Assessment Endpoints for TMDL Development in the Adirondacks Region of New York State

The results of our review of the literature on the use of four assessment endpoints – pH, dissolved reactive Al, Acid Neutralizing Capability (ANC), and the Acid Stress Index (ASI) – suggest that pH is the most appropriate endpoint for use in the development of TMDLs in the Adirondacks region of New York State. The State of New York has identified a number of water bodies in the Adirondacks that are pH-impacted; these are on the Clean Water Act Section 303(d) list. New York State standards (NYSDEC 1999) state that pH "shall not be less than 6.5 nor more than 8.5" for fresh water bodies class AA through C, the best uses of which include drinking, recreation and fishing, and "not be less than 6.0 nor more than 9.5" for class D fresh water, the best use of which is fishing. As discussed below, losses of brook trout documented in Adirondack lakes have been attributed to acidification.

According to Baker et al. (1990a, p. 3-111), the brook trout is somewhat more tolerant of low acidity than are small mouth bass alevins and rainbow trout. However, there is no doubt that brook trout have been adversely affected along with other fish populations in this region. Baker et al. (1990b) cite earlier literature to the effect that "...the critical life stage for brook trout populations is during the emergence of swim-up fry from the gravel into the overlying water column." Therefore, based on a review of the literature, they suggest a 6.0 endpoint for "...waters receiving acid peak flow from melt waters." Baker et al. (1990b, p. 4-6) offer the following statistics indicating the extent of fish mortality and its dependence on environmental circumstances:

Ninety-one percent of the lakes losing brook trout apparently as a result of acidification were classified as mounded seepage or thin-till drainage lakes; 70% were classified as low dissolved organic carbon mounded seepage or thin-till drainage lakes. Sixty-one percent of the lakes without fish were found in the Oswegatchie-Black watershed in the southwestern Adirondacks; 39% of all lakes in this watershed had no fish; brook trout was found in 52%. Of the 409 lakes with confirmed presence of brook trout in the past (before 1970), 127 (31%) appear to have lost the species. Nearly 80% of the lakes without fish had a low pH (5.0); about 90% were classified as either mounded seepage lakes or drainage lakes in watersheds with thin till.

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 models such as the ASI[1] that included pCa/pH and pAl. In a study of Ontario lakes with a pH range of 3.8-7.0, which included 37 lakes with pH below 6.0 as a result of airborne industrial pollutants, (Sprules 1975) found "a strong relationship between low levels of diversity of zooplankton and fish species and low pH levels." Sverdrup and De Vries (1994 p. 146) state that "For Scandinavian waters the pH in the runoff should in general not be less than 5.5-6.0 and the Al levels should be below 0.03-0.08 mg L^{-1}, to avoid damage on sensitive biota..." Sverdrup et al. (1992) selected 5.75 as the endpoint for brook trout in the Maryland critical load study. Sverdrup et al. (1990) suggested 6.0 as the critical pH for

[1] The ASI incorporates H, Al and Ca and ranges from zero (no acid stress) to 100 (total mortality); it represents the mortality of a particular species expected from a particular pH and concentration of Ca and monomeric dissolved Al (Baker et al. 1990a).

surface waters whereas De Vries (1993) advises a minimum pH of 5.5 and an Al concentration of 0.003 mol_c.

Certain limitations on the use of dissolved reactive Al as a chemical endpoint must be kept in mind. The Al^{3+} ion, and perhaps other aqueous Al species, rather than H^+ itself is thought to be a principal biotoxin in low pH waters. Lakes with a pH of <5.0 may have concentrations of total Al greater than 100-200 ug L^{-1}; the concentrations in some lakes are as high as 600-700 ug L^{-1} (Charles 1990). Dissolved monomeric Al has been used as a proxy for the thermodynamic activity of Al^{3+} but presents the difficulty that the quantity of organic acids, and certain other anions (e.g., F^{-1}, SO_4) reduce the activity of Al^{3+} at a given concentration as a result of complexation hence reducing its toxicity to fish. The variability of organic acid concentrations limits the value of Al as a chemical endpoint unless the Al concentration is corrected for the amount of organically complexed Al.

A further limitation is that dissolved Al tends to polymerize and even precipitate as the solubility of gibbsite decreases as the pH increases, or as the concentrations of organic acids and other complexing anions are decreased. These complications may lead to inaccurate estimates of the likelihood of Al^{3+} toxicity and suggest the use of other indicators for freshwater bodies.

