

Nutrient Loading and its Relevance to the Great Lakes Basin

A "White Paper" Literature Review
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in Great Lakes Research

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Executive Summary

Nutrient enrichment of aquatic ecosystems results in higher biological productivity and can lead to undesirable effects including algal blooms and depletion of oxygen in bottom waters. This process of eutrophication usually occurs naturally and gradually, but is greatly increased by various human activities. Phosphorus (P) and nitrogen (N) resulting from agricultural and urban activities are now recognized to be the major causes of human-driven eutrophication. This is the most common impairment of surface waters in the United States, affecting lakes, rivers and estuaries. In general, freshwater ecosystems respond most strongly to P enrichment, and coastal systems to N enrichment. Inputs are separated into point sources, such as a waste-water treatment plant which discharges through a pipe, and nonpoint sources such as fertilizer, which are delivered via hydrologic flowpaths from diffuse landscape locations. Nonpoint sources are of primary concern, and usually require management of land-use practices.

This complex topic has been the subject of multiple lines of investigation, including limnological studies of lake productivity, quantification of nutrient loads as a function of land use, and mass balance analysis of all inputs to and outputs from individual ecosystems, often using a catchment basin (watershed) as the unit of study. In recent decades, the mass balance approach has been scaled up to large basins (the Mississippi, the North Atlantic) and the globe. Mass balance analyses provide a framework for evaluating sources, determining losses and storages ('sinks'), and for refining estimates and understanding by working to resolve imbalances in estimates.

Nitrogen has attracted much recent attention, due partly to the recognition that human-fixed N now equals or exceeds naturally fixed N, and because of its multiple environmental impacts. N is a greenhouse gas, a source of acid rain, the primary cause of eutrophication in

coastal waters, and contributes to photochemical smog. Recent studies demonstrate the amenability of N to large-scale mass balance analyses of inputs to and exports from watersheds, and document that on average three-fourths of N inputs are stored, sequestered, or processed. This represents valuable ecosystem services, which some evidence indicates may be near saturation, suggesting the possibility of threshold changes in the capacity of ecosystems to process the current high loading of N from anthropogenic sources.

Eutrophication of the Great Lakes, the world's largest body of fresh water, attracted great attention in the 1970s as lake Erie experienced benthic anoxia and other water quality problems associated with nutrient enrichment. The 1972 Great Lakes Water Quality Agreement brought about reductions in point source loadings of P that dramatically lowered annual P loads and reversed many of the effects of cultural eutrophication. Today, reduced primary production, much of which is now shunted into benthic food webs by the invasive zebra mussel, has even led to calls for increased P loading to the Lakes.

Much remains to be learned about interactions between nutrients and the biota. Nutrient ratios as well as the concentrations of N and P may influence biological productivity, and migratory fishes are capable of transporting nutrients and carbon upstream in their spawning runs, thus linking the productivity of headwater streams to fish biomass accrual in open water.

Numerous opportunities remain for individual and collaborative research into a wealth of fundamental and applied issues centered around the dynamics of nutrients and linkages between terrestrial and freshwater ecosystems.

Eutrophication

Eutrophication refers to the change in state of a lake or other water body over time, whereby an increased nutrient supply results in higher biological productivity and often leads to undesirable effects including algal blooms and depletion of oxygen in bottom waters.

Eutrophication derives its name from classic studies of limnology. Early in the twentieth century, European limnologists noted that lakes in infertile basins had low biological productivity compared to lakes in fertile basins, and the terms oligotrophic and eutrophic were coined to describe attributes of low and high productivity lakes respectively. Because lakes tend naturally to acquire nutrients from their landscapes as they age, they undergo a gradual increase in productivity, or eutrophication, due to natural nutrient enrichment. Human activities can dramatically increase the nutrient supply to water bodies, giving rise to the term cultural eutrophication to describe the accelerated and human-driven process, which we now know have numerous adverse effects. Phosphorus (P) and nitrogen (N) resulting from agricultural and urban activities are now recognized to be the major causes of cultural eutrophication (Carpenter et al. 1998).

The production of new plant biomass, referred to as primary production, is critical to nearly all ecosystems. With the exception of a small number of unique systems that rely on chemosynthesis, photosynthesis supplies the energy for life, and takes place wherever light and nutrients are in sufficient supply. While photosynthetic plants, microbes and protists require a diverse array of macro-nutrients, micro-nutrients, and vitamins, N and P usually are the limiting factors for primary production. Thus, when additional N and P are made available, primary production often increases. While some increase may be beneficial, providing more energy to consumers and thus boosting secondary production, excessive algal growth frequently causes

adverse effects. As algal blooms decay, often after sinking into bottom waters, oxygen is depleted, resulting in hypoxia or anoxia and rendering bottom waters unsuitable for most life. Toxic algae may bloom under nutrient enrichment, including various cyanobacteria (blue-green algae) mainly in fresh water, and dinoflagellates in brackish and marine waters. Fish kills can result from oxygen depletion and toxins. Additional consequences include complex effects on the food chain, reduced water clarity, taste and odor problems, and degradation of the water body's aesthetic and recreational qualities (Carpenter et al. 1998, Smith 1998).

Eutrophication caused by excessive inputs of P and N is the most common impairment of surface waters in the United States, and accounts for about 50% of the impaired lake area and 60% of impaired river reaches (U.S. EPA 1990, U.S. EPA 1996). It is the most widespread pollution problem of the nation's estuaries (NRC 1993). Impairment refers to surface waters that are not suitable for designated uses including drinking, recreation, irrigation and industry (U.S. EPA 1990). Surface waters face many additional threats from chemical contamination, siltation caused by erosion from agriculture, construction and logging activities, invasive species, and alteration of hydrologic flowpaths (Carpenter et al. 1998). Nevertheless, eutrophication is one of the most serious environmental threats to fresh and coastal waters. It is best-known for algal blooms and resulting anoxia, which prominently impacted Lake Erie in the 1970s, and more recently have impacted Chesapeake Bay and the Gulf of Mexico, causing significant damage to valuable fisheries.

Eutrophication of lakes emerged as a serious issue in the 1970s, sparking a large and important investment in freshwater science aimed at resolving conflicting claims about the importance of N, P and CO₂ as the primary driver. This has been largely resolved, and for many lakes P inputs are the primary cause, although some lakes are N-limited (Schindler 1977, Wetzel

2001). Eutrophication of estuaries and coastal waters, due to large quantities of nutrients delivered by rivers, has more recently emerged as widespread and serious. Prominent examples include the hypoxic (low oxygen) and anoxic (no oxygen) bottom waters of the Gulf of Mexico and the Chesapeake Bay. N is the nutrient most limiting to primary production in most temperate estuaries and coastal ecosystems (NRC 1993, Nixon 1996).

Sources of Nutrients

Nutrients reach surface waters from many sources. It is convenient to classify chemical inputs to rivers, lakes, and oceans as point or nonpoint sources (Carpenter et al. 1998). Point sources (PS) include municipal waste water treatment plants and industrial discharges, tend to be a continuous input over time, and enter the water body through a pipe or at a specific location. This makes monitoring and pollution treatment relatively straightforward. Nonpoint sources (NPS) include agricultural runoff of fertilizers and animal waste, urban runoff such as pet waste and fertilizers from unsewered areas, atmospheric deposition, septic tank leaching, and construction runoff. They tend to be episodic, and may be linked to seasonal activity such as agriculture or construction, or irregular and associated with rainstorms. Nonpoint sources tend to occur over or be derived from large areas, and are transported via hydrologic flowpaths and by wet and dry deposition. They are difficult to measure or regulate. Due to improvements in regulations and technology, point source pollution has been significantly reduced over the last several decades. Nonpoint inputs are the major source of nutrient delivery to surface waters today (U.S. EPA 1996), and it is widely recognized that reductions in NPS pollution are needed to improve the quality of the nation's waters (Carpenter et al. 1998).

