	5.48	0.51	Implicit
WITCHOPPLE LAKE	5.14	0	70.10	89.40	12.47	5.17	78.52	Implicit
WOLF POND	5.30	0	39.95	50.95	7.11	5.32	29.84	Implicit

Appendix 17.3

Adirondacks Forest Preserve Acid Rain Lakes TMDL Air Deposition Changes Due to Planned EPA and State Programs

Air Programs Branch, USEPA Region 2

This summary describes how we calculated future changes in atmospheric deposition of nitrogen and sulfur. Recently, EPA has produced regional air pollution modeling results for ozone and particulate matter that also include deposition of various species, including nitrogen and sulfur. These model runs were completed to support EPA's Clean Air Interstate Rule (CAIR).

These modeling results are very helpful for determining the future of air deposition in the Adirondacks. Most of the nitrogen and sulfur in the lakes is from air deposition, rather than runoff from farming or other human activities. When TMDLs are prepared for Adirondack lakes, the loading from the atmosphere is the most important source of nitrogen and sulfur to these lakes. The Clean Air Act mandated reductions in nitrogen and sulfur emissions to reduce deposition. Also, additional programs in progress, and proposed programs, including CAIR, are designed to reduce ozone and fine particle pollution to protect public health. All these programs will continue to reduce deposition of acidic species into lakes and watersheds.

EPA used the Community Air Quality Model (CMAQ) to project the impacts from air pollution control programs on particulate matter and ozone concentrations, including deposition for the eastern United States. CMAQ is a dynamic gridded model using complex atmospheric chemistry and high resolution weather data. It is EPA's state-of-the-art model for air dispersion, pollution transport and atmospheric chemistry. Information on the use of this model for CAIR is at EPA's technical information page found via the http://www.epa.gov/cair/index.html web site.

Baseline deposition data are from measurements of chemicals in rainfall at the Huntington State Forest Site in the heart of the Adirondack Forest Preserve. The portion of the Adirondacks around Huntington includes most of the lakes that EPA is evaluating to see if they can recover from the depletion of acid-neutralizing soils and decades of sulfur and nitrogen deposition. The baseline deposition values are a five-year average of wet deposition data, centered around the base year of 2000. Five years of data were used to provide a robust baseline. This way year-to-year variations in weather could be averaged out.

The predicted deposition amounts are the average of the output from two grid cells surrounding the Huntington deposition monitoring site. The grid cells are 36km on each side.

The model's base case is 2000 and projected deposition data are available for 2010 and 2015. Later, predictions for 2020 were modeled. Future deposition was calculated by multiplying the percent change in modeled deposition from 2000 to 2010 times the observed deposition from Huntington. The same method was followed to calculate deposition for 2015. Since the deposition from 2020 was based on a new run of the CMAQ model, the reduction in deposition from a new 2000 base case to the 2020 predicted deposition was applied to the observed deposition from Huntington. The changes in deposition are summarized in a table of baseline deposition and future deposition for 2010, 2020 and full implementation of CAIR. A supplementary table lists the air pollution control programs that were applied by the model for the projected deposition we used.

Dry deposition data were not collected at the Huntington site, so baseline dry deposition was estimated using the model's ratio of dry to wet deposition. Specifically, the ratio of dry to wet deposition was multiplied by the wet deposition for each species from the Huntington site and used as baseline dry deposition. For the future case projected dry deposition, we reduced the base case deposition by the percentage reduction in dry deposition as predicted by CMAQ..

Since some of the sulfur emission reductions in CAIR will not be in place by 2020, the sulfate results include an estimate of deposition upon full implementation of CAIR. For nitrate and ammonium, complete implementation of CAIR is expected by 2020. Since there are no modeling results available for full implementation scenario, used the emissions reduction estimated for full implementation to linearly extrapolate the deposition for the full implementation of CAIR.

Summary of Projected Reductions from Various Programs		
Baseline Atmospheric Deposition: 1998-2002 (Based on actual Deposition Data)	Baseline deposition data includes reductions from the following 1990 Clean Air Act programs	
Wet Deposition: SO_4^{-2}: 26.28 ueq/L NO_3^{-1}: 20.46 ueq/L NH_4^{+1}: 10.09 ueq/L Dry Deposition: calculated from ratio of modeled dry to wet deposition times the observed wet deposition: SO_4^{-2}: 12.71 ueq/L NO_3^{-1}: 19.61 ueq/L NH_4^{+1}: 1.549 ueq/L	State NOx Reasonably Available Control Technology (RACT) Regulations	
	Ozone Transport Commission (OTC) Phase II NOx Controls	
	State Implementation Plans for ozone -progress toward attaining ozone standard by 2005/7	varies by state
	Title IV Acid Rain provisions	
	- Federal Motor Vehicle Control Program - States Inspection and Maintenance Programs - Regular and Enhanced - Reformulated Gasoline (lower sulfur) - Low Emission Vehicle Reg (implementation date varied by state) - Offset of new increases in NOx in ozone nonattainment areas (ratio varies from 1:1 to 1:1.15 (e.g., a 1.15 ton decrease in NOx emissions for each 1ton of new emissions) - Residential Wood Combustion	

Estimated Atmospheric Deposition in future year(s)			Reductions in nitrogen and sulfur include reductions from the following programs effective from 2001 to 2010, 2010 to 2015, 2015 to 2020 and to fully implementation (as appropriate). Reductions are a percent of 2001 base emissions for each <u>category</u> of emissions:	
Year	Wet	Dry		
<u>2010</u> SO_4^{-2}: NO_3^{-1}: NH_4^{+1}:	 18.68 ueq/L 13.93 ueq/L 9.85 ueq/L	 9.039 ueq/L 13.35 ueq/L 1.512 ueq/L	Mobile - on road - sources Ongoing programs: - Federal Motor Vehicle Control Program - States Inspection and Maintenance Programs - Regular and Enhanced - Reformulated Gasoline (lower sulfur) - Low Emission Vehicle Reg (implementation date varied by state) Programs starting after 2001, but starting before 2010: - Federal Motor Vehicle Control Program Tier II (lower NO_x, (and SO_x,)) - New Diesel Engine Standards (NOx and SOx) - EPA Clean Diesel initiative Phase II of Title IV	90 % SOx 44 %NOx
			New : - OTC Phase III NOx Controls - CAIR Ongoing: -NOx State Implementation Plan (SIP) Call (implemented starting in 2001, completed 2004/5)	44% SO2 52% NOx
			Non EGU sources: Ongoing programs: - Offset of new increases in NOx in ozone nonattainment areas (ratio varies from 1:1 to 1:1.15 (e.g., a 1.15 ton decrease in NOx emissions for each 1ton of new emissions)	2 %NOx
			Other area sources: Ongoing program - Residential Wood Combustion	increased by 10%SO2, 11%NOx
			Nonroad Federal non-road engine standards (NOx and SOx) Nonroad Engine Controls	43%SOx 17 % NOx

Estimated Atmospheric Deposition in future year(s)			Reductions in nitrogen and sulfur include reductions from the following programs effective from 2001 to 2010, 2010 to 2015, 2015 to 2020 and to fully implementation (as appropriate). Reductions are a percent of 2001 base emissions for each <u>category</u> of emissions:	
Year	Wet	Dry		
<u>2015</u> SO_4^{-2}: NO_3^{-1}: NH_4^{+1}:	16.97 ueq/L 12.33 ueq/L 9.89 ueq/L	8.208 ueq/L 11.82 ueq/L 1.519 ueq/L	Other area sources: Ongoing program - Residential Wood Combustion program.	increased by 14%SO2 16%NOx
			CAIR NOx Phase I Programs starting in 2009 - all reductions implemented by 2015 CAIR SO2 Phase I Program starting in 2010	56 % SO2 48% NOx
<u>2020</u> SO_4^{-2}: NO_3^{-1}: NH_4^{+1}:	16.18 ueq/L 10.79 ueq/L 8.78 ueq/L	7.828 ueq/L 10.34 ueq/L 1.348 ueq/L	CAIR NOx and SO2 Phase II Programs starting in 2015	64 % SO2 48 % NOx
<u>full implementation</u> SO_4^{-2}: NO_3^{-1}: NH_4^{+1}:	14.41 ueq/L 10.79 ueq/L 8.78 ueq/L	6.972 ueq/L 10.34 ueq/L 1.348 ueq/L	CAIR NOx and SO2 Phase II Programs starting in 2015	73% SO2 48% NOx

Source: USEPA Region 2, Air Programs Branch, 2006.

Appendix 17.4

New York State Forest Preserve Lakes TMDL Support Documents (Selected)

Appendix C

Geochemical Modeling Support for Developing the New York State Acid Deposition TMDL

Appendix F

Hydrology Data and Methods

These two (2) documents are taken from the larger Draft Report *New York State Forest Preserve Lakes TMDL Support Document* (Battelle, 2006a). Because this draft support document is still undergoing review and revision, it is not included in this TMDL document in its entirety. However these appendices to this draft report (Appendices C and F, specifically) provide relevant information regarding the PHREEQC modeling approach and are included as Appendix 17.4.

Appendix C

Geochemical Modeling Support for Developing the New York State Acid Deposition TMDLs

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EXECUTIVE SUMMARY

This appendix is part of a larger effort conducted by Battelle, Pacific Northwest Division to determine Total Maximum Daily Loads (TMDLs) for pH and dissolved aluminum in watersheds of the Adirondack region that are potentially affected by acidic deposition. One of the models used in the combined modeling approach of this effort is the PHREEQC geochemical model (Parkhurst and Appelo, 1999). The available PHREEQC thermodynamic databases do not contain data for the organic acid speciation, aluminum-organic acid complexation, and gibbsite [$Al(OH)_3$] solubility reactions important for representing aqueous chemistry in Adirondacks watersheds. Therefore, the recent scientific literature on soil and surface water chemistry was reviewed to identify relevant data.

Based on this review, the most appropriate model of organic acid chemistry for Adirondacks watersheds is expected to be the triprotic model developed by Driscoll et al. (1994). Thermodynamic data for reactions based on this model:

$H^+ + Orgacid^{-3} = HOrgacid^{-2}$ log K = 5.94

$2\ H^+ + Orgacid^{-3} = H_2Orgacid^-$ log K = 11.60

$3\ H^+ + Orgacid^{-3} = H_3Orgacid$ log K = 14.24

were added to the PHREEQC database, where "Orgacid" represents the organic acid anion. To obtain a representative gram formula weight for "Orgacid," the site density of 0.055 mol sites/mol C derived by Driscoll et al. (1994) was used to calculate a value of 218.2 g C/mol sites; this conversion factor can be used to convert measured DOC concentrations in mg C/L to concentrations of organic acid used by PHREEQC.

Reactions that describe aluminum complexation by organic species were included in the PHREEQC thermodynamic database. The thermodynamic data for the complexation reactions:

$Al^{3+} + Orgacid^{3-} = AlOrgacid^0$ log K = 8.39

$Al^{3+} + H^+ + Orgacid^{3-} = AlHOrgacid^+$ log K = 13.1

were selected because they are consistent with the triprotic organic acid model and were obtained by model calibration to Adirondack watershed data (Schecher, 1988; Schecher and Driscoll, 1995).

Review of the relevant literature indicated that aluminum solubility in Adirondacks watersheds is best represented by an empirical relationship for waters with pH less than about 5.5 (Sullivan and Cosby, 1998) and by the theoretical solubility of natural gibbsite for higher pH conditions. The empirical relationship between aluminum ion concentrations [Al^{3+}] and pH was written as a solubility reaction for a solid phase "Gibbsite(emp):"

$Al(OH)_2^+(s) + 2\ H^+ = Al^{3+} + 2\ H_2O$ log K = 4.5

where $Al(OH)_2^+(s)$ represents Gibbsite(emp) as a charged solid. Although such a charged solid is theoretically impossible, formulation of the reaction in this manner produces a slope of –2 for a plot of $[Al^{3+}]$ concentration as a function of pH, which is required by the empirical relationship of Sullivan and Cosby (1998), while maintaining overall charge balance for the solubility equation. In addition to the entry made for Gibbsite(emp), other potentially relevant aluminum hydroxides phases were added to the PHREEQC database to provide a complete set of the predominant phases generally used in modeling studies: natural gibbsite [Gibbsite(nat)], synthetic gibbsite [Gibbsite(syn)], microcrystalline gibbsite [Gibbsite(uc)], and amorphous aluminum trihydroxide [$Al(OH)_3$(am)].

An example soil solution composition was developed for use in PHREEQC calculations performed to verify that the thermodynamic data were entered correctly. Results of the PHREEQC calculations confirmed that the data were appropriately incorporated in the database, including control of aluminum solution concentrations by the Gibbsite(emp) reaction at pH values less than 5.5 and by gibbsite(nat) solubility at higher pH values. The calculations also confirmed the importance of aluminum complexation of organic ligands under the slightly acidic to near-neutral conditions expected for most forested watersheds.

The final compilation of PHREEQC thermodynamic data determined from this review and testing effort are provided as part of this appendix, along with the PHREEQC input and output files used in the report calculations. Methods for using PHREEQC to calculate the Gran titration acid neutralizing capacity (ANC_G), a laboratory-measured parameter often used to characterize the acid buffering capacity of Adirondack waters, were also provided.

1.0 INTRODUCTION

This appendix is part of a larger effort conducted by Battelle, Pacific Northwest Division to determine Total Maximum Daily Loads (TMDLs) for pH and dissolved aluminum in watersheds of the Adirondack region that are potentially affected by acidic deposition. The overall effort relies on a series of numerical models of atmospheric, hydrological, and geochemical processes to predict TMDLs based on rates of acid deposition received by the watersheds. One of the models used in the combined modeling approach of this effort is the PHREEQC geochemical model (Parkhurst and Appelo, 1999), which is used for simulating chemical reactions in soils and surface waters.

The original versions of the thermodynamic databases that are part of the PHREEQC package do not contain data for three types of reactions that are important for representing aqueous chemistry in Adirondacks watersheds, including:

- Organic acid speciation;
- Aluminum-organic acid complexation; and
- Natural gibbsite [$Al(OH)_3$] solubility.

Therefore, the purpose of this appendix is to provide information on reaction stoichiometries and equilibrium constants for these three types of reactions and augment the PHREEQC thermodynamic database with these data for use in the TMDL modeling effort. To accomplish this goal, the recent scientific literature on soil and surface water chemistry was reviewed to identify relevant data. Selected data were incorporated into the PHREEQC thermodynamic database and test simulations were run to verify that the data were entered correctly. The final compilation of PHREEQC thermodynamic data determined from this review and testing effort are provided as part of this appendix.

Section 2.0 provides a discussion of the literature review and a summary of the selected data. Section 3.0 contains a description of how the data were added to the PHREEQC thermodynamic database and the results of PHREEQC modeling runs that were performed to test the data.

2.0 DATA REVIEW

A review was conducted of the recent scientific literature that describes organic acid speciation, complexation of aluminum by organic anions, and aluminum solid solubility in natural waters affected by acid deposition in the northeastern U.S. and northern Europe. Based on this review, data relevant to modeling these processes have been summarized and evaluated with respect to their applicability to lakes in the New York State Adirondack Mountains region.

2.1 Organic Acid Dissociation Constants

Organic acids in soil solutions, groundwater, and surface water are naturally occurring humic substances derived from transformation of biogenic organic matter. Organic acids can affect the acidity and buffering of forest soil solutions, groundwater, and surface water and contribute organic anions that can complex metallic cations.

Aquatic humic substances are polymeric acids that can have a variety of acid functional groups, including carboxylic acids, phenols, thiols, and alcohols. These functional groups have a range of acid-base characteristics, making it difficult to characterize organic acids in terms of specific acid-base reactions (Driscoll et al., 1994). As a consequence, different modeling approaches have been developed to represent the collective acid-base properties of organic solutes in natural waters. These approaches include empirically based equations derived from potentiometric titrations and simple organic acid analogs with different pK_as (negative logarithms of the acid dissociation constants) or distributions of pK_a values (Driscoll et al., 1994).