Alkalinity/ANC is not linearly related to pH or Al^{3+} or toxicity, and hence, is not an optimum toxicity indicator. While there is no state water quality standard for alkalinity/ANC, this measure can provide a qualitative sense regarding margin of safety. Thus, pH appears to be the chemical indicator of choice for the brook trout biological indicator.[2] Where populations have been lost, critical loads could be calculated to allow successful reintroduction of the species. However, using pH as the chemical indicator does require cognizance of the pre-industrial low pH of some of these lakes. Estimates by Charles et al. (1989), using sediment diatom and chrysophyte assemblages to infer past pH in lakewater, indicate that the pH prior to 1850 in 11 of the 19 Adirondack lakes analyzed was 6.0 or below; three of the 19 lakes, it was inferred, would have had pH between 6.1 and 6.4, putting a total of 14 of the 19 lakes below the New York State standard of 6.5.

References

Baker J, DP Bernard, S Christensen, MJ Sale, J Freda, K Heltcher, D Marmorek, L Rowe, P Scanlon, G Suter, W Warren-Hicks. 1990a. Biological Effects of Changes in Surface Water Acid-Base Chemistry. NAPAP Report 13, In: National Acid Precipitation Assessment Program, Acidic Deposition: State of Science and Technology. Vol. II.

[2] Critical loads calculations are referenced to one or more biological endpoints. These endpoints can be established for individual plant species, for an ecological community, or for fauna in the surface water draining a watershed (Dijk and Roelofs 1988). The individual plant species or ecological community endpoints may be more conservative than fauna endpoints but are also generally considerably more difficult and costly to quantify.

Baker JP, SA Gherini, SW Christensen, CT Driscoll, J Gallagher, RK Munson, RM Newton, KH Reckhow, and CL Schofield. 1990b. "Summary and Conclusions." in: *Adirondack Lakes Survey: An interpretive Analysis of Fish Communities and Water Chemistry*, 1984-87. Adirondack Lakes Survey Corporation, Ray Brook, NY.

Charles, DF, RW Battarbee, I Renberg, H van Dam, and JP Smol. 1989. "Paleoecological analysis of lake acidification trends in North America and Europe using diatoms and chrysophytes." In SA Norton, SE Lindberg, and AL Page (eds.), Acid Precipitation, Vol. 4: Soils, Aquatic Processes, and Lake Acidification. Springer-Verlag, NY, NY.

Charles DF, MW Binford, ET Furlong, RA Hites, MJ Mitchell, SA Norton, F Oldfield, MJ Paterson, JP Smol, AJ Uutala, JR White, DR Whitehead, and RJ Wise. 1990. "Paleoecological investigation of recent lake acidification in the Adirondack Mountains, N.Y." *Journal of Paleolimnology* 3:195-241.

Cronan CS, DF Grigal. 1995. "Use of calcium/aluminum ratios as indicators of stress in forest ecosystems." Journal of Environmental Quality 24:209-226.

De Vries W. 1993. "Average critical loads for nitrogen and sulfur and its use in acidification abatement policy in the Netherlands." *Water, Air, and Soil Pollution* 68:399-434.

Dijk H van, and J Roelofs. 1988. "Critical loads for nitrogen on natural vegetation." pp. 313-322, in J Nilsson and P Grennfelt (eds.), Critical Loads for Sulphur and Nitrogen. Skokloster, Sweden, March 19-24, 1988.

Janicki A, D Wade, H Wilson, D Heimbuch, H Sverdrup, P Warfvinge. 1995. Maryland critical loads study volume 1: Critical loads assessment for Maryland streams. Chesapeake Bay Research and Monitoring Division, Report CBRM-AD-95-9.

New York State Department of Environmental Conservation (NYSDEC). 1999. "Water quality regulations: Surface water and groundwater, classifications and standards." New York State codes, rules and regulations Title 6, Chapter X Parts 700-706.

Shortle WC, KT Smith. 1988. "Aluminum-induced calcium deficiency syndrome in declining red spruce." *Science* 240:1017-1018.

Sprules GW. 1975. "Factors affecting the structure of limnetic crustacean zooplankton communities in central Ontario lakes." *Verh. Internat. Verein. Limnol.* 19:635-643.

Sverdrup H., and W De Vries.1994. "Calculating critical loads for acidity with the simple mass balance method." *Water, Air, and Soil Pollution* 72:143-162.

Sverdrup H, and P Warfvinge. 1996: Assessing the potential for forest effects due to soil acidification in Maryland." *Water, Air and Soil Pollution* 87:245-265.

Sverdrup H, P Warfvinge, M Rabenhorst., A Janicki, R Morgan, and M Bowman. 1992. "Critical loads and steady-state chemistry for streams in the State of Maryland." *Environmental Pollution* 77:195-203