The relative importance of different nutrient sources varies spatially and temporally. For most reaches of U.S. rivers, nonpoint sources are responsible for most N and P delivery. Of 86 rivers studied by Newman (1995), over half of the rivers studied received > 90% of their N, and one-third of the rivers studied received > 90% of their P, from nonpoint sources. However, point sources of N and P can contribute over half of the N and P load to urban river reaches (Newman 1995).

Multiple Perspectives on Nutrient Loading¹ to Aquatic Ecosystems

The topics of nutrient loading and eutrophication are tied to multiple scientific sub-fields, and we think it is useful to identify three to help us structure this review of the state of the science. (1) The need to understand and manage nutrient loads and eutrophication has led to a great deal of research into limiting nutrients and biological responses. While much excellent research continues in this sub-field, largely the domain of limnologists and biological oceanographers, a great deal has been learned in the past 30 years concerning the role of limiting nutrients in aquatic ecosystems. (2) The need to quantify the link between land-use activities and nutrient delivery, particularly from non-point sources, has led to a substantial body of research on land use and land-use change in relation to nutrient enrichment. The explosive spread of Geographic Information System technologies and the field of landscape ecology together have further stimulated research in this area. (3) An increased appreciation of human modification of

¹ Load refers to the mass or amount of a material that is exported at the mouth of a river, or the sum of inputs distributed over some land area, such as a watershed. Typically it is expressed per day, week, or year, and so is a rate. In a river, we can measure the concentration of N, P, sediments, etc. in mg/L, then multiply that concentration by river flow (in, say, m³/s multiplied by seconds per day) to obtain the load (perhaps in g or kg/day). Summed over a year, this would be the annual load discharged by the river to the lake (some would call this the annual discharge of sediments). If we wish to compare the load of two watersheds of different areas, we might standardize by dividing by area. This is referred to as the yield (e.g., kg/km²/yr). Thus instantaneous concentrations are converted to loads and yields based on total water volume exported and the area drained, and this requires a sampling program tied to variation in river flow.

regional and global cycling of carbon and other materials, with potentially disastrous impacts, together with the data bases, modeling and other scientific tools to construct comprehensive input-output budgets, has led to increased emphasis on large-scale input-output budgets. After carbon, nitrogen probably has attracted the most attention. The reasons are discussed more fully below, but include the extent of human alteration of the natural cycle, diverse and serious environmental impacts, and a fair level of tractability for investigation.

This review does not further describe the links between nutrient enrichment, enhanced biological production, and related ecosystem responses. This information can be found in any limnology text (e.g., Wetzel, 2001). We next introduce the watershed-landscape-ecosystem approach, which has been pioneered using small watersheds and the mass balance analysis of biogeochemical cycles, and subsequently extended to the regional and global scale. We will then turn to an in-depth review of nitrogen budgets because of the high level of research activity associated with N cycling. Then we examine the state of the science with regard to quantifying the link between land use and eutrophication, which can best be appreciated within the larger context of a full input-output accounting.

Watersheds and the Mass Balance Approach

The watershed approach (synonymous with catchment, drainage area, and basin) is a quantitative accounting of all inputs and outputs to a landscape (Likens 2001). Typically, one tracks the fluxes of elements such as carbon, nitrogen, calcium, etc., although some studies are based on organic matter. Boundaries for the landscape may be determined for the convenience of the question being asked, but often the boundaries coincide with a watershed unit. A watershed is an area of land where precipitation drains toward a common outlet, typically a river

mouth. The material of interest, such as C or N, cycles between living and non-living components within the boundaries of the ecosystem (Likens 1992), and its non-living forms include various species of the element, which may be in the atmosphere or in solution in water. Riverine export of the material is widely used to track losses from the watershed. Figure 1 depicts a model of nutrient relationships for a watershed-landscape ecosystem (Likens 1992, 2001).

Analysis of mass balances underlies the watershed approach by providing the accounting framework. Simply put, for any system,

$$\text{inputs} = \text{outputs} \pm \text{storage}$$

Thus, all inputs to a watershed should be balanced by equal outputs, unless changes in storage take place. For example, outputs of nitrogen from a watershed may include N dissolved in stream water and N denitrified in wetlands (thus exiting as atmospheric N₂). If outputs are less than inputs, this suggests that some N is stored, for example, in new biomass of forest trees. Outputs can theoretically exceed inputs if previously stored material is mobilized, by mining, erosion, or other processes.

Elements of greatest interest, from an ecosystem perspective, are those that are biologically reactive, and thus tend to cycle between living and non-living pools. It is generally expected that those elements most limiting to life processes will be very rapidly incorporated into living tissue whenever they become available. Conservative elements (e.g., Na⁺, Cl⁻) are not influenced in their abundance by biological processes, and often serve as useful tracers of water and air movements.

The terminology of source and sink dynamics is widely used in mass balance studies. To illustrate, C or N forced into the atmosphere by the burning of fossil fuels is a source of those

elements to a watershed-landscape. Any C or N that is converted into plant biomass represents a sink (storage, sequestration) and will not be included in riverine export. However, if that vegetation is burned, releasing its C and N, it becomes a source. Any compartment may be a source or a sink, depending on the researcher's perspective within the larger cycle.

The advantages of a complete accounting are many. If all terms but one can be estimated with confidence, the remaining term can be estimated by difference. An inability to balance the equation serves as motivation to re-examine estimates for flaws. A particularly instructive example is the "missing carbon", which refers to our current inability to account for all of the carbon pumped into the atmosphere by the burning of fossil fuels. Over the past two decades, scientific debate shifted from forest uptake (new growth) vs. release (burning), to oceanic uptake (arguable due to mixing/dispersion issues), back to forest and soil storage in temperate and boreal systems, and most recently to the possibility that the extent of missing carbon may have been over-estimated. Much exciting science has resulted from efforts to arrive at the correct balance and discover the magnitude of rates of underlying processes. Indeed, this is the main endeavor of ecosystem science.

Watersheds have been the focus of a great deal of small-scale ecosystem research. Hubbard Brook, New Hampshire, has been the focus of nearly 40 years of continuous study (see Bormann and Likens 1967, Likens 2001), and continues to be the location of intensive new research. Parenthetically, as Likens (2001) discusses in some detail, such research has an interesting bearing on how we do science. Specifically, ecosystem studies of this nature tend to be long-term, often are large-scale, and require an interdisciplinary team. These in turn pose challenges, opportunities, and fundamental requirements for the practice of science. It can be argued that the undertaking of a large-scale and long-term, team study of ecosystem processes

has important implications for institution and capacity-building, and for positioning a team of researchers to participate in the scientific advances of the next decades.

With the growth of interest in global cycles and human alteration of global patterns, probably best demonstrated by C and N, research has broadened to include comparative studies and regional and global balances. For example, Caraco and Cole (1999) constructed a model that explained the 1000-fold variation in nitrate export from major world rivers. Using estimates of point-source loading, fertilizers and atmospheric deposition, they explained over 80% of global variation in riverine export of nitrate. Intriguingly, using only human population (clearly a proxy rather than a mechanistic explanation), Cole et al. (1993) explained over 50% of this variation. Recent studies have constructed budgets for N export to the North Atlantic Ocean (Howarth et al. 1996, discussed elsewhere in this review) and to the Gulf of Mexico. Accurate accounting of the inputs to the Mississippi River are central to the politically charged and economically important arguments regarding the need to reduce fertilizer use in the upper Midwest in order to protect the livelihoods of Louisiana shrimpers.