Oliver et al. (1983) described the results of an early study of organic acids extracted from natural water samples from lakes in Ontario and Nova Scotia. These acids were analyzed to determine their carboxylic acid content and dissociation behavior. The overall pK_a value was observed to change as a function of pH:

$$pKa = 0.96 + 0.90\ pH - 0.039\ (pH)^2 \quad (1)$$

A number of subsequent studies have been carried out that developed organic acid models based on monoprotic, diprotic, and triprotic analogs of a generalized organic acid molecule (HA) based on data from watersheds in the eastern United States and northern Europe (Table 1). The monoprotic model includes the single acid dissociation reaction:

$$HA = A^- + H^+ \quad (2)$$

Diprotic models include two acid dissociation reactions:

$$H_2A = HA^- + H^+ \quad (3)$$

$$HA^- = A^{2-} + H^+ \quad (4)$$

Table 1. Example dissociation constants for organic acid analog models

pKa_1	pKa_2	pKa_3	Acid Model	Location	Reference
4.41	--	--	monoprotic	Adirondacks	Driscoll and Bisogni (1984)
4	--	--	monoprotic	Norway	Wright (1989)
4.45	--	--	monoprotic	Adirondacks	Driscoll et al. (1994)
4.3	--	--	monoprotic	Sweden	Hruška et al. (1999)
4.02	6.04	--	diprotic	Adirondacks	Driscoll et al. (1994)
3.37	6.22	--	diprotic	Eastern U.S.	Schecher and Driscoll (1995)
1.76	5.90	6.83	triprotic	Not specified	Driscoll and Schecher (1988, 1990)
2.64	5.66	5.94	triprotic	Adirondacks	Driscoll et al. (1994)
2.1	5.94	6.86	triprotic	Eastern U.S.	Schecher and Driscoll (1995)
2.1	5.6	7.0	triprotic	Norway	Cosby et al. (1995)
3.6	4.2	5.5	triprotic	Sweden	Kőhler (1999)
2.0	4.12	5	triprotic	Sweden	Hruška et al. (1999)
4.5	8.0	16.0	triprotic	Norway	Wright (2001)

Triprotic models include three acid dissociation reactions:

$$H_3A = H_2A^- + H^+ \tag{5}$$

$$H_2A^- = HA^{2-} + H^+ \tag{6}$$

$$HA^- = A^{3-} + H^+ \tag{7}$$

The most recent study of organic acid dissociation that utilized data from the Adirondacks was Driscoll et al. (1994). In that study, Driscoll et al. (1994) used data from the Adirondack Lake Survey to calibrate organic acid analog models, including the Oliver et al (1983) model and also monoprotic, diprotic, and triprotic representations of organic acids. The triprotic model provided the best fit to the observed data and was consistent with observed changes in organic solute charge density as a function of pH. Sullivan et al. (1996) used the Driscoll et al. (1994) triprotic organic acid model to predict the pH in three Adirondacks data sets and found that it provided a reasonably good representation of historical acidification. Because the triprotic organic acid model developed by Driscoll et al. (1994) was obtained using data from watersheds in the Adirondacks, it is the most appropriate for geochemical modeling of organic acids in this investigation.

2.2 Dissolved Organic Carbon Site Density

The organic content of natural waters is generally reported in terms of total organic carbon (TOC, obtained from unfiltered water samples) or dissolved organic carbon (DOC, obtained from filtered water samples). Although laboratory analyses provide a measure of the carbon content per unit of solution, the organic acid functional groups that are available in the dissolved organic carbon must be estimated when modeling the chemical behavior of dissolved organic carbon in natural waters. The number of organic acid dissociation sites per unit weight of dissolved organic carbon is referred to as the site density, and representative values have been reported in a number of investigations (Table 2).

The organic carbon site density values most likely to be applicable to modeling lakes in the Adirondacks are the values that are consistent with the triprotic organic acid model derived for watersheds in the northeastern U.S by Driscoll et al. (1994) and Schecher and Driscoll (1995). The Driscoll et al. (1994) value of 4.6 μeq/mg DOC (0.055 mol sites/mol C) was used with the triprotic organic acid analog model by Sullivan et al. (1996) to evaluate historical acidification of lakes in the Adirondacks, and provided reasonably good agreement between model predictions of pH and the historical lake water pH values inferred from the sediment diatom record. The Driscoll et al. (1994) value is also consistent with the selected triprotic organic acid model data (Section 2.1). Therefore, the Driscoll et al. (1994) organic carbon site density value will be used to model the surface waters in this investigation.

Table 2. Representative organic carbon site densities

Site Density (μeq/mg DOC)	Location	Reference	Comments
4.5	Maine	Kahl et al. (1989)	Average value calculated from charge balance of waters in data set
4.5	Norway	Wright (1989)	Maximum value estimated from charge balance of waters in data set
6.5	Not specified	Munson and Gherini (1991)	Monoprotic acid model, data source not cited
9.7	Finland	Kortelainen and Saukkonen (1995)	Oliver et al. (1983) acid model
4.6	Adirondacks	Driscoll et al. (1994)	Triprotic acid model, fit to Adirondack Lake Survey data
4.5	Eastern U.S.	Schecher and Driscoll (1995)	Diprotic acid model, fit to Eastern Lake Survey and RILWAS data
3.6	Eastern U.S.	Schecher and Driscoll (1995)	Triprotic acid model, fit to Eastern Lake Survey and RILWAS data
6.5 to 7.7	Maine	David et al. (1999)	Used model similar to Oliver et al. (1983), titrated DOC from forest-floor samples

2.3 Aluminum Complexation by Organic Species

Aluminum can be complexed in solution by dissolved organic carbon species. If a triprotic acid analog model is used to describe organic acid chemistry, the reactions:

$$Al^{3+} + Orgacid^{3-} = AlOrgacid^{0} \quad (8)$$

$$Al^{3+} + H^{+} + Orgacid^{3-} = AlHOrgacid^{+} \quad (9)$$

may be used to describe the aluminum complexation reactions, where $Orgacid^{3-}$ is a triprotic organic acid (Schecher and Driscoll, 1995).

Limited data are available regarding the thermodynamic equilibrium constants for reactions (8) and (9). A log value of 11.08 for the equilibrium constant was included in the ILWAS model for reaction (8), but the model did not include reaction (9) (Eary et al., 1989). Driscoll and Schecher (1988; 1990) reported equilibrium constants of 8.39 and 13.09 (log K) for reactions (8) and (9), respectively; these equilibrium constants were calibrated using the ALCHEMI model and field data collected from the Adirondack region (Schecher, 1988). Schecher and Driscoll (1995) derived virtually the same equilibrium constants (8.38 and 13.1 for reactions (8) and (9), respectively) from an optimization of the ALCHEMI model to data from the eastern U.S. Because the thermodynamic constants derived by Schecher (1988) were developed using data from the Adirondack region, these data were selected for use in the current investigation.

2.4 Gibbsite Solubility

In surface waters affected by acid deposition, aluminum concentrations can be an order of magnitude higher than in circumneutral surface waters (Sullivan and Cosby, 1998). Because of the toxicity of dissolved aluminum species to aquatic biota and terrestrial vegetation, extensive research has been conducted to identify the processes controlling aluminum concentrations in soil solutions, surface waters, and groundwater in watersheds that may have been affected by acid deposition.

Discussions of aqueous chemistry of watersheds generally use the term total monomeric (dissolved) aluminum to refer to the sum of the inorganic (labile) and organically complexed (nonlabile) monomeric aluminum species present in solution. Numerical models of aqueous chemistry, such as PHREEQC, are capable of representing chemical reactions involving total monomeric aluminum through principles of chemical equilibrium. In general, total monomeric aluminum concentrations tend to be relatively low in moderate-pH solutions because of the low solubilities of naturally forming minerals, such as gibbsite [$Al(OH)_3(s)$], which is often referred to as aluminum trihydroxide (Driscoll and Schecher, 1990; Langmuir, 1997; Schecher and Driscoll, 1995). However, aluminum mobility increases in more acidic solutions (pH less than about 6) and in the presence of complexing ligands such as fluoride (F^-) and organic acids (Langmuir, 1997).

A number of studies have focused on the possible control of total monomeric aluminum concentrations by the solubility of gibbsite in acid-deposition-affected watershed soils and surface water. Gibbsite solubility can be described by the reaction:

$$Al(OH)_3(s) + 3\ H^+ = Al^{3+} + 3\ H_2O \qquad (10)$$

For this reaction, the theoretical solubility constant (K_{s0}) is defined as:

$$K_{s0} = \{Al^{3+}\}/\{H^+\}^3 \qquad (11)$$

where the brackets refer to activities. Assuming that aluminum concentrations $[Al^{+3}]$ closely approximate aluminum activities $\{Al^{+3}\}$ in the dilute waters of most forested watersheds, equation (11) is typically expressed in a more convenient log form as:

$$\log [Al^{+3}] = \log K_{s0} - 3\ pH \qquad (12)$$

Equation (12) defines the solubility of gibbsite in terms of the concentration of the Al^{3+} species, from which the concentrations of other dissolved aluminum species that comprise total monomeric aluminum can be calculated with the relevant speciation reactions. This type of calculation is performed with geochemical models, such as PHREEQC, for conditions of chemical equilibrium.

Based on determinations of solution chemical composition and conditions, various studies have derived solubility constants (K_{s0}) for aluminum trihydroxide solids that range from 6.5 to 10.8 (Table 3). This reported solubility range is a consequence of both the methods used to determine the aluminum trihydroxide solubilities and the solid phase that is assumed to control total monomeric aluminum concentrations. A number of the studies listed in Table 3 used solubility constants from the literature for different forms of gibbsite that appeared to work best for the systems examined. The different forms range from amorphous aluminum trihydroxide to synthetic gibbsite, resulting in different values for log K_{s0} ranging from 8.1 to 10.8 (Driscoll et al. 1984; Reuss and Johnson, 1985; Cronan et al., 1986; Eary et al., 1989; Sullivan and Cosby, 1998). Other values of log K_{s0} for aluminum trihydroxide have been calculated empirically using surface-water data (Driscoll and Bisogni, 1984) or adjusted during calibration of various watershed models (Warfvinge and Sverdrup, 1992; Cosby et al., 1995; Mol-Dijkstra and Kros, 2001; Wright, 2001), resulting in a range of values from 6.5 to 10.1. In addition, some aluminum trihydroxide solubility constants were experimentally determined using catchment soils under controlled conditions (Dahlgren and Walker, 1993; Berggren and Mulder, 1995).

Although some soil solutions in forested watersheds reportedly have monomeric aluminum concentrations consistent with gibbsite solubility, most soil solutions and surface waters with low pH values (less than about 4.2 to 4.5) are undersaturated with respect to gibbsite solubility (Berggren and Mulder, 1995; Mulder and Stein, 1994; Sullivan and Cosby, 1998; de Wit et al. 1999). The undersaturation conditions have

Table 3. Reported aluminum trihydroxide solid solubility constants

Log Solubility Constant[1]	Solubility-Controlling Phase	Reference	Location	Comments
8.49	Aluminum trihydroxide	Driscoll and Bisogni (1984)	Adirondacks	Calculated value using lake and stream data
8.11	Synthetic gibbsite	Driscoll et al. (1984)	Adirondacks	Solubility constant from May et al. (1979)
8.77	Natural gibbsite	Driscoll et al. (1984)	Adirondacks	Solubility constant from May et al. (1979)
9.35	Microcrystalline gibbsite	Driscoll et al. (1984)	Adirondacks	Solubility constant from Hem and Robertson (1967)
10.80	Amorphous aluminum trihydroxide	Driscoll et al. (1984)	Adirondacks	Solubility constant from Stumm and Morgan (1970)
8.5	Aluminum trihydroxide	Reuss and Johnson (1985)	Model system	Specified solubility between gibbsite and amorphous $Al(OH)_3(s)$
8.77	Aluminum trihydroxide	Cronan et al. (1986)	North America and Europe	Solubility constant from May et al. (1979)
8.18	Unspecified gibbsite	Eary et al. (1989)	Model system	Solubility constant in ILWAS model close to value reported by May et al. (1979) for synthetic gibbsite
6.5 to 9.27	Gibbsite	Warfinge and Sverdrup (1992)	Sweden	Solubility constants calibrated with PROFILE model increased with depth in soil horizons
8.1	Synthetic gibbsite or hydroxy-Al interlayer in soil layered silicates	Dahlgren and Walker (1993)	Maine and New Hampshire	Experimentally determined solubility at pH 3 to 5 using Bs horizon soils; slope of 2.7 compared to. ideal slope of 3 for gibbsite
8.85	Amorphous aluminum trihydroxide	Berggren and Mulder (1995)	Sweden	Experimentally determined solubility in mineral soils above pH 4.1 at 8ºC
7.6 (soil) 6.6 (lake)	Aluminum trihydroxide	Cosby et al. (1995)	Norway	Risdalsheia catchment, calibrated value using MAGIC model at 7ºC
8.8 (soil) 7.5 (lake)	Aluminum trihydroxide	Cosby et al. (1995)	Norway	Skjervatjern catchment, calibrated value using MAGIC model at 6.6ºC
6.5 to 8.5	Gibbsite	Hodson et al. (1996)	Scotland	Solubility constants were default values in PROFILE model or based on reports on similar soils
8.1 (25ºC) 9.1 (8ºC)	Synthetic gibbsite	Sullivan and Cosby (1998)	Model system	Solubility constant from May et al. (1979)
7.2	Aluminum trihydroxide	Mol-Dijkstra and Kros (2001)	Norway	Calibrated value using the SMART2 model, Risdalsheia catchment
8.8 (soil) 10.1 (surface runoff)	Aluminum trihydroxide	Wright (2001)	Norway	Vikedal river catchment, calibrated value using MAGIC model at 6.6ºC
8.1 (soil) 9.3 (surface runoff)	Aluminum trihydroxide	Wright (2001)	Norway	Tovdal river catchment, calibrated value using the MAGIC model at 5ºC

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[1] Log solubility constants for aluminum trihydroxide as defined in Equation (3)

been attributed to aluminum complexation and adsorption by soil organic matter; processes that reportedly may limit aluminum concentrations to values less than predicted by gibbsite solubility in acidic, organic surface soils (Cronan et al. 1986; Walker et al., 1990; Mulder and Stein, 1994; Berggren and Mulder, 1995). Because slightly acidic surface waters (pH less than about 5.5) are often reported to be undersaturated with gibbsite solubility (Sullivan et al. 1986; Sullivan and Cosby, 1998), watershed models such as MAGIC that rely on gibbsite solubility as defined by equation (12) have generally over-predicted aluminum concentrations in acidic watersheds (Sullivan and Cosby, 1998).

Based on observations that gibbsite solubility generally does not accurately represent aluminum in the acidic waters of Adirondacks watersheds, Sullivan and Cosby (1998) analyzed surface water chemical compositions from the Adirondacks to derive a more reliable predictor of monomeric aluminum concentrations. In their analysis, Sullivan and Cosby (1998) observed that the log of measured concentrations of total inorganic monomeric aluminum[1] ($[Al_i]$) had a slope of approximately -1 when plotted as a function of pH. Sullivan and Cosby (1998) developed a series of empirical relationships that related total monomeric inorganic aluminum concentration to pH based on their analyses of different surface water datasets from the Adirondacks, Catskills, and Northern Appalachians. For the Adirondacks surface waters, these empirical relations are:

$$\log [Al_i] = 0.2 - 1.09 \text{ pH (spring sampling period)} \qquad (13)$$

and

$$\log [Al_i] = -1.3 - 0.81 \text{ pH (fall sampling period)} \qquad (14)$$

Holmberg et al. (2001) developed similar empirical equations to predict $[Al_i]$ as a function of pH in forest-floor and upper mineral soil horizons.

Sullivan and Cosby (1998) also observed that $\log [Al^{3+}]$ had a slope of about –2 when plotted as a function of pH. Based on this observation, Sullivan and Cosby (1998) recommended that applications of chemical models to Adirondacks watersheds use the following empirical relationship to describe gibbsite solubility as a function of pH:

$$\log [Al^{3+}] = \log K_{s0(emp)} - 2 \text{ pH} \qquad (15)$$

Depending on whether data from the Adirondacks spring or fall sampling period were used in their analysis, Sullivan and Cosby (1998) derived values of $\log K_{s0(emp)}$ equal to 5.8 and 4.0, respectively. Sullivan and Cosby (1998) used a value of $K_{s0(emp)}$ equal to 4.0 as being most representative of aluminum in the Bear Brook watershed and a value of 2.6 for the Risdalsheia watershed in Norway. In comparison, additional analyses by Sullivan and Cosby (1998) yielded values of $K_{s0(emp)}$ equal to 2.2 and 4.6, for Catskill and

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[1] $[Al_i] = [Al^{3+}] + [AlOH^{2+}] + [Al(OH)_2^+] + [Al(OH)_3^0] + [Al(OH)_4^-] + [AlSO_4^+] + [Al(SO4)_2^-] + [AlF^{2+}] + [AlF_2^+] + [AlF_3^0] + [AlF_4^-]$

Northern Appalachian streams, respectively. The MAGIC model was recently revised to allow more flexibility in modeling aluminum concentrations through the use of empirical relationships (e.g., equations 13 through 15 above) rather than solely relying on the theoretical equation for gibbsite solubility (Cosby et al. 2001).

Equation (15) is similar to equation (12) that describes the theoretical solubility of gibbsite as a function of pH with the difference of a slope of –2 with pH instead of –3. A slope of –2 with pH infers a non-stoichiometric reaction when compared to the reaction shown in equation (10). Hence, although the relationship shown in equation (15) more accurately predicts aluminum concentrations in Adirondacks watersheds, it should be noted that it is empirically derived and not based on theoretical thermodynamic relationships.

Based on the wide range of gibbsite solubility constants that have been reported in the literature (Table 3), it is recommended that equation (15) developed by Sullivan and Cosby (1998) specifically for Adirondacks watersheds be included in the PHREEQC thermodynamic database for geochemical modeling of groundwater and surface water with pH less than about 5.5. Above a pH of about 5.5, the theoretical solubility of natural gibbsite ($\log K_{s0} = 8.77$ at 25˚C) has generally been found to provide a better representation of aluminum concentrations (Cronan et al. 1986; de Wit et al. 2001; Driscoll et al. 1984; Lawrence et al. 1986; Walker et al. 1990). However, as concentrations of dissolved aluminum approach analytical determination limits with increasing pH, the resulting scatter in the analyzed aluminum concentrations can make discerning distinct trends in solubility data difficult at near-neutral pH values (Sullivan and Cosby, 1998).