The integration of lakes and streams within a landscape perspective is another important extension of mass balance studies of aquatic ecosystems. Studies by Kling et al. (1997), Kratz et al. (1997) and Soranno et al. (1999) examine inland lakes in a flowpath of surface or groundwater, and argue that a landscape perspective is preferable to treating lakes as independent entities. Lake chains (lakes in a series connected through surface or groundwater flow) exhibit common spatial patterns for a wide range of variables. Lake synchrony was greatest when water residence times were short, indicating high inter-connectedness (Soranno et al. 1999). Kling et al. (1997) studied chemical constituents in 14 stream sites and ten lake sites in a lake district in arctic Alaska. In-lake processing tended to consume alkalinity, conductivity, and most anions

and cations measured, and produce K^+ and dissolved organic carbon (DOC). In-stream processing resulted in the opposite trends. They argue for the concept of a landscape mass balance, linking lakes and streams in a downslope flowpath across the landscape, and employing the mass balance budgeting approach to changes in mass or concentration of substances.

One last example demonstrates how a mass balance approach can be brought into a novel context. Baker et al. (2001) developed a nitrogen balance for Phoenix and its surroundings. They found that humans mediate 88% of N inputs, and argue that effective N management will require a full understanding of the interplay of inputs, local environmental conditions, and internal processes that influence the fate of N.

Finally, it should be emphasized that watershed-landscape mass balance studies are powerful aids in identifying key uncertainties. In their N budget for the North Atlantic Ocean, Galloway et al. (1996) identified key uncertainties: (1) storage vs denitrification losses in the watershed, (2) natural N-fixation in the watershed, (3) N-fixation in the open ocean, and (4) N exchange between the North and South Atlantic Oceans. In their Phoenix-Central Arizona N budget, Baker et al. (2001) emphasized uncertainties in (1) regional variation in dry deposition of NO_x , (2) soil N dynamics, and (3) factors controlling denitrification in urban landscapes and cropland. By requiring the integration of information on all aspects of the ecosystem, including inputs, outputs, transformations and storage, the watershed-landscape mass balance provides a powerful organizing concept for systematic advancement of knowledge.

Global Modification of the Nitrogen Cycle

Although a key element in many biogeochemical processes and potentially limiting to aquatic and terrestrial ecosystem processes, almost all (~99%) of global N exists as stable atmospheric N₂ (Schlesinger 1991, Mackenzie et al. 1993). To be available to ecosystems, N₂ must be converted into a reactive N species (NH₃, NH₄⁺, organic N, NO, NO₂, HNO₃, NO₃, N₂O₅, HNO₄, HNO₂, NO₂⁻, NO₃⁻). Once created, one species of reactive N can be converted into another, and reactive N species are very mobile via atmospheric and hydrologic pathways (Galloway et al. 1996). Denitrification is the only process that converts reactive species of N back to unreactive N₂. This is an anaerobic process, and occurs at significant rates only in certain types of ecosystems, including wetlands and anaerobic locations within soils. Reactive N is created naturally by lightening and by biological fixation carried out by specific microbes. Humans augment the formation of reactive N by fertilizer production, legume and rice cultivation, and fossil fuel combustion (Galloway et al. 1996). Vitousek et al. (1997) provide a thorough review of human alteration of the N cycle, and its consequences.

Human domination of the nitrogen cycle is an alarming and recent aspect of global environmental change. Prior to human alterations of the N cycle, it is estimated that natural fixation of N (the bonding of atmospheric N₂ to hydrogen or oxygen, forming compounds such as NH₄ and NO_x that plants can use) by terrestrial organisms totaled about 90-140 Tg (1 Tg = 10¹² metric tons) annually (Vitousek et al. 1997). Today that amount is doubled as a consequence of human activities. Industrial fixation of nitrogen for use as fertilizer is currently about 80 Tg annually. Humans have replaced large areas of natural vegetation with nitrogen-fixing leguminous crops, adding an estimated 40 Tg annually. Burning of fossil fuels is estimated to add more than 20 Tg annually of fixed nitrogen to the atmosphere. Human

activities liberate nitrogen from long-term biological storage by burning of vegetation (40 Tg/yr), draining of wetlands (10 Tg/yr), and clearing of land for crops, which mobilizes 20 Tg/yr from soils. Together, these sources reflect at least a doubling over the upper bound estimate on natural nitrogen fixation (Vitousek et al. 1997).

Human-driven alterations of the nitrogen cycle have regional and global impacts (Vitousek et al. 1997). Nitrous oxide is a long-lived greenhouse gas (GHG). Nitric oxides contribute to acid rain and photochemical smog. Intensive fertilization of soil affects microbial processes and produces surplus runoff of nitrates, causing eutrophication of estuarine and coastal waters and altering the N:P ratio of fresh waters. On the positive side, by stimulating terrestrial plant growth, increased N may stimulate crop productivity and aid carbon uptake and sequestration by terrestrial vegetation. As soils become saturated with nitrogen, the potential for harmful effects to both terrestrial and aquatic ecosystems is attracting increased attention. Excess nitrogen can decrease soil fertility through leaching away of other minerals, including calcium, magnesium and potassium. Changes in leaf nutrient ratios may have positive or negative effects on consumers of leaves and leaf litter.

The impacts of an altered N cycle on aquatic ecosystems is profound. Total nitrogen (TN) in the North Atlantic Ocean and rivers of the North Sea region has increased two- to 20-fold, has more than doubled since 1965 in the Mississippi River, and has risen three- to ten-fold since the early 1900s in major rivers of the northeastern U.S. (Vitousek et al. 1997). Nitric acid is a major contributor to the acidification of lakes and streams, high nitrate loading is the principal cause of eutrophication and anoxia of estuarine and coastal waters, and high levels of nitrate in drinking water (> 10 mg/L standard set by U.S. Public Health Service) can lead to an anemic condition that is life-threatening to infants.

Management options include reduction in the production and use of fertilizers, and reduced burning of fossil fuels, neither of which will be easily attained. Significant mitigation and adaptation may be possible, but these require an improved understanding of the inputs, outputs, and sinks for N in natural systems. As the following section will show, there is enormous opportunity for scientific investigation, spanning terrestrial and aquatic ecosystems as well as scale from local processes to whole-system accounting, to elucidate the important ecosystem services that affect N. Current evidence indicates that most of the N received by watersheds is processed or sequestered, but as this capacity becomes saturated, the potential exists for threshold changes in ecosystem responses and human impact.

In a widely cited article that appeared in a series of large-basin studies published in the journal *Biogeochemistry*, Howarth et al. (1996) calculated nitrogen and phosphorus budgets of the North Atlantic Ocean and its watershed. Using relatively pristine regions as an indicator of pre-settlement conditions, they estimated that riverine nitrogen fluxes have increased 2 to 20-fold in many disturbed regions. On a per area basis, the largest nitrogen fluxes are found in the highly disturbed watersheds around the North Sea, in northwestern Europe, and in the northeastern US, where riverine N fluxes exceed $1,000 \text{ kg N km}^{-2}\text{yr}^{-1}$. Non-point sources of nitrogen dominate riverine fluxes in all regions and are due mainly to anthropogenic influences (fertilizer application, atmospheric deposition, fixation by leguminous crops and other agricultural activities). Overall, only about 25% of these anthropogenically derived nitrogen inputs are exported by rivers to coastal waters. Denitrification in wetlands and aquatic ecosystems are important sinks. With a few exceptions, riverine N is consumed in estuaries and continental shelves, and is not exported to the open ocean.

A recent series of articles in the journal *Biogeochemistry* (volume 57/58, 2002), derived from the International Scope Nitrogen Project, demonstrates the opportunities when good science involving diverse specialists is focused on an environmental issue of national importance. Focusing on 16 river basins (Fig. 2) along the northeastern coast of the U.S. from Maine to Virginia, and covering a total area of 250,000 km² (for comparison, the entire Great Lakes basin drains 522,000 km²), these articles document nitrogen inputs, export, and the fate of the roughly 75% of inputs that do not appear as river export. Losses through biological uptake, denitrification, and other forms of sequestration represent an enormous service performed by terrestrial and aquatic ecosystems. These ecosystem services may decline due to nitrogen saturation of system capacity, and there may be management approaches that could increase nitrogen removal.

Boyer et al. (2002) constructed budgets for inputs and losses of N for all 16 watersheds (Figure 2). Inputs included atmospheric deposition, nitrogenous fertilizers, biological nitrogen fixation, and import of N in food and feed. N losses were quantified as river export. The relative importance of N sources varied among watersheds in accordance with land use: atmospheric deposition predominated in forested watersheds, fertilizer application in agricultural watersheds, and import of food in urban watersheds. Over the combined area, net atmospheric deposition contributed 31%, net imports of food and feed 25%, biological fixation on agricultural lands 24%, fertilizer use 15%, and forest fixation 5%. Riverine export correlated with N inputs, but accounted for only 25% of inputs, similar to the earlier estimate by Howarth et al. (1996).

Mayer et al. (2002) demonstrate the feasibility of using nitrogen (^{15}N) and oxygen (^{18}O) isotope ratios of nitrate to elucidate sources and transformations of riverine nitrate. Analysis showed that riverine nitrate was almost exclusively derived from soil nitrification

processes, with only minor contributions from atmospheric deposition. Isotope analysis also implicated nitrate from wastewater as a significant source of riverine nitrate. Surprisingly, nitrate-containing fertilizers were not implicated as a significant source of riverine nitrate in agricultural watersheds by this method.

Van Breeman et al. (2002) attempt to assess the fate of the missing nitrogen by constructing empirical and process models of a complete N budget. They independently estimated all fates except for denitrification from land, which was determined by difference. Of total storages and losses, loss of N in gaseous form (mainly by denitrification) accounted for 51%, riverine export for 20%, and food and wood exports 6% and 5% respectively. Increased storage of N in soil organic matter (9%) and wood (9%) complete the budget. Such a large change in the storage term (18% of "missing" N) indicates the system is not in steady state, and once those storages are saturated, it is likely that denitrification and/or riverine export will increase.

Goodale et al. (2002) quantify the role of forests as nitrogen sinks in these 16 watersheds. They quantified forest N sinks as biomass accumulation and export of harvested wood; relatively young forests showed the highest net uptake. Wood export and new biomass together amounted to 73% of atmospheric deposition of N.

N retention vs. export by rivers is a topic of much interest and uncertainty. Studies conducted within local reaches of small streams generally estimate relatively short transit distances, of the order of 10's to 100's of meters. These studies use the conceptual model of nutrient spiraling (see Allan 1995), in which the cycle between abiotic and biotic pools involved downstream transport ("spiraling distance"), as the nutrient cycle interacts with water movement. Studies of large river basins put more emphasis on the river as a pipe than as a processing site.

Alexander et al. (2000) help to reconcile these approaches, which represent studies at vastly different spatial scales. In a study of spatial variation in N transport within the Mississippi basin, they showed a rapid decline in the rate of nitrogen loss with increasing channel size (using depth as their measure). At river depths > 1 m, transport distance increased greatly. Seitzinger et al. (2002) extend this analysis to the 16 North Atlantic watersheds. They conclude that about half of the N removed within river channels takes place in 1st through 4th order streams (which account for 90% of total stream length), and the other half from 5th order and higher rivers of the network. Due to the cumulative effect of continued N removal along the entire flow path, more N is removed than would be expected from reach-scale estimates.

This series of papers nicely demonstrates the power of a landscape mass balance accounting of element inputs and losses. Similar to the case of the carbon cycle and the "missing" carbon, a careful accounting of sources and sinks reveals limitations in our current understanding, pushes forward the opportunity to develop process-based models and mechanisms to explain fluxes, and ultimately provides the practical knowledge on which management intervention can be based. In Calvert County, Maryland, a watershed model developed under a U.S. EPA STAR grant has produced a spatially explicit model of nitrogen loading in response to various development scenarios, showing the potential to assist decision-makers confronting further growth in their region (<http://www.uvm.edu/giee/PLM/>).

Land Use and Nutrient Loading

Loading of surface waters with N and P is a well-recognized cause of their degradation (Carpenter et al. 1998, Correll 1998), and much of this N and P delivery is the consequence of changing land use. The replacement of forest or other natural vegetation by agricultural land is a

well-established correlate of elevated nutrient levels (Jordan et al. 1997a). Omernik et al.'s (1977) comparison of 175 small watersheds differing in land use and lacking point source inputs demonstrated a strong correlation of N and P concentrations with fraction of land in agriculture. Percentage of cropland explained 75% of the variation in nitrate concentrations in watersheds of the coastal plains adjoining Chesapeake Bay (Jordan et al. 1997a), and 73% in piedmont watersheds (Jordan et al. 1997b). In small sub-watersheds of the Saginaw Basin, land use explained over half of the variation in nitrate and TN (Johnson et al. 1997). In Illinois, the ratio of forest to agricultural land explained as much as 92% of the variance in nitrate, or a non-significant fraction, depending on season (Osborne and Wiley 1988). Across tributary and mainstem sites of the River Raisin in southeastern Michigan, the ratio of agricultural to forested land explained nearly 94% of total variance in nitrate concentrations (Castillo et al. 2000).

In general, phosphorus concentrations and loads do not correlate with land use as consistently as does nitrogen. Smith et al. (1987) analyzed water quality data from more than 300 U.S. rivers from 1974 to 1981, and found few trends in P concentrations. Johnson et al. (1997) reported that shared land use and geology correlated with P concentrations throughout the Saginaw River Basin. In the Raisin River, soluble reactive phosphorus was best predicted by geology and point sources, rather than land use (Castillo et al. 2000).

There are several reasons why relationships are less clear between P and land use, and measurement difficulties may partly explain weak relationships reported in some studies. Phosphorus cycling is highly dynamic, cycling rapidly among its four basic fractions: reactive (inorganic) dissolved P, reactive (inorganic) particulate P, dissolved organic P, dissolved particulate P (Vaithyanathan and Correll 1992). It adheres readily to sediments, and so is exported mainly in particulate form during episodic stormflows, which can be difficult to

measure accurately. Comparing a cornfield to a hardwood forest and by intensive sampling of all P fractions, Vaithyanathan and Correll (1992) estimated watershed export to be seven times greater from the agricultural vs. the forested watershed. Particulate P accounted for 94% of total P export from the agricultural watershed and 77% from the forested watershed. Thus studies that measure only dissolved reactive phosphorus in the water column may provide insufficient data to examine this issue.

Literature-derived export coefficients for N and P from different land use/cover types are now widely used in planning and modeling studies. A classic review (Beaulac and Reckhow 1982) reported median values for TP export of about $2 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ for row crops, $1 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ for pastures, and $0.2 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ for forests. Local terrain, climate and geology of course result in some variation, but these coefficients compare well with a detailed study of some Chesapeake Bay watersheds. Jordan et al. (1997) report TP yields to range from 0.073 to $0.47 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ for inner Delmarva and outer Coastal Plains watersheds, $0.61\text{-}1.3 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ for central Coastal Plain, and $0.30\text{ to }4.0 \text{ kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ for watersheds of the Rhode River.