2.5 Selected Data

The data selected for incorporation into the PHREEQC database are summarized in Table 4. These data are relevant to the soils and surface waters of the Adirondacks because they were generated based on fitting the MAGIC model to data obtained in the Adirondacks. These data are also internally consistent because they were generated using a triprotic organic acid analogue model.

2.6 Representative Solution Chemistry

To verify that the additions of thermodynamic constants to the PHREEQC database resulted in reasonable depictions of aqueous chemistry, a representative solution chemistry was developed (Table 5). A soil solution described by Rustad et al. (1996) had a relatively complete chemical description, so this composition was used as a starting point. However, the fluoride and DOC concentrations and carbon dioxide partial pressure were not provided, so these values were estimated as described in Table 5.

Table 4. Data selected for inclusion in the PHREEQC database

Organic Acid Model: $H^+ + H_2Orgacid^- = H_3Orgacid$ log $Ka_1 = 2.64$ $H^+ + HOrgacid^{2-} = H_2Orgacid^-$ log $Ka_2 = 5.66$ $H^+ + Orgacid^{3-} = HOrgacid^{2-}$ log $Ka_3 = 5.94$ Driscoll et al. (1994)
Organic Carbon Site Density: 4.6 µequivalents/mg DOC (0.055 mol sites/mole C) Driscoll et al. (1994)
Aluminum Complexation by Organic Anions: $Al^{3+} + Org^{3-} = AlOrg^0$ log K = 8.39 $Al^{3+} + H^+ + Org^{3-} = AlHOrg^+$ log K = 13.1 Schecher (1988), Schecher and Driscoll (1995)
Aluminum Solubility: $pH < 5.5$: $\log [Al^{3+}] = \log K_{s0(emp)} - 2\ pH$ Sullivan and Cosby (1998) $pH > 5.5$: $\log [Al^{3+}] = 8.77 - 3\ pH$ (25°C) Driscoll et al. (1984); Cronan et al. (1986)

Table 5. Solution composition used for verification tests of the phreeqc_tmdl.dat thermodynamic data

Constituent	Value	Reference
pH (s.u.)	5.5	Rustad et al. (1996), Table 3, Bear Brook, Maine
Ca (mg/L)	2.16	Rustad et al. (1996), Table 3, Bear Brook, Maine
Mg (mg/L)	0.12	Rustad et al. (1996), Table 3, Bear Brook, Maine
K (mg/L)	0.35	Rustad et al. (1996), Table 3, Bear Brook, Maine
Na (mg/L)	1.98	Rustad et al. (1996), Table 3, Bear Brook, Maine
Al (mg/L)	0.19	Rustad et al. (1996), Table 3, Bear Brook, Maine
NH_4 (mg/L)	0.018	Rustad et al. (1996), Table 3, Bear Brook, Maine
SO_4 (mg/L)	9.89	Rustad et al. (1996), Table 3, Bear Brook, Maine
NO_3 (mg/L)	0.68	Rustad et al. (1996), Table 3, Bear Brook, Maine
Cl (mg/L)	1.6	Rustad et al. (1996), Table 3, Bear Brook, Maine
F (mg/L)	0.04	Lawrence et al. (1986), RILWAS lake average
DOC (mg/L)	5	Kahl et al. (1989); Cronan et al. (1988)
log PCO_2(g) (atm)	-2.4	Norton et al. (2001), Bear Brook, Maine

3.0 PHREEQC DATABASE DEVELOPMENT

This section describes additions made to the thermodynamic data used by the PHREEQC geochemical model for forested watershed systems of the Adirondacks, based on the review presented in the preceding section. Tests that were carried out to verify the database additions are also described in this section.

3.1 PHREEQC Code and Database

PHREEQC is a computer program that is widely used to perform low-temperature geochemical speciation and reaction calculations (Parkhurst and Appelo, 1999). PHREEQC Version 2.8 is the most recent version available from the U. S. Geological Survey.[1] This version was used for all calculations and examples provided in this appendix.

The PHREEQC 2.8 package contains five different thermodynamic data files. For the purposes of this study, the "phreeqc.dat" thermodynamic data file was chosen as the starting database to which data were added. The phreeqc.dat data file was selected because it is the most compact and most thoroughly verified thermodynamic dataset for the major cationic and anionic species normally found in aqueous systems (Ball and Nordstrom, 1991; Nordstrom et al. 1990; Parkhurst et al. 1980). Additional data necessary for simulating important processes in forested watershed systems were added to the database, as described in the following subsections. This revised thermodynamic data file was renamed "phreeqc_tmdl.dat."

3.2 Dissolved Organic Acid Speciation

Based on the literature review, the constants developed by Driscoll et al. (1994) for dissolved organic acid speciation for the Adirondacks were selected as the most representative model of organic acids for this study (Table 4). Because a triprotic organic acid model was selected, an entry was made in the SOLUTION_MASTER_SPECIES list of in the phreeqc_tmdl.dat data file to define the organic acid as follows:

```
#element species        alk    gfw_formula     element_gfw
Orgacid  Orgacid-3      0.0     Orgacid          218.2
```

An entry was also made in the SOLUTION_SPECIES list of the phreeqc_tmdl.dat to complete the definition of Orgacid-3 as the master species for organic acid, i.e.,

```
Orgacid-3 = Orgacid-3
        log_k           0.000
```

This definition allows organic acid to be represented by the string "Orgacid" in other reactions defined in phreeqc_tmdl.dat.

---

[1] Available for download at http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html

Representations of the reactive functional groups associated with organic acids in soil chemical systems typically use an empirical relationship between the concentration of DOC and the site density of the organic acid to give the total concentration of active sites (Orgacid_T), i.e.,

$$\text{Orgacid}_T = m[\text{DOC}] \tag{16}$$

where m is the site density in moles of sites per moles of carbon (Section 2.2) and [DOC] is the concentration of DOC in moles per liter. However, in the PHREEQC nomenclature, concentrations are converted to mole equivalents using the gram formula weight (g/mol) defined for each dissolved species. To obtain a representative gram formula weight for "Orgacid," the site density of 0.055 mol sites/mol C derived by Driscoll et al. (1994) was used (Table 4). Using this value for the site density for organic acid, the representative gram formula weight for "Orgacid" for the entry in phreeqc_tmdl.dat was calculated as follows:

$$(12\text{ g C/mol C})(\text{mol C}/0.055\text{ mol sites}) = 218.2\text{ g C/mol sites} \tag{17}$$

The log K values for the triprotic organic acid model and reaction stoichiometries selected from the review described above and summarized in Table 5 are shown in Table 6, recast as protonation reactions. Typically, reactions in PHREEQC are defined as summed reactions, so the data from Driscoll et al. (1994) were recast as the summed protonation reactions as shown in Table 6 for reactions (D) through (F). Representation of reactions (D) through (F) in Table 6 were added to phreeqc_tmdl.dat in the SOLUTION_SPECIES section as the following blocks of data:

```
#HOrgAcid  from Driscoll et al. (1994) Water Res. Res. 30, 297-306.
        H+ + Orgacid-3 = HOrgacid-2
        log_k          5.94
        delta_h        0.0
#H2OrgAcid  from Driscoll et al. (1994) Water Res. Res. 30, 297-306.
        2H+ + Orgacid-3 = H2Orgacid-
        log_k          11.60
        delta_h         0.0
#H3OrgAcid  from Driscoll et al. (1994) Water Res. Res. 30, 297-306.
        3H+ + Orgacid-3 = H3Orgacid
        log_k          14.24
        delta_h         0.0
```

Note that lines starting with "#" are comments and not actual data used by PHREEQC. Data for the enthalpy of reaction (delta_h) or empirical measurements of the temperature dependence of the log K values were not available from Driscoll et al. (1994). Hence, values of 0.0 kcal/mol were used for delta_h.

An aqueous speciation calculation was conducted for "Orgacid" with PHREEQC using the added thermodynamic data to ensure that reasonable results were obtained and that mass was conserved. The PHREEQC calculations were performed to determine the

Table 6. Summary of Reactions and Log K Values for the Triprotic Organic Acid Model Used in PHREEQC

Reaction	Stoichiometry	Log K	Source
A	$H^+ + Orgacid^{3-} = HOrgacid^{2-}$	5.94	Driscoll et al. (1994)
B	$H^+ + HOrgacid^{2-} = H_2Orgacid^-$	5.66	Driscoll et al. (1994)
C	$H^+ + H_2Orgacid^- = H_3Orgacid$	2.64	Driscoll et al. (1994)
D	$H^+ + Orgacid^{-3} = HOrgacid^{-2}$	5.94	From reaction (1)
E	$2\ H^+ + Orgacid^{-3} = H_2Orgacid^-$	11.60	Sum of reaction (1) and (2)
F	$3\ H^+ + Orgacid^{-3} = H_3Orgacid$	14.24	Sum of reaction (3) and (5)

change in speciation as a function of pH using the soil solution composition given in Table 5.

The speciation results showed that mass was conserved, indicating no errors in entries for the reactions involving "Orgacid" in phreeqc_tmdl.dat. The results also show that $H_2Orgacid^-$, $HOrgacid^{-2}$, and $Orgacid^{-3}$ are the dominant ionic species in the slightly acidic to near-neutral pH range of 4.9 to 6.5 expected for most surface and soil solutions present in forested watersheds (Figure 1).

3.3 Aluminum-Organic Acid Complexation Constants

In their calibration of the triprotic organic acid model to Adirondacks lakes, Driscoll et al. (1994) accounted for the complexation of dissolved aluminum by organic acid using the two reactions listed in Table 4. To remain consistent with the adoption of the triprotic organic acid model of Driscoll et al. (1994) in this study, the above two reactions were incorporated into phreeqc_tmdl.dat with the following blocks in the section for SOLUTION_SPECIES:

```
#AlOrgacid from Schecher and Driscoll (1995) ALCHEMI; SSSA Special
Publication 42.
        Al+3 + Orgacid-3 = AlOrgacid
        log_k           8.38
        delta_h         0.0
#AlHOrgacid+ from Schecher and Driscoll (1995) ALCHEMI; SSSA Special
Publication 42.
        Al+3 + H+ + Orgacid-3 = AlHOrgacid+
        log_k           13.1
        delta_h         0.0
```

The results of a PHREEQC calculation of dissolved aluminum speciation as a function of pH using the added Al-Orgacid complexation data are shown in Figure 2 for the soil solution composition listed in Table 5. The results showed that mass was conserved in

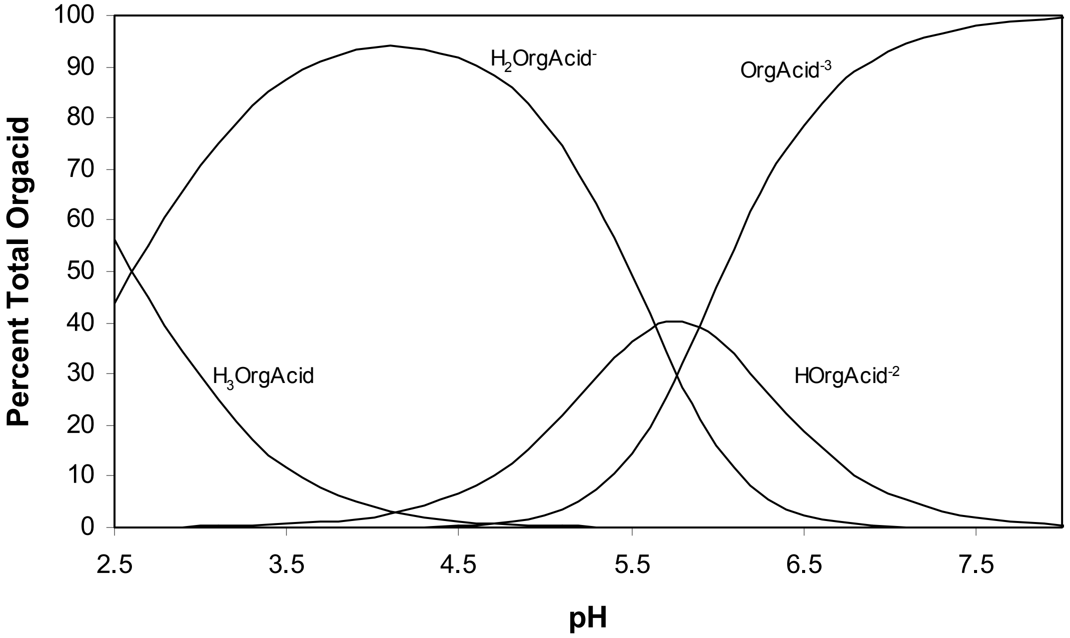

Figure 1. PHREEQC speciation results for triprotic "Orgacid."

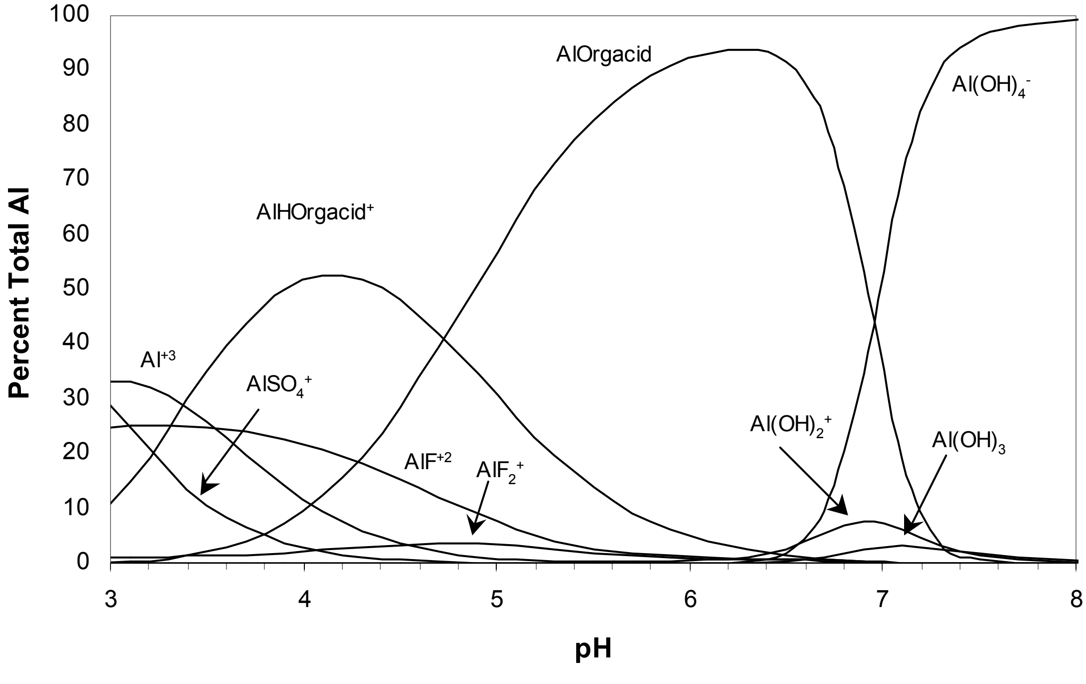

Figure 2. PHREEQC speciation results for dissolved aluminum. Species less than 1.0 % of total Al are not shown, including $AlOH^{2+}$, $Al(SO_4)_2^-$, $AlHSO_4^{2+}$, AlF_3^0, AlF_4^-, AlF_5^{2-}, and AlF_6^{3-}.

the calculations, indicating that the reactions were entered correctly. In addition, the results show the importance of including organic acid complexation of dissolved aluminum as indicated by the predominance of $AlHOrgacid^+$ and AlOrgacid under slightly acidic to near-neutral pH conditions expected for most forested watersheds.

3.4 Representation of Gibbsite Solubility

The review of relevant literature on gibbsite solubility (Section 2.4) indicates that Al^{+3} concentrations are best represented by an empirical relationship for waters with pH less than about 5.5 and by the theoretical solubility of natural gibbsite for higher pH conditions. To achieve this combined representation of gibbsite solubility with PHREEQC, a number of additions were made to the phreeqc_tmdl.dat database.

To represent the empirical relationship between $[Al^{+3}]$ and pH developed by Sullivan and Cosby (1998), a solid phase named Gibbsite(emp) was added to the "PHASES" section of phreeqc_tmdl.dat. To match the slope of –2 recommended by Sullivan and Cosby (1998) for the change in $[Al^{+3}]$ with pH (see equation 15), the solubility reaction for Gibbsite(emp) was written as:

$$Al(OH)_2^+(s) + 2\ H^+ = Al^{3+} + 2\ H_2O \qquad (18)$$

In equation (18), Gibbsite(emp) is represented by a solid with a charge of +1. Although a charged solid phase is theoretically impossible, writing the reaction in this way produces a slope of –2, as required by the empirical relationship of equation (15), while maintaining overall charge balance for the solubility reaction.

With Gibbsite(emp) solubility defined by equation (18), a series of PHREEQC calculations were carried out with the solution composition in Table 5 to adjust the value of log $K_{s0(emp)}$ iteratively until concentrations of total monomeric inorganic aluminum[1] $[Al_i]$ matched the empirical relationships developed by Sullivan and Cosby (1998) for data from the ELS(II) spring and fall sampling periods for Adirondacks surface waters (equations 13 and 14) for the pH range of 4.5 to 5.5 (Figure 3). The vast majority of Adirondacks surface waters have pH values greater than 4.5 (Sullivan and Cosby, 1998). The PHREEQC runs were made with the added reactions for organic acid dissociation and aluminum complexation by organic acids (Sections 3.2 and 3.3).