Similarly, TN export coefficients demonstrate the strong impact of land use. According to Beaulac and Reckow (1982), the average for row crops is $9 \text{ kg N ha}^{-1}\cdot\text{yr}^{-1}$ and for mixed agricultural lands is $15 \text{ kg N ha}^{-1}\cdot\text{yr}^{-1}$, although these values are somewhat lower than other studies have found. Jordan et al. (1997) estimated an N discharge of $2.9 \text{ kg N ha}^{-1}\cdot\text{yr}^{-1}$ for non-cropland and $18 \text{ kg N ha}^{-1}\cdot\text{yr}^{-1}$ for cropland. These estimates compare well with other estimates of N inputs to Chesapeake Bay of $20 \text{ kg N ha}^{-1}\cdot\text{yr}^{-1}$ for cropland, $5.8 \text{ kg N ha}^{-1}\cdot\text{yr}^{-1}$ for pasture, and $1.4 \text{ kg N ha}^{-1}\cdot\text{yr}^{-1}$ for forest. Clearly, variation in export of TN is mostly explained by the proportion of cropland in watersheds.

Eutrophication in the Great Lakes

The Laurentian Great Lakes system is the largest body of freshwater in the world, and includes within their combined watersheds nearly 25% of the U.S. and Canadian population. Despite their tremendous volumes, even the Great Lakes are not immune to the process of cultural eutrophication. Beeton (1965) was able to document chemical and biological changes associated with increases in sodium, chloride, sulfate and total dissolved solids in all of the Great Lakes except for Lake Superior. Water quality problems associated with eutrophication in the Great Lakes have been well described (IJC 1970), including issues related to excessive algal growth, changes in phytoplankton composition, turbidity, taste and odor problems, and promotion of anoxic conditions (Burns and Ross 1972). Historically, the demands placed on this freshwater resource and conflicts concerning its use have resulted in reduced water quality and impaired beneficial uses.

One of the most significant impacts of eutrophication in the Great Lakes was the creation of anoxic zones in the central basin of Lake Erie, as well as in various embayments such as Green Bay and Saginaw Bay. Increased production of organic matter resulting from increased nutrient supplies resulted in increased oxygen consumption due to respiration and decomposition. Once the lakes are thermally stratified a significant portion of the oxygen depletion occurs in the hypolimnion as particulate matter settles through the thermocline. The hypolimnion is essentially isolated from the surface and from re-oxygenation, thus oxygen-consuming processes ultimately lead to anoxia depending on such factors as temperature, volume of the hypolimnion, and the flux of organic matter. The development of anoxia impacts the entire benthic community as well as coldwater pelagic fish species that may be trapped there because of thermal requirements.

The historical depletion of silica concentrations is another example of the impact of eutrophication in the Great Lakes. In Lake Michigan, dissolved silica concentrations have been depleted from levels of 5 mg/L to maximums of only 1.5 mg/L. This change resulted from the increased diatom productivity associated with phosphorus inputs and the subsequent loss of silica through sedimentation and burial. This depleted silica supply has forced a shift in species composition of phytoplankton to non-siliceous forms, including less desirable forms of bluegreen species (Schelske and Carpenter 1992).

Great Lakes Management

In 1972 the Great Lakes Water Quality Agreement (GLWQA) was established between Canada and the U.S to restore and maintain the chemical, physical, and biological integrity of the Great Lakes. An original assessment by the IJC Water Quality Board in 1973 resulted in the listing of 42 Areas of Concern (AOC) where specific beneficial use impairments were identified including such issues as fish advisories, toxic contamination, degraded aquatic communities and eutrophication (Freedman and Monson 1989). AOCs remain a top priority for the federal, state, and provincial managers and each have been subjected to the development of remedial action plans. Another important policy aspect of the GLWQA was the establishment of Lakewide Management Plans (LAMPs) for each of the lakes. These management plans are intended to provide a systematic and comprehensive approach to managing the ecosystem and are designed to identify sources, pathways, and concentrations of critical pollutants. The plans are intended to address remedial actions for reducing pollutant loading including a watershed management plan for nonpoint source pollutants.

The initial Great Lakes Water Quality Agreement of 1972 identified phosphorus as the nutrient of primary concern and defined target phosphorus loads for each of the lakes based on a

technological approach of requiring all municipal discharges with flows in excess of 1 MGD (million gallons per day) to reduce their effluent TP concentration to less than 1 mg/L (Figure 3). In addition to upgraded sewage treatment plants, a program was initiated to greatly limit the amount of phosphorus in laundry detergents. This approach was estimated to have cost approximately 10 billion dollars to implement.

Subsequent research in the area of eutrophication led to the development of the nutrient loading concept. This concept proposes that quantifiable relationships exist between the quantity of phosphorus entering a water body and the responses to this input as expressed through specific water quality parameters or trophic indices (Vollenweider et al. 1980). Water quality modeling efforts initially focused on establishing predictive relationships between phosphorus loading and resulting in-lake phosphorus concentrations. Statistical relationships then were utilized to establish predictions in key water quality parameters such as algal biomass, water clarity, and hypolimnetic dissolved oxygen concentrations (see Bierman 1980). Based on this improved understanding and quantitative assessment, new target loading rates for each lake were established in the 1978 GLWQA Amendment on the basis of achieving specific phosphorus concentrations that would result in desired water quality conditions. A major focus was to restore year-round aerobic conditions in the bottom water of Lake Erie, to reduce algal biomass to levels that would not produce nuisance conditions, and to maintain the upper lakes in oligotrophic conditions.

Phosphorus control programs implemented as part of the GLWQA were successful in reducing annual phosphorus loads in all five of the Great Lakes (Fig. 3). Current phosphorus loads for Superior, Michigan, and Huron are at or below the specified target levels in the GLWQA and are near target levels for Erie and Ontario (SOLEC 1995). Similarly, in-lake

phosphorus concentrations in the upper lakes and Lake Ontario have been reduced as expected from the modeling estimates. Concentrations in the Lake Erie have been more variable and have fluctuated around the stated objective. This discrepancy reflects the smaller volume of Lake Erie as well as the greater influence of nonpoint source loads in this lake. Since the adoption of phosphorus control strategies in response to the GLWQA, an increasingly significant portion of the phosphorus load to the lakes can be attributed to land-derived nonpoint sources. Between 1968 and 1976, remedial measures reduced Lake Erie annual point source load from 18,200 to 6,600 mtons (IJC 1980). Despite this tremendous reduction, the Phosphorus Management Task Force of the IJC concluded that point-source control programs alone would not result in meeting set target load of 11,000 mtons (Richards 1985). It should also be noted that current loading rates have not resulted in establishing year-round aerobic conditions in central Lake Erie. Indeed, there have been several recent newspaper articles about the increase in the extent of anoxia and there appears to be a significant increase in research funding and activity directed towards this issue. One hypothesis is that the increased anoxia is resulting from a fundamental shift in how energy and organic matter production is cycled now that zebra mussels are present. However, an earlier governmental report (SOLEC 1995) stated that loads as low as 5000 mton/yr may be needed to achieve this objective. There is even some evidence to suggest that seasonal periods of anoxia may be inherent to the basin and that they existed even before European settlement.

Current Paradigm

Since the establishment and spread of dreissenid mussels it has become more and more recognized that the fundamental relationships between phosphorus concentrations and water quality that have guided over 3 decades of management are no longer valid. Filtering activity by

mussels dramatically impacts phytoplankton standing stocks and composition and has resulted in a de-coupling of previously described chlorophyll-phosphorus relationships (Mellina et al. 1995). For example, Nicholls et al. (1999) documented that the amount of variance in chlorophyll concentrations in Lake Erie that could be explained by variance in TP was reduced from 75% to only 14% after mussels become established. Holland et al. (1995) documented a 90% reduction in the abundance of diatoms in post-mussel years in western Lake Erie despite no significant changes in TP and actually increased concentrations of dissolved nutrients. The authors termed this phenomena “biological oligotrophication” to denote a reduced level of biomass and productivity despite an adequate or unchanging supply of nutrients. These fundamental shifts in the ecology of the lakes have profound implications for how the lakes should be managed and whether the capacity of our valuable sports and commercial fisheries may be irreversibly changed. A special symposium at the 1999 IAGLR conference debated a proposal to increase levels of phosphorus into the lower lakes in order to increase their productivity and support the thriving sport fishing industry. This notion would directly contradict the basic management strategy of the Great Lakes over the past 35 years and would undermine the more than \$10 billion investment in infrastructure and technology applied to phosphorus loading control. More importantly, the complexity of the ever changing food-web structure in the lakes does not permit for such a direct manipulation of increased nutrients to generate increased production of desirable fish species. Fisheries management and water quality management operate at opposite ends of the spectrum (top-down vs. bottom-up) and generally evolved independently in the Great Lakes. To fully protect all of the beneficial uses of this tremendous resource we need to develop a holistic, ecologically oriented management approach that addresses the complex food-web interactions and the multiple stressors that occur within the basin.

Nutrient Ratios and Stoichiometry

The role of nitrogen in lake eutrophication has received little attention relative to the role of phosphorus. Yet numerous studies, at scales from algal cultures to whole lake manipulations, have demonstrated that interactions between N and P can impact algal productivity (see Smith 1982). Sakamoto (1966) noted that chlorophyll yield in Japanese lakes was in balance with both TN and TP concentrations when the ratio of the two nutrients was between 10 and 17, whereas yield was dependent only on TN when ratios were <10 and only on TP when ratios were >17 . An empirical analysis of 228 north temperate lakes revealed that chlorophyll yield was best described by both P concentration and the TN:TP ratio (Smith 1982), suggesting that variability in the TN:TP ratio may directly effect phosphorus-chlorophyll relationships. Similarly, Downing and McCauley (1992) reported that TN:TP varied significantly with lake trophic status. They found that TN:TP ratios were high in oligotrophic lakes and declined in a curvilinear fashion as the amount of TP increased. They also concluded that variation in the TN:TP ratio was mainly a function of nutrient sources supplying the lake. Lakes with high TN:TP ratios tended to exist in mostly natural, undisturbed watersheds with very little point source inputs.

Competition theory suggests that the ratio of the supply rates of two biologically limiting nutrients can strongly influence species dominance (Tilman 1982). For aquatic ecosystems, the N:P supply ratio has been shown to be a key determinant of the variation in community structure (Hecky and Kilham 1988; Kilham 1990). Beyond the immediate effect on primary producers, seston N:P ratio is an important determinant of food quality and has also been shown to significantly effect the growth and reproduction of certain zooplankton species (Sterner et al. 1993). Furthermore, the structure of a lake's food-web itself will exert considerable influence on the cycling and availability of nutrients (Sterner et al. 1992). The supply of nutrients into the

dissolved, biologically available pools is regulated by many interactions. Allochthonous loading from rainfall, runoff, and groundwater are mediated by autochthonous sources, sinks, and transformations through various processes such as N-fixation, nitrification, denitrification, sedimentation, and transport. On a regional scale, the addition of lakes to the landscape will increase the C:P and N:P ratios in streams, as lakes selectively retain P relative to N (Schindler et al. 1976).

The effects of N:P ratios on algal biomass result from differences in the nutrient physiology of different algal species. Smith (1982) summarized previous work in this area and noted that the optimal N:P ratio of various algae ranged from a minimum of 4 for the blue-green alga *Microcystis* to nearly 38 for the chlorophyte *Scenedesmus*. The approximate 10-fold variation in N:P ratios for phytoplankton is however significantly less than the range of N:P ratios found in lakes and nutrient sources, which may vary by 100 to 1000-fold (Downing and McCauley 1992). This disparity in supply versus demand again indicates how the N:P ratio can influence algal production and composition. One can even conclude that the N:P ratio itself may be 'limiting' i.e. mis-matched to the population of algae present in the lake and reduce expected levels of production (Smith 1982). However, Smith recognized that eutrophication management in fresh water should not focus on nitrogen because it is much less economical to control and has a much more complicated biogeochemistry with respect to its biological reactivity in the gases phase. Furthermore the typical dissolved N:P ratio in river water supplying lakes is generally replete with N relative to the required stoichiometry for optimum algal growth (Heckey et al. 1993) and P has clearly shown to be the most critical nutrient limiting production in most lakes (Schelske and Stoermer 1971; Schelske 1986).

Nutrients and Fish Production

The influence of nutrient and carbon loading from river estuaries on fish production has received increased attention in many ecosystems. The history of cultural eutrophication, then oligotrophication (Stockner et al. 2000, Hjerne and Hansson 2002) of the Great Lakes indicates that terrestrial inputs can strongly contribute to the net productivity of these systems, and suggests that in the future estuarine loading may play an increasingly important role in overall Lake metabolism and fisheries production. However, there is, at present, little direct measurement of the pertinent flux rates and almost no quantification of extent of riverine influence in the coastal zones.

Since 1970, Great Lakes aquatic ecosystems have been characterized by dramatic changes in fish communities due to coincident reductions in nutrient loadings, introductions of exotic species, and fisheries regulations. Nutrient reductions imposed by the Clean Water Act of 1970, introduction of Pacific salmonids and rehabilitation of native predator stocks (lake trout *Salvelinus namaycush*, walleye *Stizostedion vitreum*), control of sea lamprey *Petromyzon marinus*, and an ecosystem-based approach to fisheries management have improved water quality and balanced predator and prey fish communities. In western Lake Erie, for example, reduced phosphorus loadings (Neilson et al. 1995) have resulted in lowered primary and secondary production, reduced bottom anoxia, and recovery of benthic macroinvertebrate species. As in most lakes, the effects of nutrient reduction in Lake Erie coincided with recent invasion by zebra mussel *Dreissena polymorpha* which increased water clarity in shallow water areas and shunted primary production from the planktonic food web into benthic pathways. The resultant changes in physical habitat and lower trophic levels are believed to have altered fish community composition, with recovery of species intolerant of eutrophic conditions and decline

of eutrophy-tolerant species (Ludsin et al. 2001), and altered population dynamics of selected fish species (Gopalan et al. 1998, Pothoven et al. 2001, Tyson and Knight 2001). The relative contributions of zebra mussel invasion and nutrient reduction to the recovery of the Lake Erie ecosystem are unclear, as most significant changes occurred after 1990. Growth and recruitment of omnivorous yellow perch *Perca flavescens* increased since 1990 with increased consumption of *Hexagenia* mayflies, a large benthic organism that disappeared from the lake under eutrophic conditions and recovered as water clarity improved, macrophyte density increased, chlorophyll a declined, and sediments became well oxygenated (Ludsin et al. 2001). The observed increase in yellow perch growth was higher than would be expected from a density-dependent growth response to reduced abundance, suggesting mayflies significantly improved perch growth.

Recent research by Ludsin and Stein (2001) suggests an improved correlation between upland nutrient sources and fisheries recruitment in western Lake Erie. Before 1987, there was no significant relationship between river discharge and young yellow perch abundance. After 1987, the relationship is positive and significant (Figure 4), suggesting watershed nutrient loadings may act to increase perch survival through stimulation of lower trophic levels. Ludsin et al. (2001) found a unimodal relationship between phosphorus concentrations and fish species diversity in western and central Lake Erie (Figure 5). The reduction in nutrient loadings from 1970s to present caused an increase in species diversity in the eutrophic western basin, and a decrease in diversity in the more oligotrophic central basin.