Based on visual comparison of the PHREEQC iterations to the ELS(II) data, a value of log $K_{s0(emp)} = 4.5$ was determined (Figure 3), yielding the following equation for Gibbsite(emp) solubility:

$$\log [Al^{3+}] = 4.5 - 2\ pH \qquad (19)$$

---

[1] $[Al_i] = [Al^{3+}] + [AlOH^{2+}] + [Al(OH)_2^+] + [Al(OH)_3^0] + [Al(OH)_4^-] + [AlSO_4^+] + [Al(SO4)_2^-] + [AlF^{2+}] + [AlF_2^+] + [AlF_3^0] + [AlF_4^-]$

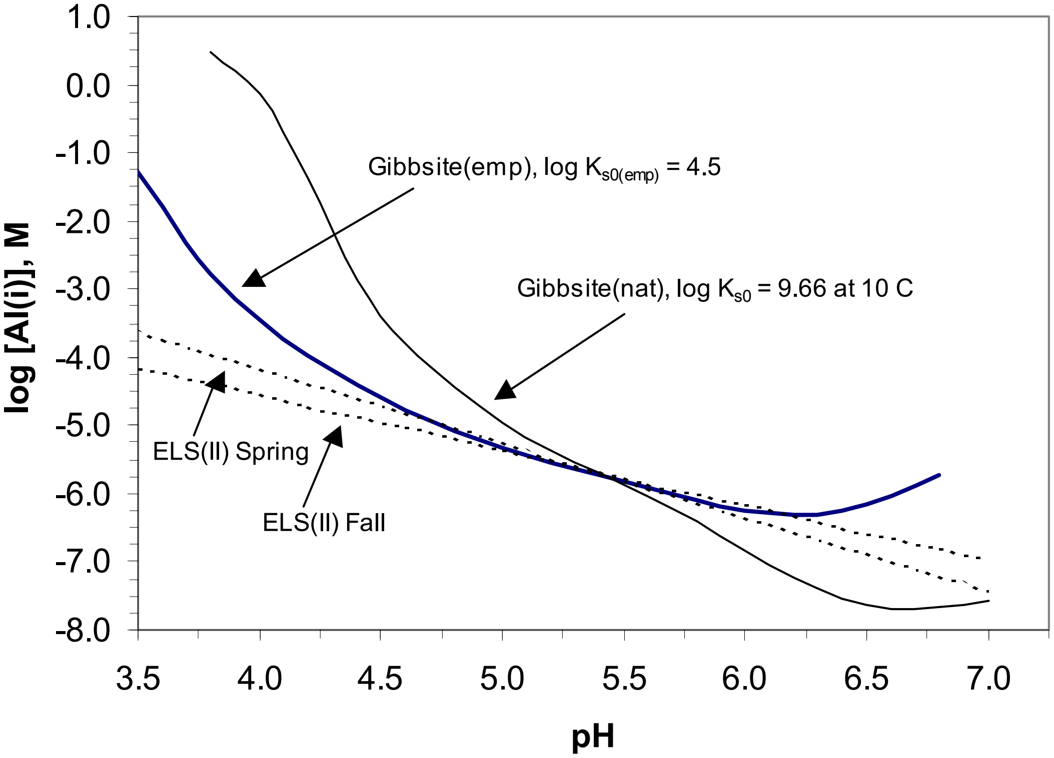

Figure 3. PHREEQC results for [Al_i] as a function of pH for Gibbsite(emp) and Gibbsite(nat) solubility compared to the empirical data of Sullivan and Cosby (1998) for Adirondacks surface waters for the ELS(II) spring and fall sampling periods

This final result was incorporated into phreeqc_tmdl.dat with the following entry in the PHASES section:

```
   Gibbsite(emp)
         Al(OH)2+ + 2H+ = Al+3 +  2H2O
         log_k        4.5
         delta_h      0.0 kcal
```

An enthalpy of reaction (delta_h) of 0.0 is used for Gibbsite(emp) because it is assumed that the empirical relationships of Sullivan and Cosby (1998) are relevant to the ambient temperatures (≈ 10˚C) of the surface waters when samples were collected.

In addition to the entry made for Gibbsite(emp) in phreeqc_tmdl.dat, other potentially relevant aluminum hydroxides phases were added to provide a complete set of the predominant phases generally used in modeling studies. These include natural gibbsite [Gibbsite(nat)], synthetic gibbsite [Gibbsite(syn)], microcrystalline gibbsite [Gibbsite(uc)], and amorphous aluminum trihydroxide [$Al(OH)_3$(am)]. The complete set of phases added to phreeqc_tmdl.dat is shown below:

```
#Gibbsite(emp) from empirical data of Sullivan and Cosby (1998) ELS(II)
#Adirondack waters
```

```
Gibbsite(emp)
         Al(OH)2+ + 2H+ = Al+3 +  2H2O
         log_k       4.5
         delta_h     0.0 kcal
#Gibbsite(syn) from May et al. 1979
Gibbsite(syn)
        Al(OH)3 + 3 H+ = Al+3 + 3 H2O
        log_k           8.110
        delta_h -22.800 kcal
#Gibbsite(nat) from May et al. 1979
Gibbsite(nat)
        Al(OH)3 + 3 H+ = Al+3 + 3 H2O
        log_k           8.770
        delta_h -22.800 kcal
#Gibbsite(uc) from Hem et al. 1973
Gibbsite(uc)
        Al(OH)3 + 3 H+ = Al+3 + 3 H2O
        log_k           9.35
        delta_h -22.800 kcal
#Al(OH)3(a) from Stumm and Morgan (1981)
Al(OH)3(a)
        Al(OH)3 + 3 H+ = Al+3 + 3 H2O
        log_k           10.800
        delta_h -26.500 kcal
```

A PHREEQC calculation was conducted to define the solubility of natural gibbsite [Gibbsite(nat)] as a function of pH and to locate the intersection of its solubility curve with the solubility curve for Gibbsite(emp). The solubility of Gibbsite(nat) is described by equations (10) through (12). At 25˚C, log K_{s0} equals 8.77 for Gibbsite(nat); however according to PHREEQC, log K_{s0} equals 9.66 for Gibbsite(nat) at 10˚C. At a temperature of 10˚C, a comparison of the two solubility curves shows that Gibbsite(nat) is the less soluble phase at pH values greater than 5.5 (Figure 3). This result is consistent with information in the literature reviewed in Section 2.4.

In practical terms for PHREEQC input, the combined solubility controls for gibbsite can be applied to modeling efforts through the use of an entry block for “EQUILIBRIUM_PHASES” where phases expected to be equilibrium are defined. For equilibrium with Gibbsite(emp) and Gibbsite(nat), an example of this block in a PHREEQC input file would be:

```
EQUILIBRIUM_PHASES 1
       Gibbsite(emp) 0.0    0.0
       Gibbsite(nat) 0.0    0.0
```

In the above block, the first “0.0” fixes the saturation index for Gibbsite(emp) and Gibbsite(nat) at 0.0 or exactly at equilibrium if aluminum concentrations reach a level high enough to achieve saturation. The second “0.0” indicates that there is no initial amount of Gibbsite(emp) or Gibbsite(nat)present in the system.

3.5 Calculation of ANC from PHREEQC Results

Output from a PHREEQC calculation typically includes a calculated alkalinity. For most aqueous systems, this alkalinity is generally comprised primarily of carbonate alkalinity and is not directly comparable to the Acid Neutralizing Capacity (ANC) that is typically used to characterize the acid buffering capacity of the dilute waters present in forested watersheds of the Adirondacks. Laboratory determinations of ANC involve a Gran titration (ANC_G) to a pH endpoint generally between 4.8 and 5.2. A consideration of the aqueous species that would be present at the pH endpoint range yields an operational definition of ANC_G as (Driscoll et al. 1994):

$$\begin{aligned} ANC_G = {} & [HCO_3^-] + 2[CO_3^{2-}] + [Al(OH)_2^+] + 3[Al(OH)_4^-] + [HOrgacid^{2-}] \\ & + 2[Orgacid^{3-}] + [AlOrgacid] + [OH^-] - [H^+] \end{aligned} \tag{20}$$

To be consistent with this operational definition of ANC, equation (20) should be used to represent the results of PHREEQC calculations of solution chemistry.

There are at least two available options for using PHREEQC to output the values relevant to $ANC_{G.}$ The first is to use the SELECTED_OUPUT option of a PHREEQC input file to specify that the various species in the above equation be sent to a tab-delimited file named SampleANC.sel with an input block like:

```
SELECTED_OUTPUT
        -file SampleANC.sel
        -molalities HCO3- CO3-2 AlOH+2 Al(OH)4- HOrgacid-2
                    Orgacid-3 AlOrgacid OH- H+
```

The data from this output option in SampleANC.sel can be imported into a spreadsheet to calculate ANC_G according to the equation (20).

The second option for using PHREEQC to calculate ANC_G is to use the programmable options in a PHREEQC input file to calculate the ANC_G directly and output the data to a file. This method requires the use of a USER_PUNCH block with an embedded section of Basic code to calculate ANC_G from equation (20), e.g.:

```
USER_PUNCH
-start
-head pH ANC
  10 ANC1 = MOL("HCO3-") + 2*MOL("CO3-2") + MOL("AlOH+2") + 3*MOL("Al(OH)4-")
  20  ANC2 = ANC1 + MOL("HOrgacid-2") + 2*MOL("Orgacid-3") + MOL("AlOrgacid")
  30  ANC3 = ANC2 + MOL("OH-") - MOL("H+")
  40  PUNCH LA("H+"), ANC3
-end
SELECTED_OUTPUT
        -file SampleANC.sel
        -reset true
```

This method produces a list of pH and ANC_G in a tab-delimited file named SampleANC.sel.

4.0 SUMMARY AND CONCLUSIONS

The thermodynamic databases provided with the PHREEQC geochemical model do not contain data for some reactions that are important for representing the aqueous chemistry in Adirondacks watersheds. Therefore, a review of the literature was carried out to summarize the available thermodynamic data and to identify data that are most applicable to modeling the chemistry of groundwater and surface water in Adirondacks watersheds.

The reactions identified for addition to the PHREEQC database were organic acid speciation, complexation of aluminum by organic acid species, and the solubility of aluminum solids. Thermodynamic data for these reactions were selected based on their applicability to the Adirondack region. The selected data were incorporated into the PHREEQC database, and a series of modeling calculations were performed to verify that the reactions were correctly included in the database. Methods for using PHREEQC to calculate the acid neutralizing capacity of the modeled solution were also identified and tested. A summary of the modifications made to the thermodynamic database is provided in Appendix I and the input files used in the calculations in this appendix are included as Appendix II.

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Appendix I

Thermodynamic Data Added to PHREEQC Database

Thermodynamic data for simulating important processes in forested watershed systems were added to the phreeqc.dat database to create the phreeqc_tmdl.dat database. The additions to the database are summarized below for each data section (SOLUTION_MASTER_SPECIES, SOLUTION_SPECIES, and PHASES).

SOLUTION_MASTER_SPECIES

```
#element species        alk    gfw_formula     element_gfw
Orgacid  Orgacid-3      0.0     Orgacid          218.2
```

SOLUTION_SPECIES

```
Orgacid-3 = Orgacid-3
        log_k           0.000
#HOrgAcid  from Driscoll et al. (1994) Water Res. Res. 30, 297-306.
        H+ + Orgacid-3 = HOrgacid-2
        log_k           5.94
        delta_h         0.0
#H2OrgAcid  from Driscoll et al. (1994) Water Res. Res. 30, 297-306.
        2H+ + Orgacid-3 = H2Orgacid-
        log_k           11.60
        delta_h          0.0
#H3OrgAcid  from Driscoll et al. (1994) Water Res. Res. 30, 297-306.
        3H+ + Orgacid-3 = H3Orgacid
        log_k           14.24
        delta_h          0.0
#AlOrgacid from Schecher and Driscoll (1995) ALCHEMI; SSSA Special
Publication 42.
        Al+3 + Orgacid-3 = AlOrgacid
        log_k            8.38
        delta_h          0.0
#AlHOrgacid+ from Schecher and Driscoll (1995) ALCHEMI; SSSA Special
Publication 42.
        Al+3 + H+ + Orgacid-3 = AlHOrgacid+
        log_k            13.1
        delta_h          0.0
```

PHASES

```
#Gibbsite(emp) from empirical data of Sullivan and Cosby (1998) ELS(II)
#Adirondack waters
Gibbsite(emp)
         Al(OH)2+ + 2H+ = Al+3 +  2H2O
         log_k       4.5
         delta_h     0.0 kcal
#Gibbsite(syn) from May et al. 1979
Gibbsite(syn)
        Al(OH)3 + 3 H+ = Al+3 + 3 H2O
        log_k           8.110
        delta_h -22.800 kcal
```

```
#Gibbsite(nat) from May et al. 1979
Gibbsite(nat)
        Al(OH)3 + 3 H+ = Al+3 + 3 H2O
        log_k           8.770
        delta_h -22.800 kcal
#Gibbsite(uc) from Hem et al. 1973
Gibbsite(uc)
        Al(OH)3 + 3 H+ = Al+3 + 3 H2O
        log_k           9.35
        delta_h -22.800 kcal
#Al(OH)3(a) from Stumm and Morgan (1981)
Al(OH)3(a)
        Al(OH)3 + 3 H+ = Al+3 + 3 H2O
        log_k           10.800
        delta_h -26.500 kcal
```

Appendix II

PHREEQC Input Files

File: OrgAcidSpeciation.inp used for calculating speciation of “Orgacid” for Figure 1.

```
TITLE Triprotic organic acid test input file.
#Bear Brook Bs Horizon soil solution chemistry from Rustad et. al. (1996),
# Soil Sci Soc Am J 60:1933-1943, Table 3.
# Orgacid conc of 5 mg/L selected as generalized average
# F estimated from Hubbard Brook (Lawrence et al. 1986;
#  Schecher and Driscoll, 1988(RILWAS Lakes))
#  PCO2(g)=10**-2.4 atm or 0.4% taken from Norton et al. 2001 from
#  estimated average measured in B-horizon soils at Bear Brook.
SOLUTION 1
        -units  mg/L
        temp   10.0
        pH      5.5
        Ca      2.16
        Mg      0.12
        K      0.35
        Na      1.98
        N(-3)   0.018 as NH4
        S(6)    9.89 as SO4 charge
        N(5)    0.68 as NO3
        Cl      1.60
        F       0.04
        Orgacid 5.0
#Define a fixed-pH phase for speciation calculation as function of pH
PHASES
        Fix_H+
        H+ = H+
        log_k  0.0
END
#Define an output file for speciation results
SELECTED_OUTPUT
        -file OrgAcidSpeciation.sel
        -molalities Orgacid-3 HOrgacid-2 H2Orgacid- H3Orgacid
KNOBS
    -iterations 150
    -step_size    5
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -2.50   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -2.70   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -2.9   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -3.1   H2SO4    10.0
        CO2(g)   -2.4    1.0
```

```
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -3.3   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -3.5   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -3.7   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -3.9   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -4.1   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -4.3   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -4.5   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -4.7  H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -4.9   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -5.1  H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -5.3   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
```

```
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -5.5   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -5.7   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -5.9   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -6.1   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -6.3   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -6.5   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -6.7   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -6.9   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -7.1   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -7.3   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -7.5   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
```

```
EQUILIBRIUM_PHASES 1
       Fix_H+   -7.7   NaOH    10.0
       CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
       Fix_H+   -7.9   NaOH    10.0
       CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
       Fix_H+   -8.1   NaOH    10.0
       CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
       Fix_H+   -8.3   NaOH    10.0
       CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
       Fix_H+   -8.5   NaOH    10.0
       CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
       Fix_H+   -8.7   NaOH    10.0
       CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
       Fix_H+   -8.9   NaOH    10.0
       CO2(g)   -2.4    1.0
END
```

File: AlSpeciationInput.inp used for calculating speciation of aluminum for Figure 2.

```
TITLE Aluminum speciation test input file.
#Bear Brook Bs Horizon soil solution chemistry from Rustad et. al. (1996),
# Soil Sci Soc Am J 60:1933-1943, Table 3.
# Orgacid conc of 5 mg/L selected as generalized average
# F estimated from Hubbard Brook (Lawrence et al. 1986;
#   Schecher and Driscoll, 1988(RILWAS Lakes))
#  PCO2(g)=10**-2.4 atm or 0.4% taken from Norton et al. 2001 from
#  estimated average measured in B-horizon soils at Near Brook although
#  PCO2(g) has no real effect on organic acid speciation and is only
#  entered here to complete the soil solution chemical composition.
SOLUTION 1
        -units  mg/L
        temp   10.0
        pH      5.5
        Ca      2.16
        Mg      0.12
        K       0.35
        Na      1.98
        N(-3)   0.018 as NH4
        Al      0.19
        S(6)    9.89 as SO4 charge
        N(5)    0.68 as NO3
        Cl      1.60
        F       0.04
        Orgacid 5.0
# Defined fixed pH phase
PHASES
        Fix_H+
        H+ = H+
        log_k  0.0
END
#Define an output file for speciation results
SELECTED_OUTPUT
        -file AlSpeciation.sel
        -molalities Al+3 AlOH+2 Al(OH)2+ Al(OH)3 Al(OH)4-
                    AlSO4+ Al(SO4)2- AlHSO4+2
                    AlOrgacid AlHOrgacid+
                    AlF+2 AlF2+ AlF3 AlF4- AlF5-2 AlF6-3
KNOBS
    -iterations 150
    -step_size    5
EQUILIBRIUM_PHASES 1
        Fix_H+   -2.50   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -2.70   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -2.9   H2SO4    10.0
        CO2(g)   -2.4    1.0
```

```
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -3.1   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -3.3   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -3.5   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -3.7   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -3.9   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -4.1   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -4.3   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -4.5   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -4.7  H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -4.9   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -5.1  H2SO4    10.0
        CO2(g)   -2.4    1.0
END
```

```
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -5.3   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -5.5   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -5.7   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -5.9   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -6.1   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -6.3   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -6.5   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -6.7   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -6.9   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -7.1   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -7.3   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
```

```
EQUILIBRIUM_PHASES 1
        Fix_H+   -7.5   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -7.7   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -7.9   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -8.1   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -8.3   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -8.5   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -8.7   NaOH    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -8.9   NaOH    10.0
        CO2(g)   -2.4    1.0
END
```

File: al(OH)2Plus.inp used for calculating the solubility of gibbsite(emp) [$Al(OH)_2^+(s)$] for Figure 3.

```
TITLE Solubility calculation for Gibbsite(emp)
# Gibbsite(emp) = Al(OH)2+(s) empirical solid
SOLUTION 1
        -units  mg/L
        temp   10.0
        pH      5.5
        Ca      2.16
        Mg      0.12
        K      0.35
        Na      1.98
        N(-3)   0.018 as NH4
        S(6)    9.89 as SO4 charge
        N(5)    0.68 as NO3
        Cl      1.60
        F      0.04
        Orgacid 5.0
# Defined fixed pH phase
PHASES
      Fix_H+
        H+ = H+
        log_k  0.0
END
USER_PUNCH
-start
-head pH log10(Al(i)) log10(Al+3)
10  Ali_1 = MOL("Al+3") + MOL("AlOH+2") + MOL("Al(OH)2+") + MOL("Al(OH)3")
20  Ali_2 = Ali_1 + MOL("Al(OH)4-") + MOL("AlSO4+") + MOL("Al(SO4)2-")
30  Ali_3 = Ali_2 + MOL("AlF+2") + MOL("AlF2") + MOL("AlF3") + MOL("AlF4-")
40  PUNCH -LA("H+"), log10(Ali_3), log10(MOL("Al+3"))
-end
SELECTED_OUTPUT
        -file al(OH)2plus.sel
        -reset true
KNOBS
     -iterations 150
     -step_size    5
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -3.4   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -3.6   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -3.8   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
```

```
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -4.0  H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -4.2  H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -4.4   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -4.6   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -4.8   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -5.0   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -5.2   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -5.4   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -5.6   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
```

```
        Fix_H+      -5.8   H2SO4    10.0
        CO2(g)      -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+      -6.0   H2SO4    10.0
        CO2(g)      -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+      -6.2   NaOH    10.0
        CO2(g)      -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+      -6.4   NaOH    10.0
        CO2(g)      -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+      -6.6   NaOH    10.0
        CO2(g)      -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+      -6.8   NaOH    10.0
        CO2(g)      -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+      -7.0   NaOH    10.0
        CO2(g)      -2.4   1.0
        Gibbsite(emp) 0.0   1.0
END
```

File: gibbsiteNat.inp used for calculating the solubility of gibbsite(nat) [$Al(OH)_3(s)$] for Figure 3.

```
TITLE Solubility calculation for Gibbsite(nat)
# Gibbsite(nat) = Al(OH)3(s)
SOLUTION 1
        -units  mg/L
        temp   10.0
        pH      5.5
        Ca      2.16
        Mg      0.12
        K      0.35
        Na      1.98
        N(-3)   0.018 as NH4
        S(6)    9.89 as SO4 charge
        N(5)    0.68 as NO3
        Cl      1.60
        F      0.04
        Orgacid 5.0
# Defined fixed pH phase
PHASES
      Fix_H+
        H+ = H+
        log_k  0.0
END
USER_PUNCH
-start
-head pH log10(Al(i))
10  Ali_1 = MOL("Al+3") + MOL("AlOH+2") + MOL("Al(OH)2+") + MOL("Al(OH)3")
20  Ali_2 = Ali_1 + MOL("Al(OH)4-") + MOL("AlSO4+") + MOL("Al(SO4)2-")
30  Ali_3 = Ali_2 + MOL("AlF+2") + MOL("AlF2") + MOL("AlF3") + MOL("AlF4-")
40  PUNCH -LA("H+"), log10(Ali_3)
-end
SELECTED_OUTPUT
        -file gibbsiteNat.sel
        -reset true
KNOBS
     -iterations 150
     -step_size    5
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -3.8   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(nat) 0.0   10.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -4.0  H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(nat) 0.0   10.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -4.2  H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(nat) 0.0   10.0
END
```

```
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -4.4   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(nat) 0.0   10.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -4.6   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(nat) 0.0   10.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -4.8   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(nat) 0.0   10.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -5.0   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(nat) 0.0   10.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -5.2   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(nat) 0.0   10.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -5.4   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(nat) 0.0   10.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -5.6   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(nat) 0.0   10.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -5.8   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(nat) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+       -6.0   H2SO4    10.0
        CO2(g)       -2.4   1.0
        Gibbsite(nat) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
```

```
	Fix_H+      -6.2   NaOH    10.0
	CO2(g)      -2.4   1.0
	Gibbsite(nat) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
	Fix_H+      -6.4   NaOH    10.0
	CO2(g)      -2.4   1.0
	Gibbsite(nat) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
	Fix_H+      -6.6   NaOH    10.0
	CO2(g)      -2.4   1.0
	Gibbsite(nat) 0.0   1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
	Fix_H+      -6.8   NaOH    10.0
	CO2(g)      -2.4   1.0
	Gibbsite(nat) 0.0   1.0
END

USE solution 1
EQUILIBRIUM_PHASES 1
	Fix_H+      -7.0   NaOH    10.0
	CO2(g)      -2.4   1.0
	Gibbsite(nat) 0.0   1.0
END
```

File: SampleANC.inp example of the use of USER_PUNCH and PHREEQC’s Basic interpreter code for calculating ANC according to Driscoll et al. 1994.

```
TITLE Example input file for calculating ANC with USER_PUNCH.
# ANC equation from Driscoll et al. 1994.
#Bear Brook Bs Horizon soil solution chemistry from Rustad et. al. (1996),
# Soil Sci Soc Am J 60:1933-1943, Table 3.
# Orgacid conc of 5 mg/L selected as generalized average
# F estimated from Hubbard Brook (Lawrence et al. 1986;
#   Schecher and Driscoll, 1988(RILWAS Lakes))
#  PCO2(g)=10**-2.4 atm or 0.4% taken from Norton et al. 2001 from
#  estimated average measured in B-horizon soils at Near Brook although
#  PCO2(g) has no real effect on organic acid speciation and is only
#  entered here to complete the soil solution chemical composition.
SOLUTION 1
        -units  mg/L
        temp   10.0
        pH      5.5
        Ca      2.16
        Mg       0.12
        K       0.35
        Na      1.98
        N(-3)   0.018 as NH4
        Al      0.19
        S(6)    9.89 as SO4 charge
        N(5)    0.68 as NO3
        Cl      1.60
        F       0.04
        Orgacid 5.0
# Defined fixed pH phase
PHASES
        Fix_H+
        H+ = H+
        log_k  0.0
END
USER_PUNCH
-start
-head pH ANC
10  ANC1 = MOL("HCO3-") + 2*MOL("CO3-2") + MOL("AlOH+2") + 3*MOL("Al(OH)4-")
20  ANC2 = ANC1 + MOL("HOrgacid-2") + 2*MOL("Orgacid-3") + MOL("AlOrgacid") + MOL("OH-
")
30  ANC3 = ANC2 - MOL("H+")
40  PUNCH -LA("H+"), ANC3
-end
SELECTED_OUTPUT
        -file SampleANC.sel
        -reset true
KNOBS
     -iterations 150
     -step_size    5
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -4.0   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
```

```
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -5.0   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -6.0   H2SO4    10.0
        CO2(g)   -2.4    1.0
END
USE solution 1
EQUILIBRIUM_PHASES 1
        Fix_H+   -7.0   NaOH    10.0
        CO2(g)   -2.4    1.0
END
```

Appendix F

Hydrology Data and Methods

Appendix F: Hydrology Data and Methods

This appendix describes the hydrology of the simulated watershed-lake system. An overview of the method and key assumptions are given first, followed by more detail on the methods and results.

F.1 Overview

Hydrology in each watershed was simulated as a system of soil and shallow groundwater, deep groundwater, and a lake (Figure F.1). The PNNL Watershed Model (PWM) was run at a daily timestep for water year 1952, a representative year selected from the period of record for available meteorology data (see Section F.2.1 for more detail on meteorology input to the model.) For each day in the year, the water cycle was simulated as precipitation falling on the land surface and lake, evaporation from canopy interception, evapotranspiration (ET) from soil, surface runoff to the lake, shallow groundwater flow to the lake, percolation from shallow to deep groundwater, deep groundwater flow to the lake, and outflow from the lake. Precipitation and evapotranspiration fluxes were estimated by the meteorology input, simulated available soil moisture, and the ET relationship used in PWM. Outflow from the lake was adjusted to maintain a constant lake volume at all times. All other fluxes in the model were governed by the storage-discharge relationships in PWM.

Hydrologic characteristics of a sample watershed, Donut Pond, are listed in Table F.1 along with the extreme values for each metric and the corresponding watershed ID. Watershed size metrics ranged over 2 orders of magnitude. Lake depth and residence time ranged over 1 and 3 orders of magnitude, respectively.

For Donut Pond, fluxes to and from the soil/shallow groundwater store were the most variable (Figure F.2). Precipitation was greatest in November and July, and shallow groundwater flow to the lake was greatest during April due to snowmelt. Percolation down to the deep groundwater store followed the trend of shallow groundwater flow but was less variable. Deep groundwater flow to the lake was nearly constant. Quick runoff, modeled as overland flow from rocky areas and as overflow from non-primary lakes in the same watershed as the primary lake, made a significant contribution to lake inflows during all months of the year, but especially during April and July.

The Donut Pond storage volumes were greatest in deep groundwater and least in shallow groundwater, and the lake volume was several times that of shallow groundwater (Figure F.3). On a percentage basis, the shallow groundwater storage fluctuated the most, while deep groundwater storage was nearly constant, and the lake storage was assumed constant.

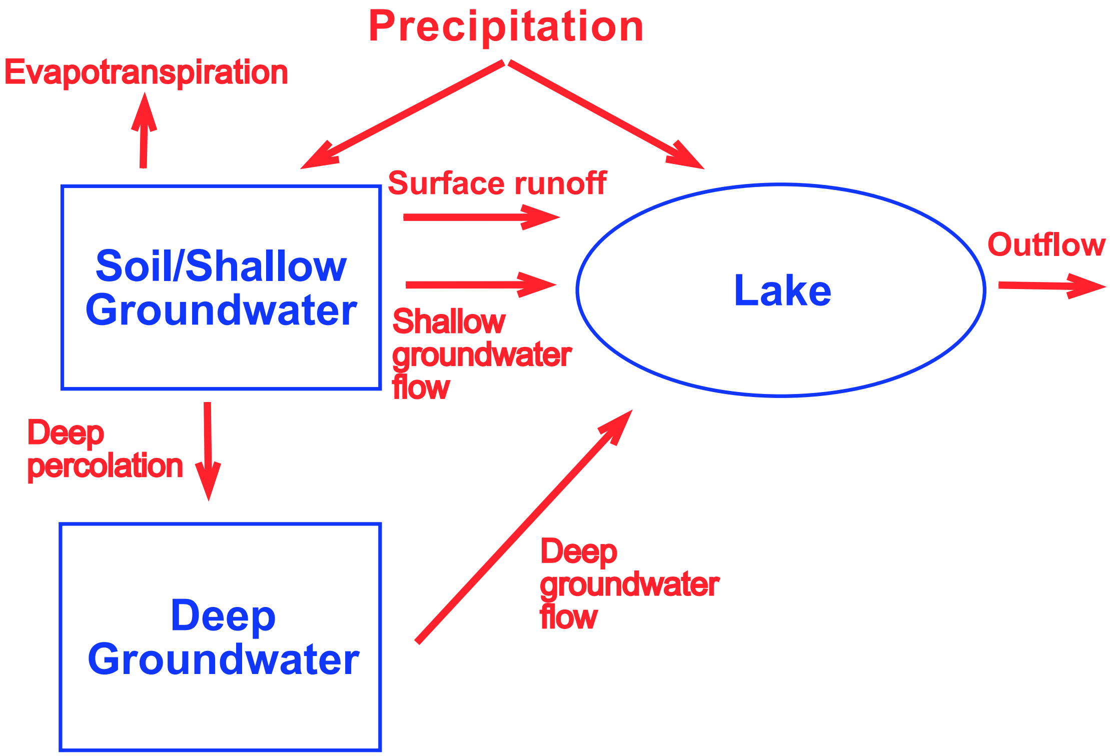

Figure F.1. Hydrology model flowchart. State variables (water storage terms) are in blue, fluxes are in red.

Table F.1. Hydrologic characteristics of watersheds. Values are listed for Donut Pond (WS ID=70), sample watershed, and for the extreme cases.

Characteristic	Donut Pond (70)	Minimum Value	Minimum WS ID	Maximum Value	Maximum WS ID
Total watershed area(a) (km^2)	0.71	0.029	127	27.1	41
Runoff area(b) (km^2)	0.66	0.02	127	26.8	41
Lake area(c) (km^2)	0.047	0.001	32	0.5	137
Lake depth (m)	3.49	0.8	32	8.3	137
Watershed/Lake area ratio(d)	14.12	2.4	127	1988	32
Thin soil fraction of watershed area	0.08	0.01	13	0.36	142
Deep soil fraction of watershed area	0.85	0.63	32	0.99	64
Direct runoff fraction of watershed area	0.07	0	3	0.34	32
Direct runoff fraction of lake inflow	0.17	0.02	90	0.52	66
Shallow groundwater fraction of lake inflow	0.35	0.19	66	0.46	142
Deep groundwater fraction of lake inflow	0.48	0.29	66	0.58	90
Lake residence time (weeks)	11	0.1 days	32	106	128

(a) Total watershed area includes the primary lake.
(b) Runoff area is all watershed area other than primary lake.
(c) Lake area refers to primary lake, the water body at the bottom of the watershed that is being modeled.
(d) Ratio = (land + non-primary lake area)/primary lake area.

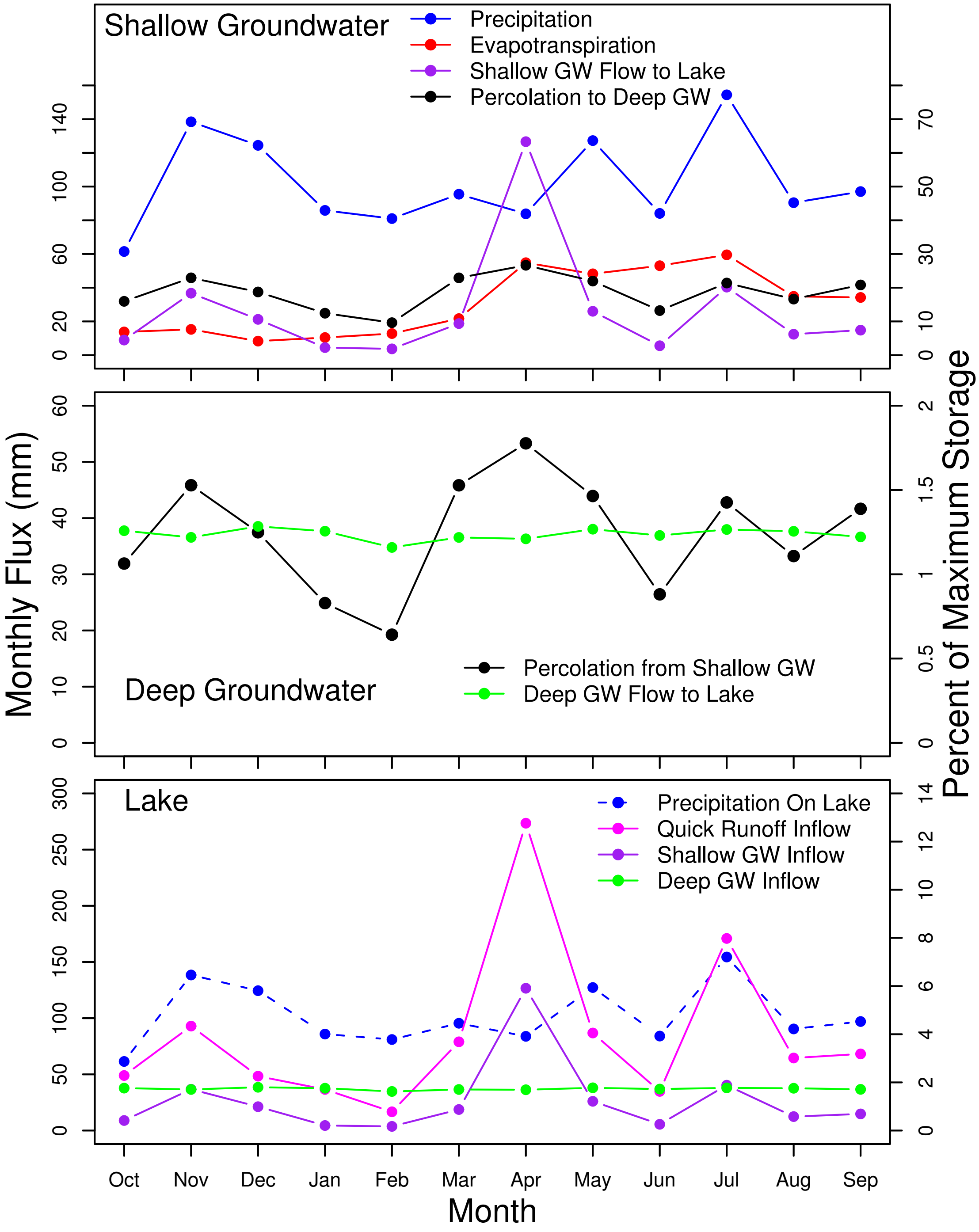

Figure F.2. Mean monthly fluxes for Donut Pond, a sample watershed. Fluxes relevant to each water compartment are shown. For the lake, inflows are scaled to units of depth per lake area.