Fishes can have important effects on aquatic nutrient cycles because they can advect nutrients through immigration or emigration from spawning and nursery habitats, or alter zooplankton communities through size selective predation, which may affect the rate of N and P recycling. Fish also excrete nutrients that can be important to phytoplankton, especially for

benthivorous fishes which may translocate nutrients from the bottom to the pelagia. In some lakes, over half of the epilimnetic biomass of phosphorus is concentrated in fish biomass (Nakashima and Leggett 1980, Kraft 1992). Salmon and eel migrations have been recognized as important nutrient and energy transport mechanisms in coastal stream and lakes (eg Kline et al. 1990, Bilby et al. 1996), as has migration of clupeids into tidal streams and coastal marshes (eg. Durbin et al. 1979). Nutrient and energy inputs to coastal ecosystems by clupeids have been greater than eventual loss through juvenile emigration, although for some species the export is a significant fraction of the total estuarine production. Deegan (1993) calculated that N and P exports by gulf menhaden (*Brevoortia patronus*) from a Louisiana estuary to coastal Gulf of Mexico waters were of the same magnitude and more biologically available than passive waterborne exports. The menhaden biomass exported amounted to 5-10% of total estuarine primary production. Durbin and Durbin (1998) estimated that nitrogen exported in juvenile menhaden emigrating from Narragansett Bay comprised between 3-7% of total annual nitrogen exports.

The importance of fish to nutrient export to Great Lakes coastal systems is relatively unknown but potentially significant. Many Great Lakes potamodromous fishes (salmonids, walleyes, lake sturgeon, suckers) convey carbon and nutrients from Lake Michigan to tributaries during spawning migrations, and convey nutrients back to Lake Michigan during larval drift or active out-migrations. Jude and Pappas (1992) suggested that up to 90% of all Great Lakes fishes are dependent on coastal wetlands for some part of their life histories. Despite the perceived importance, there are few actual measurements to support or deny the hypothesis that fish are important mediators of nutrient transport in Great Lakes systems. Rand et al. (1992) estimated that anadromous spawning runs of chinook salmon contributed a negligible fraction of

the total phosphorus available to the Salmon River, a Lake Ontario tributary. Brazner et al. (2001) estimated the net flux of nutrients mediated by migrating fishes from coastal wetlands to nearshore zone in Lake Superior. They calculated a net efflux of carbon, nitrogen and phosphorus by fishes from the wetlands to the nearshore zone, primarily attributed to emigration of juvenile yellow perch and brown bullhead *Ictalurus nebulosus* during summer. The net contribution of nutrients transported by fishes was relatively minor compared to background nutrient levels in the nearshore zone. Nitrogen and phosphorus export by fish was 1-2 orders of magnitude lower than estimated dissolved exports observed in fish. The net export of carbon, nitrogen and phosphorous in fish amounted to no more than 0.002% of the estimated total nutrient biomass in the nearshore zone.

We (Rutherford et al., in progress) have attempted to estimate potential loadings of nutrients advected by anadromous fishes to Lake Michigan from three tributaries where fish have been sampled. The Muskegon River, Manistee River, and Pere Marquette River each drains into wetlands and lakes that connect to eastern Lake Michigan through relatively narrow channels. Abundance and biomass estimates of migrating juvenile or adult fishes were converted to nutrient biomass estimates through average weights of fish and assumed weight-specific nutrient composition values (9.52% for carbon, 2.54% for nitrogen, 0.5% for phosphorus – Schindler and Eby 1997, Brazner et al. 2001). The estimates made of juveniles emigrating from tributaries to Lake Michigan come from electrofishing surveys (Carl 1982, Rutherford unpublished data) or traps (Zafft 1992, Seelbach 1993, Rutherford unpublished data), or were estimates made from spawning adults and assumed fecundities and survival of eggs and migrating fry. Estimates of salmonid smolts stocked into tributaries were available from Michigan DNR records. The estimates of numbers of adults migrating up rivers to spawn come from Michigan DNR creel

surveys or weir counts, or from electrofishing surveys conducted by hydropower relicensing programs (Lawler et al. 1991).

Although the numbers of migrating juveniles and adults were quite large in each river, the import or export of nutrients mediated by fish migration was insignificant relative to total loading estimates (Tables 1-3). Total loadings of nutrients exported from these rivers ranged from 5 to 15 million kg organic Carbon, from 0.7 to 1.3 million kg total Nitrogen, and from 41 to 66,000 kg total phosphorus (Table 3). Seasonally, the highest pulse of nutrients occurs in spring, coinciding with the spring plankton bloom that precedes hatch and migration of many lake fishes (rainbow smelt *Osmerus mordax*, alewife *Alosa pseudoharengus*, yellow perch, lake whitefish *Coregonus clupeaformis*, salmonids) into the nearshore zone to forage (Jude et al. 1987).

Numbers of emigrating fry and juveniles ranged from 20 to 25 billion individuals in the 3 rivers examined. The emigrating species groups included salmonids, suckers, walleye, and alewife, and in the un-impounded Pere Marquette River, juvenile northern pike *Esox lucius* and burbot *Lota lota*. Although numerous, the emigrating juveniles were small in mass, and the total biomass of nutrients exported through fish outmigration contributed a relatively minor fraction of total terrestrial input to nearshore Lake Michigan. For example, in the Muskegon River, juvenile fishes transported approximately 0.01% of organic C, 0.08% of total N, and 0.16% of total P estimated from loading measurements (Tables 2, 3).

The contribution of anadromous adult fishes through spawning, death and decomposition to upstream nutrient habitats represented a higher fraction of total nutrient loadings exported to Lake Michigan, but was still insignificant. In the Muskegon River, nutrients deposited through mortality and decomposition of spawning anadromous fishes may contribute 0.09% of organic C, 0.5% of total N and 1.1% of total P exported from the watershed. Therefore, the estimated

input of nutrients to the watershed via spawning adults is approximately 5 to 9 fold higher than the output mediated by migrating juveniles. On a relative basis, the proportional contributions of fish to tributary nutrient fluxes were similar in the three Lake Michigan tributaries examined.

Although the actual transport of nutrients by fishes is small relative to total loading measurements, it may be disproportionately important to the ecology of upland and coastal ecosystems. For example, small emigrating juveniles represent highly available sources of nutrients to larger fishes and invertebrates in the coastal ecosystem, and eggs from spawning adults can provide high energy food source to macroinvertebrates and fishes in rivers.

Growth rates of some aquatic taxa can be limited by accumulation rate of an element rather than by energy. If a consumer has a higher growth requirement of an element than is provided in its food, the consumers' growth may become limited by the availability of that element. Laboratory studies have suggested that zooplankton growth can be limited by quality of their phytoplankton prey (low N:C or P:C ratios – Sterner and Hessen 1994). Schindler and Eby (1997) explored the potential for fishes to be limited by the stoichiometric ratios of their prey. Specifically, they investigated whether growth of fishes be limited by phosphorus content of their prey. Through energetics analysis of fish growth and analysis of N:P ratios of fishes and their prey, they found that P-limitation of fish growth is extremely rare in nature. Fish growth is almost always limited by availability or consumption of energy.

Fish may play an important role in recycling nutrients in lakes through consumption of biota at lower trophic levels and excretion in the pelagic zone. In oligotrophic systems, fish may significantly influence the amount of chlorophyll available through consumption and excretion. Experimental studies of nutrient and fish additions to oligotrophic streams in Alaska indicated

that fish significantly increased chlorophyll concentrations through alteration of the stream food web in addition to nutrient excretion.