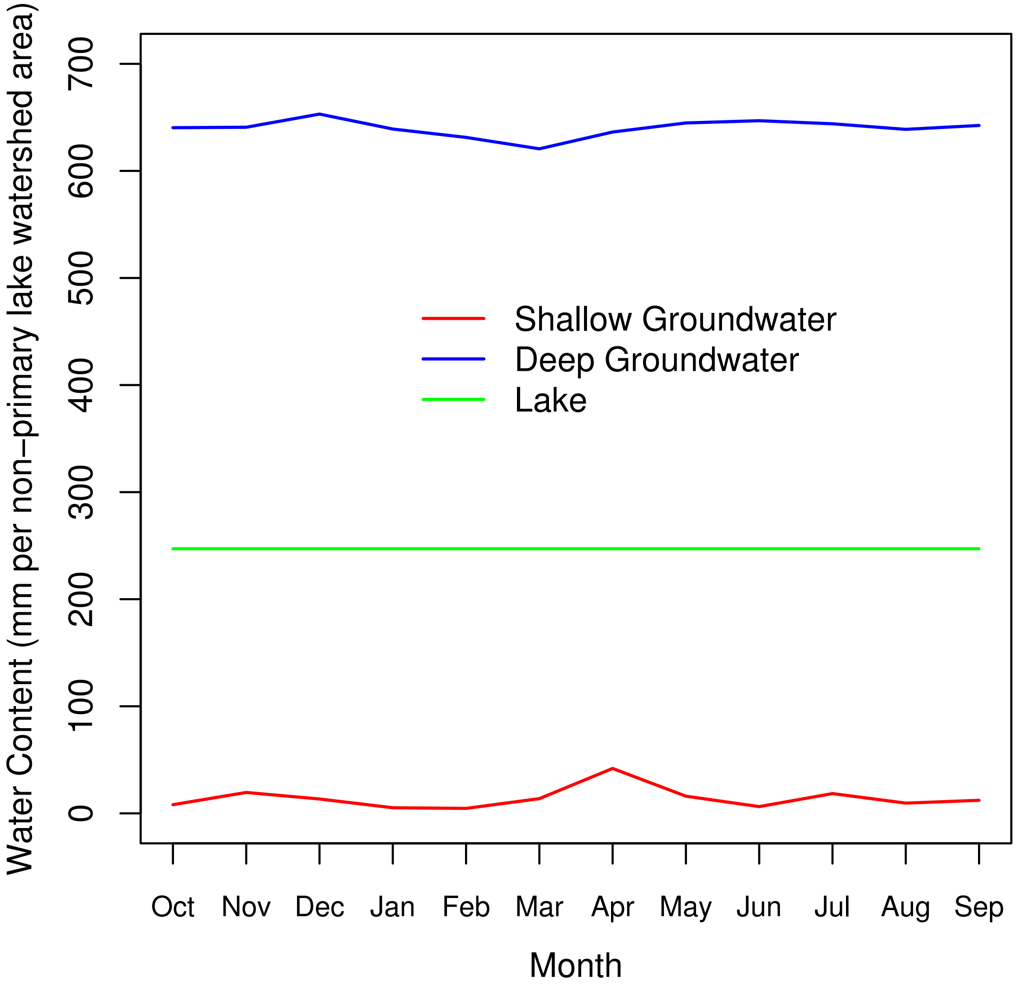

Figure F.3. Mean monthly storage volumes for Donut Pond, a sample watershed. Volumes are given as depth per watershed (non-primary lake) area.

F.2 Methods

The first step in simulating Adirondacks hydrology was to identify locations that were representative of regional conditions and which had meteorology, streamflow, and snowpack data that could be used to characterize actual hydrology, provide input to the model, and provide a verification dataset with which to compare model output. Two watersheds were identified as having the necessary data and being characteristic of thin soil and thick soil basins, respectively: Woods Lake and Panther Lake (Church and others, 1989). Four meteorology stations were selected from the region for their long periods of record and proximity to the above watersheds: Stillwater Reservoir, Old Forge, Indian Lake 2 SW, and Wanakena Ranger School. Details of the selected watersheds and meteorology stations are listed in Table F.2.

After identifying suitable locations for testing the model, the next step was to develop the meteorology input for PWM. Subsequent steps involved acquisition and processing of streamflow and snowpack data and an approximate calibration of PWM to these data. From the decades-long meteorology that was developed, a single representative year was selected and cycled as necessary to generate a dynamic steady-state hydrology. PWM was run for two generic hillslope cases, thin till and thick till, with daily hydrologic state and flux variables as the output. A third hillslope case was developed without modeling to represent the direct runoff that occurs from rocky areas and water bodies other than the primary lake. The direct runoff daily hydrology consisted of the precipitation record as the quick runoff component, and zero-valued infiltration, groundwater flow, and evapotranspiration.

The twelve original land cover classes from the GIS analysis were consolidated into the three hillslope types used in the hydrologic modeling: thin soil area, deep soil area, and direct runoff area. Then for the geochemical modeling, inflows to the lake were computed from direct precipitation on the lake and each hillslope type's contribution of quick runoff, shallow groundwater flow, and deep groundwater flow, weighted by the proportional area of the thin soil, thick soil, and direct runoff land classes. The year-long watershed hydrology was recycled as many times as necessary for each watershed to generate a dynamic steady-state geochemistry in the lake over the course of the year.

F.2.1 Meteorology

Data from the four meteorology stations listed in Table F.2 were obtained in the National Climate Data Center (NCDC). All station records included the three variables necessary to drive PWM: daily precipitation (P), daily minimum temperature (T_{min}), and daily maximum temperature (T_{max}). Because the hydrology model requires a complete meteorology input with no missing records, three methods to fill in missing data were developed and tested: 1) categorical means based on a missing day's precipitation status (wet/dry) and its month; 2) regression model to predict the missing value at a station from the values at the other stations; and 3) autocorrelation model to predict the missing value from data at that station alone.

In the categorical means method (1), monthly means of daily P served as the predictors of missing precipitation: $\hat{P}[\text{month}] \Rightarrow 12$ predictors. For air temperature, wet day and dry day means

Table F.2. Test watersheds and meteorology stations. Sources: Church and others (1989) and USGS (http://waterdata.usgs.gov).

Characteristic	Woods Lake	Panther Lake	Stillwater Reservoir	Old Forge	Indian Lake 2 SW	Wanakena Ranger School
Type of station	Stream gage	Stream gage	Met	Met	Met	Met
Near	Stillwater Res.	Old Forge	Woods Lake	Panther Lake	Nate Pond	
Station #	04256845	04253275	8248	6184	4102	8944
Latitude	43° 51' 56"	43° 41' 5"	43° 52' 59"	43° 42' 4"	43° 45' 0"	44° 9' 0"
Longitude	74° 57' 19"	74° 55' 8"	75° 1' 59"	74° 59' 6"	74° 16' 59"	74° 54' 0"
Elevation (ft)	1980	1650	1690	1720	1660	1510
Period of record	WY78-92	WY78-81	WY49-97	WY49-97	WY49-97	WY27-97
Till thickness (m)	2.3	24.5				
Drainage area (km^2)	2.1	1.2				
Mean annual precip (mm)			1198	1247	1008	1094

Table F.3. Comparison of model skill for three methods used to fill in missing daily meteorology values. Five jackknife tests were applied to each method, where for each test a random sample of days having data was collected and compared to the model prediction for that day. First-degree efficiency E_1 is defined in Section F.2.3. The grand mean used in the calculation of E_1 and against which the models are compared was the mean of the observed values for that sample, not the mean of the total dataset, resulting in a fairly stringent test.

Variable and Method	Mean E_1	Min E_1	Max E_1
Stillwater Reservoir meteorology station			
T_{min} [month,precip] Means (method 1)	0.636	0.616	0.658
T_{min} Regression (method 2)	0.792	0.775	0.815
T_{max} [month,precip] Means (method 1)	0.680	0.649	0.728
T_{max} Regression (method 2)	0.835	0.821	0.847
P [month] Means (method 1)	-0.068	-0.266	0.133
P Regression (method 2)	0.312	0.056	0.468
P Exponential-Markov Chain (method 3)	-0.31	-0.872	0.029
Old Forge meteorology station			
T_{min} [month,precip] Means (method 1)	0.454	0.435	0.466
T_{min} Regression (method 2)	0.478	0.473	0.485
T_{max} [month,precip] Means (method 1)	0.565	0.541	0.583
T_{max} Regression (method 2)	0.470	0.448	0.478
P [month] Means (method 1)	-0.011	-0.047	0.007
P Regression (method 2)	0.426	0.400	0.453
P Exponential-Markov Chain (method 3)	-0.205	-0.252	-0.161

of T_{min}, T_{max} were computed from the data for each month and were used as the predictors for missing days: $\hat{T}_{\text{min}}$[month,precip], $\hat{T}_{\text{max}}$[month,precip] $\Rightarrow$ 24 predictors each. If precipitation data was also missing for a day with missing air temperature, then its precipitation status was predicted first using one of the methods described below.

In the regression and autocorrelation methods (2,3) for predicting missing precipitation, the first step was to predict wet or dry day status. If the day's status was predicted to be wet, then a separate model was used to determine the depth of the precipitation. This two step process reduced the "smearing" of precipitation and the number of falsely wet days at a given location. In the autocorrelation method, a two-state, lag-one Markov Chain model was used to decide daily precipitation status; and the daily depth on wet days was determined from an exponential distribution.

Testing of all three methods indicated that the regression model had the most skill (Table F.3). Therefore, the regression method was used to fill in the missing values of P, T_{min}, and T_{max} in the meteorology records at Stillwater Reservoir, Old Forge, Indian Lake 2 SW, and Wanakena Ranger Station. The Stillwater Reservoir timeseries was used in subsequent hydrologic modeling with PWM.

Table F.4. Final PWM parameter values. Thin soil values were calibrated to a simulation of Woods Lake. Thick soil values were the same as thin soil values except where noted; these were modified from the thin soil values using trial-and-error and judgment to obtain a hydrograph with a larger baseflow component.

Parameter	PWM Variable	Thin Soil	Thick Soil
Maximum canopy interception	maxInt	0.0007	
	sPet	0.035	
Snowmelt coefficient	meltFactor	0.002	
Snowmelt coefficient	baseTemp	0.0	
Maximum flux	qMax	0.01	0.0075
Groundwater storage capacity	sMax	0.1	0.125
Exponent in groundwater flow equation	expon	1.0	
Infiltration rate	kL	0.001	0.002
Effective lateral hydraulic conductivity	kEffL	0.001	0.002

F.2.2 PWM Calibration

PWM was tested and underwent a limited calibration (adjustment of model parameters) prior to application with the geochemical model. Parameter adjustment was done in three phases focused on particular aspects of the water balance: 1) evapotranspiration, 2) snowpack accumulation and melt, and 3) streamflow generation (runoff). Although these aspects are interrelated, some simplifying assumptions were made to allow adjustment of a subset of parameters in each phase. Woods Lake was selected as a representative thin soil watershed (Church and others, 1989), and because it has daily streamflow data (WY78-92). Woods Lake is also located near the Stillwater Reservoir meteorology station, which in addition to providing data needed for forcing PWM, also has snowpack data which was used for calibration and verification.

First, the target (real) runoff ratio (Q/P, Q = annual streamflow, P = annual precipitation) was estimated from the regional annual streamflow reported by the US Geological Survey (USGS), and the mean annual precipitation calculated for the four meteorology stations above. The resulting runoff ratio was 760 mm/1137 mm = 0.67. A similar runoff ratio of 0.61 was found for Hubbard Brook, New Hampshire during 1964–1987 (Federer et al., 1990). Assuming no change in storage and a water balance equation of P = Q + ET, it follows that annual ET depends only P and Q, and the runoff ratio is a suitable proxy for ET. The primary model parameters that govern simulated ET are canopy interception capacity (maxInt) and soil moisture at which actual ET = potential ET (sPet). These were adjusted by trial-and-error to reproduce the estimated runoff ratio of 0.67. Final values of all calibrated parameters are given in Table F.4.

Snow survey data obtained from the Northeast Regional Forecast Center was used to calibrate the two snow parameters in PWM, meltFactor and baseTemp. The objective was to maximize efficiency E_1 of the snowpack water content at Stillwater Reservoir and Old Forge during WY49-97, and the final results are shown in Figures F.4–F.5.

Streamflow hydrographs from Woods Lake and Panther Lake are shown in Figure F.6 along with their baseflow components as estimated with an algorithm. Panther Lake, the watershed with deeper soil, does exhibit greater baseflow overall, although during some years and months the difference from thin soil Woods Lake is minor.

The final model of Woods Lake was successful, especially considering we had limited soil and vegetation information and assumed constant lake volume and an unfrozen lake surface (Figures F.7–F.10). Daily first-degree, baseline-adjusted streamflow efficiency (E'_1, see Appendix F.2.3) was 0.221 with bias less than 3%, and the corresponding monthly values were 0.45 and 3%. Model skill during the verification period was similar to the calibration period.

For the geochemical modeling with PHREEQC, the hydrology for water year 1952 (10/1/1951–9/30/1952) was selected as an “average” water year on the basis of mean annual streamflow and the standard deviation of daily streamflow as predicted by PWM. Daily hydrographs for the thin soil, thick soil, and direct runoff hillslope types are shown in Figure F.11. The daily hydrograph for thin soil was based on the calibration to Woods Lake; the hydrograph for thick soil was based on the Woods Lake parameter set modified to generate more deep groundwater flow, and the direct runoff record consisted only of quick runoff equal to precipitation.

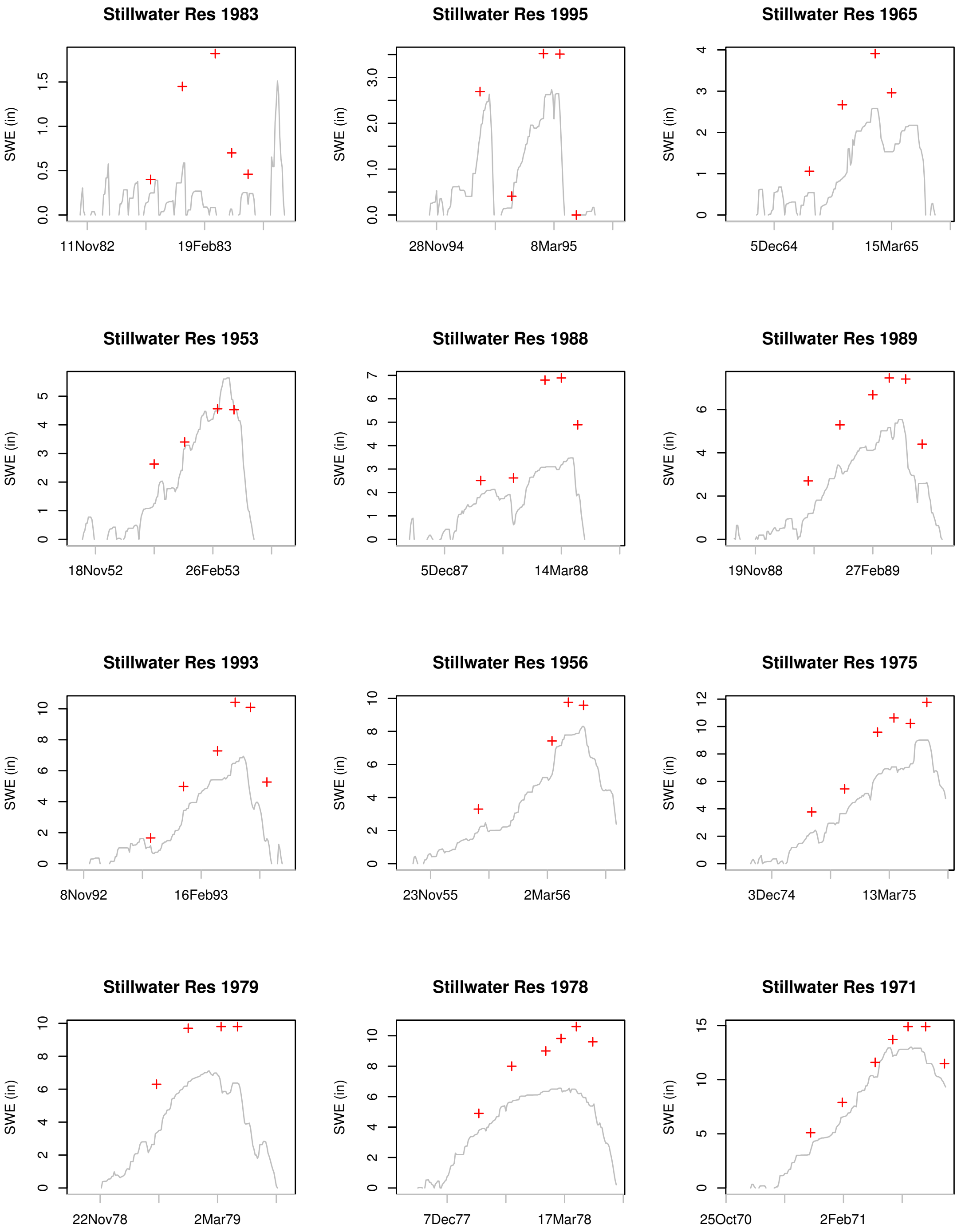

Figure F.4. Simulation of snow water equivalent at Stillwater Reservoir. Gray line is simulation from Nov 1 to Apr 30; red markers are data. Selected years represent the range of minimum to maximum snow years, with years closest to regular increments in between.

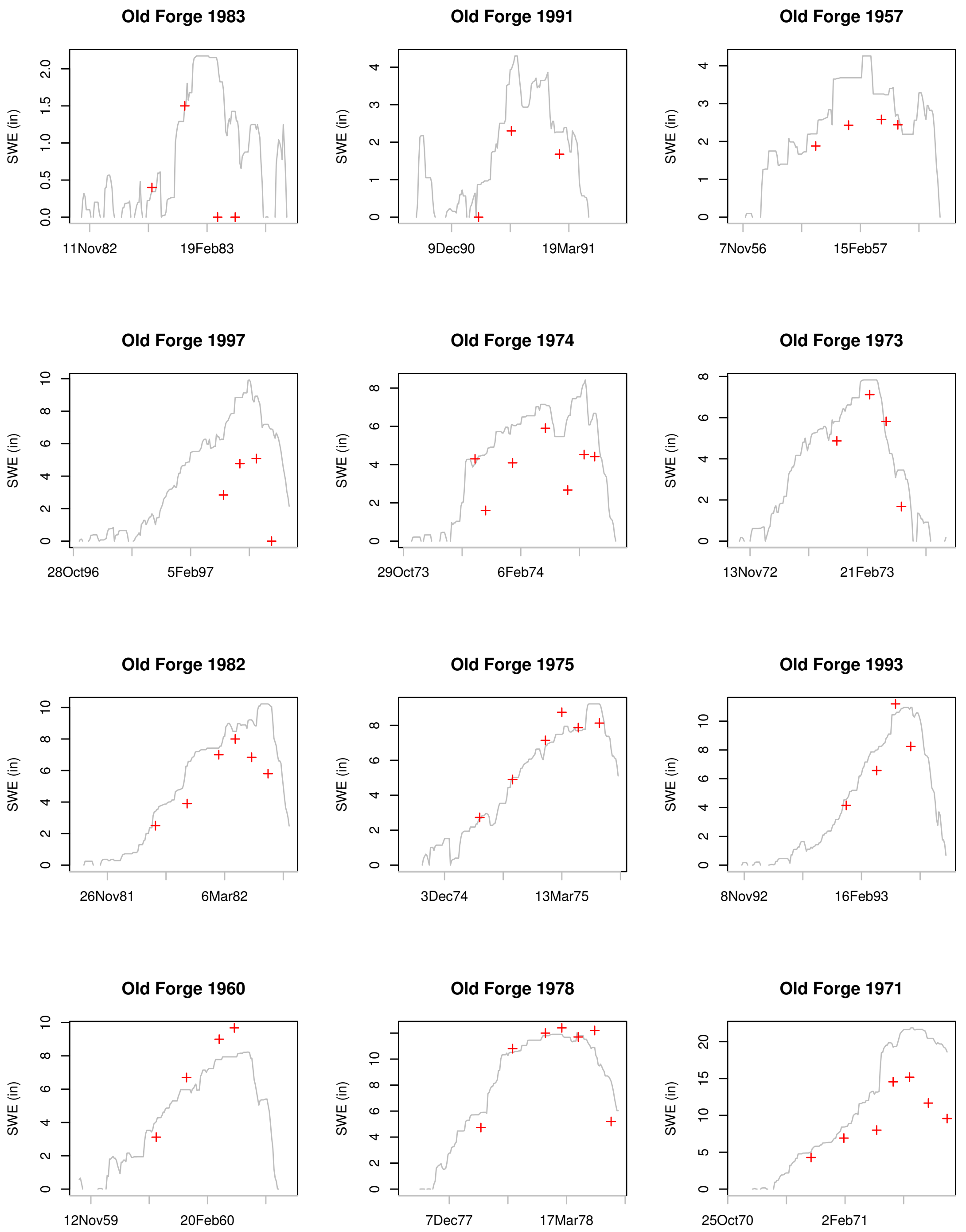

Figure F.5. Simulation of snow water equivalent at Old Forge. Gray line is simulation from Nov 1 to Apr 30; red markers are data. Selected years represent the range of minimum to maximum snow years, with years closest to regular increments in between.

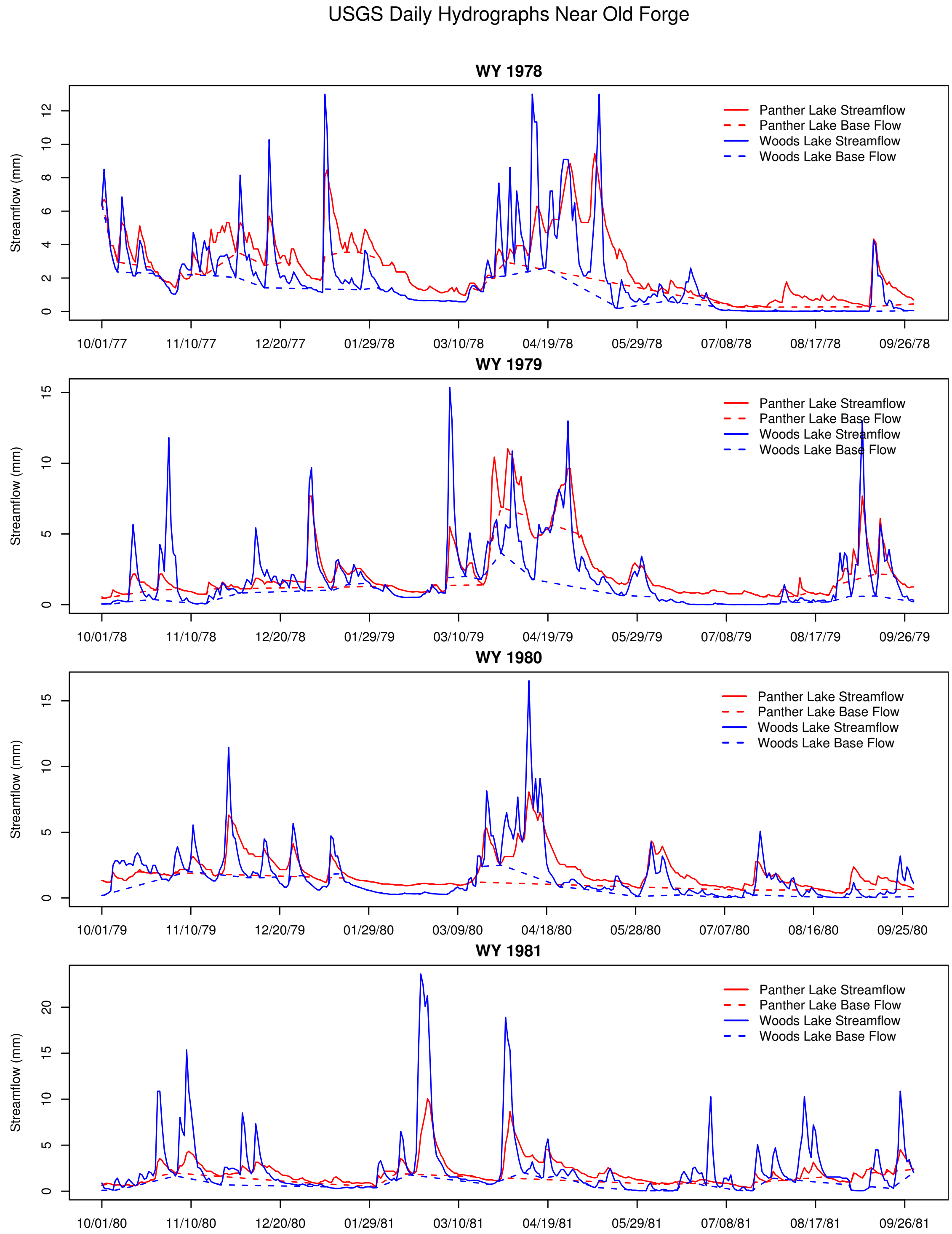

Figure F.6. Observed streamflow at Woods Lake and Panther Lake. Baseflow is computed from an algorithm.

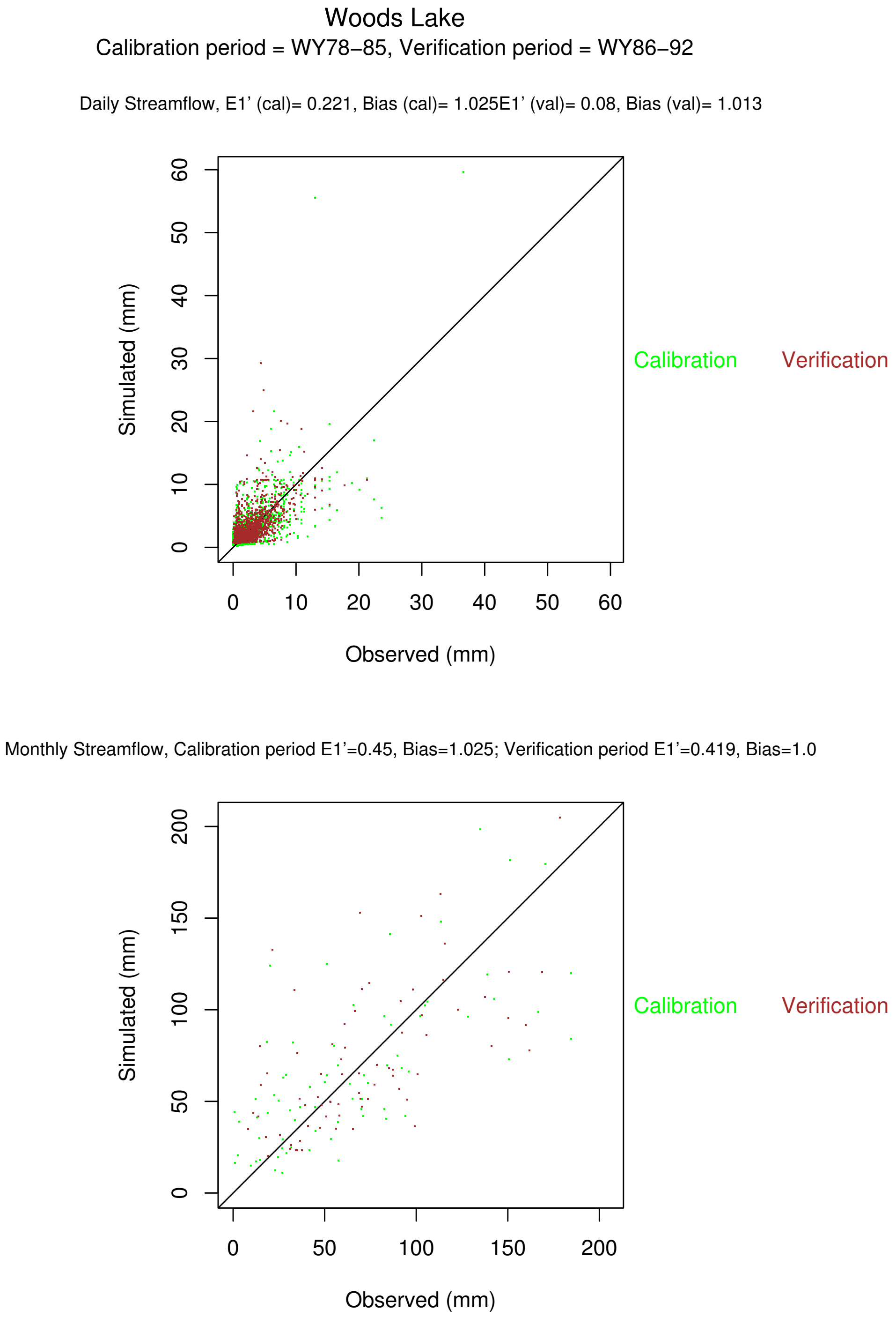

Figure F.7. Woods Lake streamflow simulation efficiency, 1:1 plots. Daily streamflow top, monthly streamflow bottom. Calibration period was WY78-85, Verification period was WY86-92. See Section F.2.3 for definitions of model skill statistics.

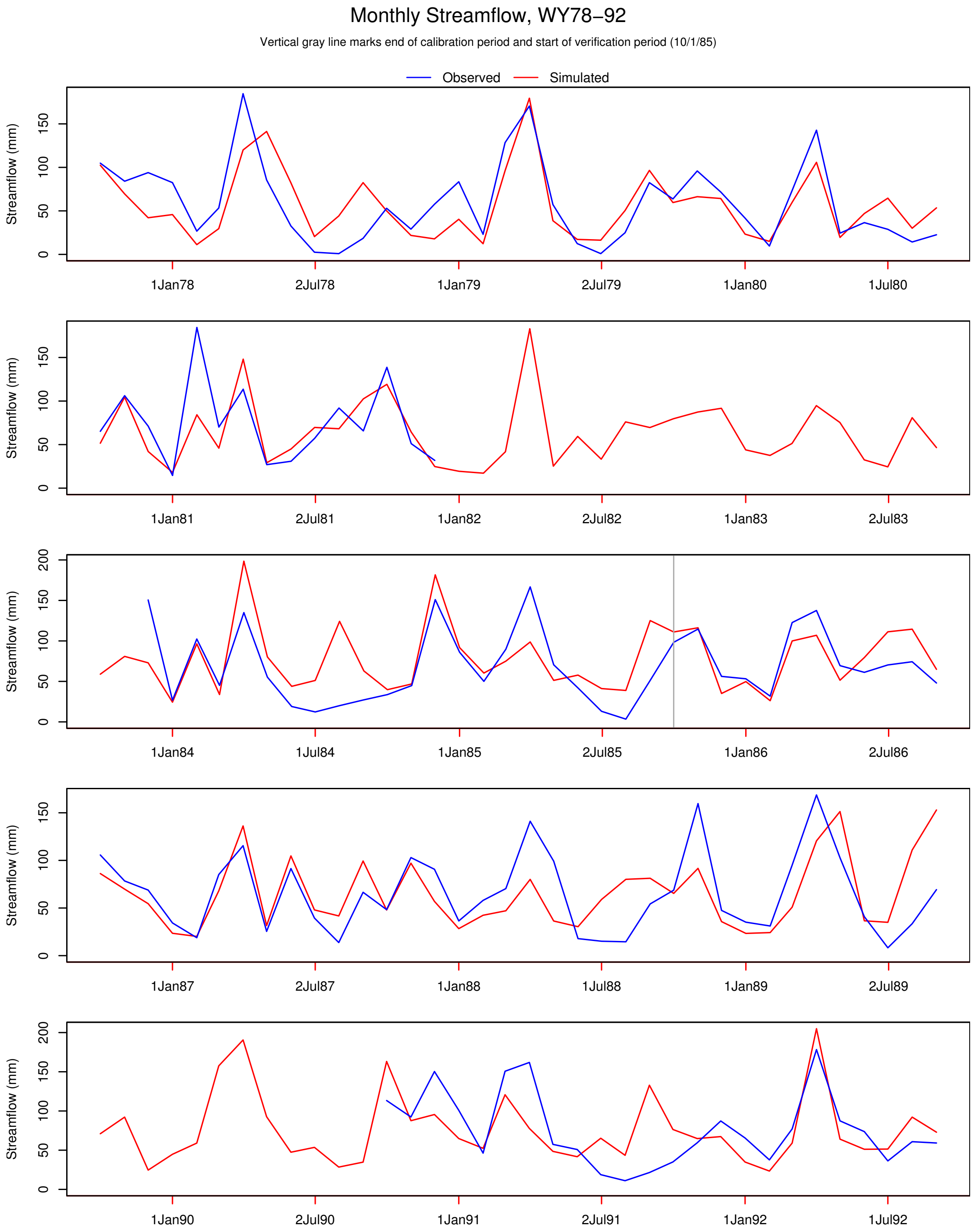

Figure F.8. Woods Lake streamflow simulation efficiency, timeseries of monthly flow. Calibration period was WY78-85, Verification period was WY86-92.

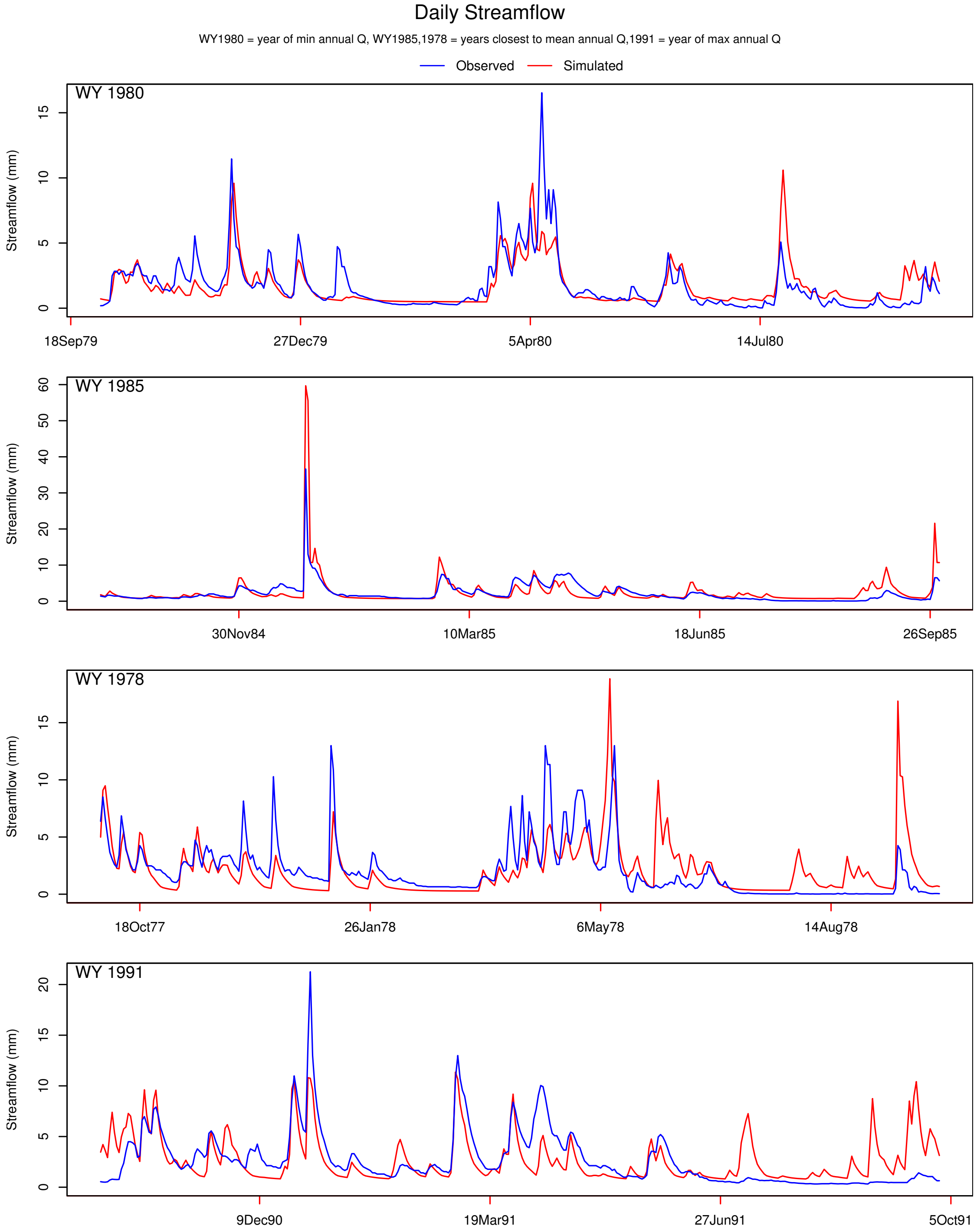

Figure F.9. Woods Lake streamflow simulation efficiency, timeseries of daily flow, part 1. Years were selected for presentation based on representativeness of annual streamflow. Calibration period was WY78-85, Verification period was WY86-92.

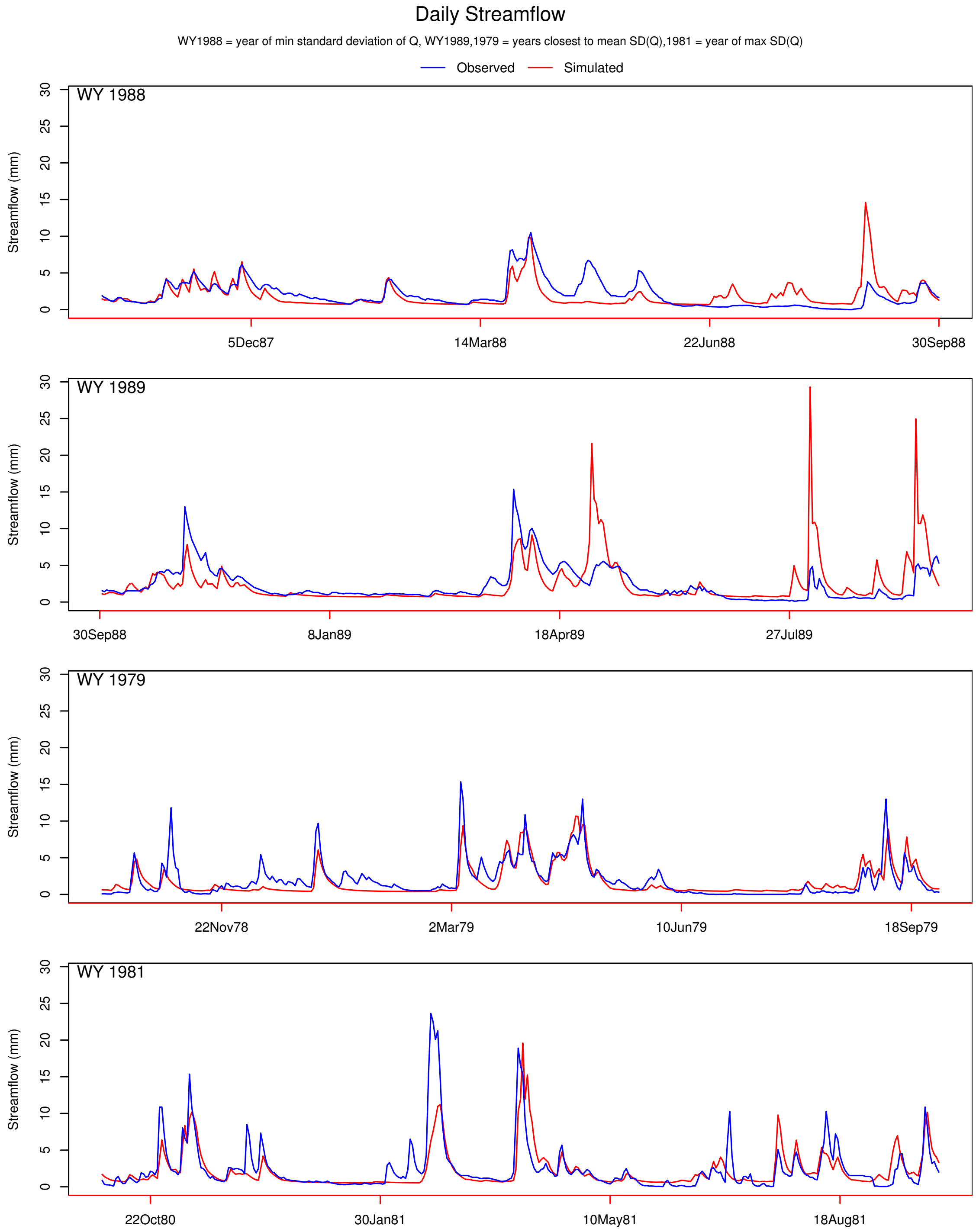

Figure F.10. Woods Lake streamflow simulation efficiency, timeseries of daily flow, part 2. Years were selected for presentation based on representativeness of the standard deviation of daily streamflow. Calibration period was WY78-85, Verification period was WY86-92.

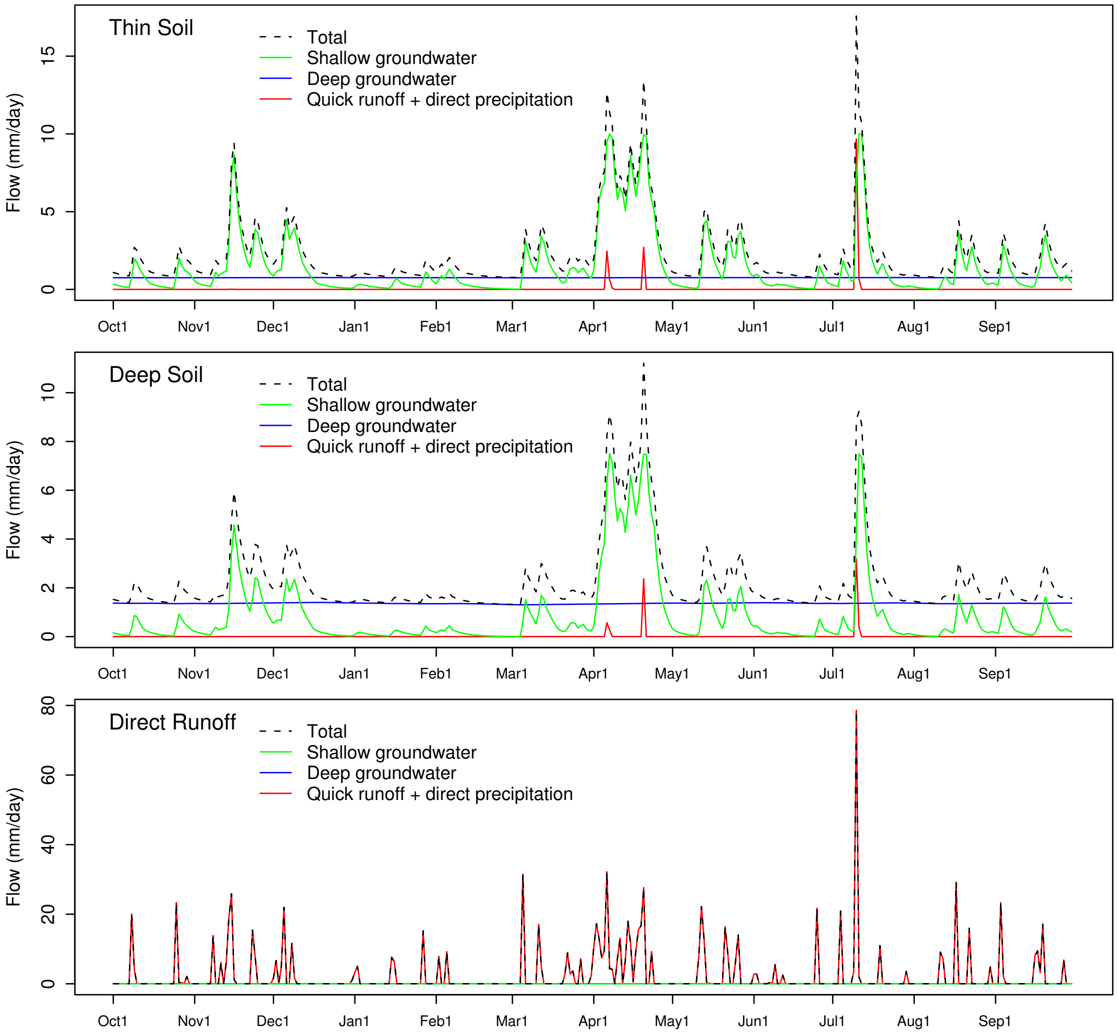

Figure F.11. Daily hydrographs for thin soil, thick soil, and direct runoff hillslope types, water year 1952. These are the daily water fluxes that were used in the geochemical modeling with PHREEQC.

F.2.3 Statistics for evaluating model skill

Bias and several goodness-of-fit measures were the primary statistics used to evaluate model skill at reproducing climate variables and streamflow. The overall approach and certain definitions are taken from Legates and McCabe (1999), an excellent reference on goodness-of-fit measures.

Bias was defined as the ratio of predicted (simulated) mean to observed mean

$$bias = \frac{\bar{P}}{\bar{O}} \tag{F.1}$$

where

$\bar{P} =$ mean of the predictions
$\bar{O} =$ mean of the observations

The traditional R^2, or square of Pearson's product-moment correlation coefficient, describes the portion of total variance in the observed data that can be explained by the model, and ranges from 0.0 to 1.0:

$$R^2 = \left\{ \frac{\sum_{i=1}^{N} (O_i - \bar{O})(P_i - \bar{P})}{\left[\sum_{i=1}^{N} (O_i - \bar{O})^2\right]^{0.5} \left[\sum_{i=1}^{N} (P_i - \bar{P})^2\right]^{0.5}} \right\}^2 \tag{F.2}$$

where

$N =$ number of timesteps
$O_i =$ observed value at timestep i
$\bar{O} =$ mean of the observations
$P_i =$ the predicted value at timestep i
$\bar{P} =$ mean of the predictions.

There are two disadvantages of R^2 for describing model skill: 1) any linear relationship between the observations and the predictions, not necessarily a 1:1 relationship, results in a high value of R^2; 2) the squaring of terms gives too much weight to large values. In the case of streamflow, a high R^2 value may indicate good fit of peakflows, but may mask poor model skill during baseflow periods.

The Nash and Sutcliffe (1970) efficiency E is a tougher test than R^2 and casts the mean of the observations as a benchmark for the model:

$$E = 1.0 - \frac{\sum_{i=1}^{N} (O_i - P_i)^2}{\sum_{i=1}^{N} (O_i - \bar{O})^2}. \tag{F.3}$$

Values of E tend to be slightly less than R-squared in the case of streamflow.

Three first-degree goodness-of-fit measures from Legates and McCabe (1999) use absolute values of differences instead of squares. The first-degree efficiency is defined as

$$E_1 = 1.0 - \frac{\sum_{i=1}^{N} \mid O_i - P_i \mid}{\sum_{i=1}^{N} \mid O_i - \bar{O} \mid}. \tag{F.4}$$

E_1 is an improvement over E when evaluating model skill at low and moderate streamflow levels is important, but the grand mean is still the basis of comparison. A further discrimination can be gained by using a baseline mean involving some kind of seasonal or other categorical variation inherent in the data. Here, the the baseline mean was defined as the mean for each month of the year, where the mean is taken across all years in the simulation. Avoidance of squaring and use of baseline mean instead of the grand mean provides tougher, more revealing tests of model skill.

The baseline-adjusted, first-degree efficiency is

$$E_1' = 1.0 - \frac{\sum_{i=1}^{N} \mid O_i - P_i \mid}{\sum_{i=1}^{N} \mid O_i - \overline{O'} \mid} \tag{F.5}$$

where

$\overline{O'} =$ baseline mean of the observations, variable in time.

All of the above measures of efficiency have a possible range of $-\infty$ to 1.0. When efficiency=0, the model is no better or worse than the observed mean as a predictor. The closer the baseline mean is to the individual observations, the lower the efficiency is likely to be.

The baseline-adjusted modified index of agreement is

$$d_1' = 1.0 - \frac{\sum_{i=1}^{N} \mid O_i - P_i \mid}{\sum_{i=1}^{N} \left(\mid P_i - \overline{O'} \mid + \mid O_i - \overline{O'} \mid \right)}. \tag{F.6}$$

d_1' has the advantage of having the same range as the familiar R^2, 0 to 1.0.

F.3 References

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Appendix 17.5

Support Document for Liming Calculation

Liming Assessment Approach

From earlier simulations using an end-member approach with the PHREEQC model (Battelle Duxbury Operations 2006), a representative year-long time series of lake water chemistries were estimated for a range of deposition loads from current to pre-industrial sulfate and nitrate levels. These simulations were performed for each of the listed Forest Preserve lakes. The average daily lake water chemistries and daily chemistry associated with the minimum pH were selected for each lake. The PHREEQC model was again used to estimate the equilibrated water chemistries for a range of increments of added lime to the original (current deposition level) lake water chemistries. The lime increment per liter of water was scaled by the discharge from the lake to estimate the total lime required to bring the water to a new chemical state.

Assessment Results

The liming estimate was based on the estimated minimum daily pH once the Clean Air Interstate Rule (CAIR) (http://www.epa.gov/cair/) is fully implemented and on the discharge from the lake. Full implementation will decrease the anthropogenic loading of sulfate and nitrate by approximately 40 percent. The amount of lime required to raise the pH to 5.5 from the presumed steady minimum pH value is estimated. Two explicit conservative assumptions are included in this approach: 1) pH 5.5 is higher than the actual standard of 5.4 and 2) the actual pH value will exceed the minimum pH value at all times except during the particular instant of the minimum, therefore, at all other times the actual instantaneous liming requirement would be lower than assumed. Additionally, an implicit conservatism results from the insensitivity of the lake pH to deposition with the end-member approach. This means that the assessment methodology likely underestimates the pH response that could result from full implementation of the Clean Air Interstate Rule.

The estimates assume a 100 percent efficiency of lime delivery. In actual practice, depending on the material and the method of dispersion, the delivery efficiencies may be as low as 50 percent.