Research and Management Challenges

Clearly the intertwined topics of nutrient loading, eutrophication, and regional-scale mass balance analyses offer enormous opportunities for research and challenges for management. With a collective volume of 24,620 km³, the Laurentian Great lakes are the largest body of freshwater in the world, exceeding even Lake Baikal's 23,000 km³ volume. Impacts to the lakes are intertwined and ever-changing. Nutrient supply has been enormously altered by human urban, agricultural and industrial developments, affecting both P and N, the dominant nutrients of cultural eutrophication in fresh and coastal waters respectively. The Great Lakes nutrient dynamics have been strongly influenced by P loading, prompting hugely expensive and highly successful control measures aimed at point sources. Today, in a surprising reversal, this success combined with altered energy pathways brought about by the zebra mussel invasion has prompted some to argue for increases rather than decreases to P loads. Management of Great Lakes nutrient levels is further complicated by uncertainties regarding the importance of nutrient ratios vs. nutrient levels, and by the translocation of nutrients by fishes, including during upstream migrations whereby anadromous fishes can strongly influence productivity in upper watersheds.

Mass balance analyses have emerged as a powerful approach to understand nutrient inputs, outputs, and transformations at scales ranging from small watersheds, to regions such as the Laurentian Great Lakes Basin, to the globe. Nitrogen in particular has attracted much

attention because of the extent of human alteration of N supply, its many environmental impacts, and its suitability for such accounting. A full understanding of the multiple impacts of altered N cycling on the coupled terrestrial-aquatic ecosystems of the Great Lakes is a major scientific challenge of great practical importance.

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Table 1. Estimated numbers (No.) and wet weights (wt., kilograms) of immigrating adults by species in the Muskegon, Manistee and Pere Marquette River tributaries to Lake Michigan.

Species	Muskegon		Manistee		Pere Marquette	
	Wt (kg)	No.	Wt. (kg)	No.	Wt. (kg)	No.
Chinook	4.5	20,000	4.5	20,000	4.5	20,000
Steelhead	2.3	20,000	2.3	20,000	2.3	20,000
Coho	2.5	500	2.5	500	2.5	500
Suckers	0.9	42,340	0.9	38,000	0.9	48,780
Walleye	1.0	200,000	1.0	30,000	1.0	128,400
Alewife	0.3	73,500	0.3	73,500	0.3	107,000

Table 2. Estimated numbers (No.) and average wet weights (Wt., grams) of emigrating juveniles by species in the Muskegon, Manistee and Pere Marquette River tributaries to Lake Michigan. ***indicates average weight of wild and stocked hatchery juveniles.

Species	Muskegon		Manistee		Pere Marquette	
	Wt.	No.	Wt.	No.	Wt.	No.
Chinook	3.3***	510,260	2.1***	252,576	5.3	88,285
Steelhead	53.4***	77,000	53.4***	60,000	53.4	42,372
Suckers	0.0005	$105.8 * 10^6$	0.0005	$193.9 * 10^6$	0.0005	$882.8 * 10^6$
Walleye	0.0020	$1.35 * 10^9$	0.002	$506.3 * 10^6$	0.0020	$2.31 * 10^9$
Alewife	0.0005	$1.47 * 10^9$	0.0005	$470.0 * 10^6$	0.0005	$2.14 * 10^9$
Nor. Pike					5.1	180,000
Burbot					1.0	200,000

Table 3. Estimates of annual loadings (1,000 kg/yr) of organic carbon (POC, DOC), total nitrogen and total phosphorus from the Muskegon, Manistee and Pere Marquette River tributaries to Lake Michigan, and nutrients transported by fish migrations. Major migratory species groups were salmonids (chinook salmon, rainbow trout, coho salmon), walleye, suckers (white sucker, longnose sucker, redhorses), alewife, and in the Pere Marquette, northern pike and burbot. Juvenile or adult fish abundance estimates were converted to nutrient estimates through average weights of fish and assumed weight-specific nutrient composition values (9.52% for carbon, 2.54% for nitrogen, 0.5% for phosphorus – Schindler and Eby 1997, Brazner et al. 2001). Numbers of adults (Table 1) were adjusted by estimated spawning mortality rates to calculate nutrient biomass imported by fishes.

River	Total Loadings			Export by Fish			Import by Fish		
	C	N	P	C	N	P	C	N	P
Musk.	15,130	672	66	1.964	0.542	0.107	13.2	3.5	0.7
Manis.	13,000	1,160	74	0.482	0.129	0.025	11.6	3.0	0.6
P.M.	5,000	1,335	41	0.843	0.225	0.044	16.2	4.3	0.9

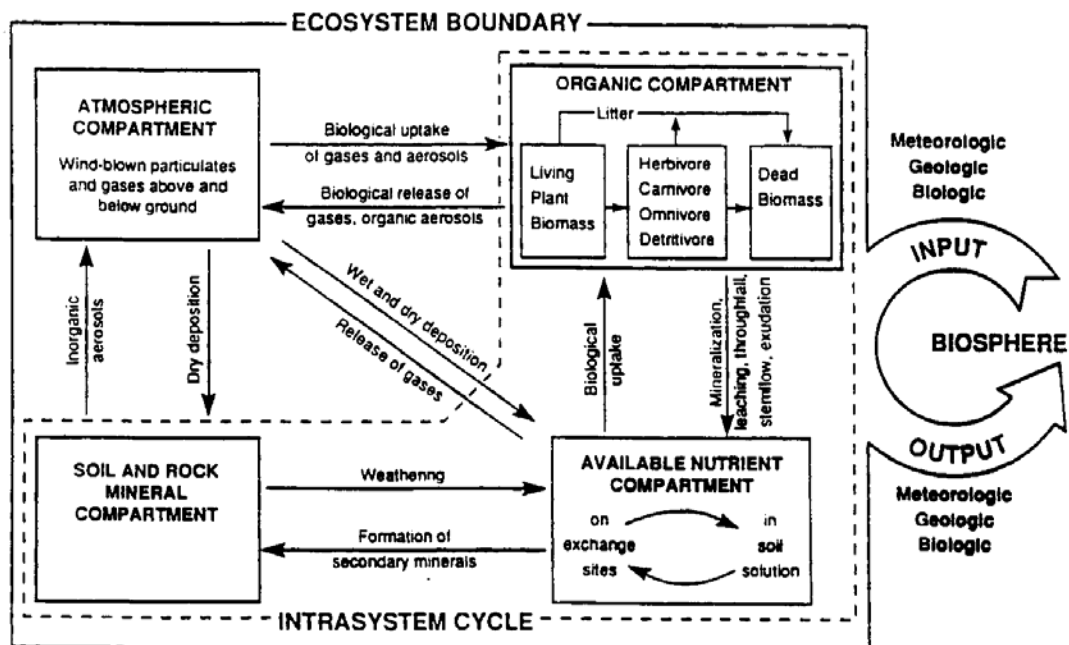


Figure 1. Model of nutrient relationships for a landscape-watershed ecosystem. From Likens 1992 and 2001.

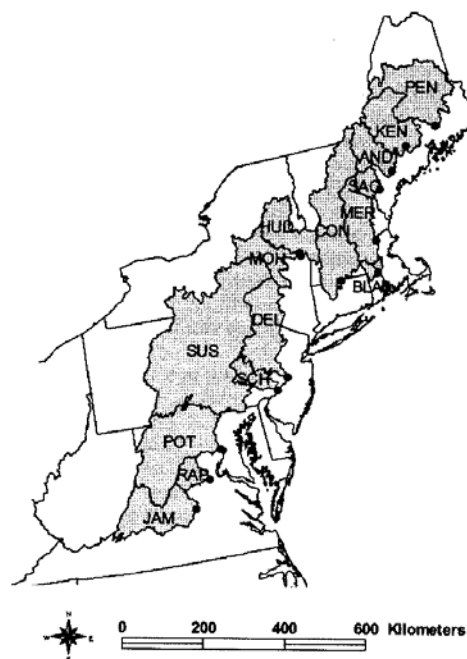


Figure 2. The sixteen river basins from Maine to Virginia that were examined for nitrogen inputs, exports, and sinks. From Boyer et al. 2002.

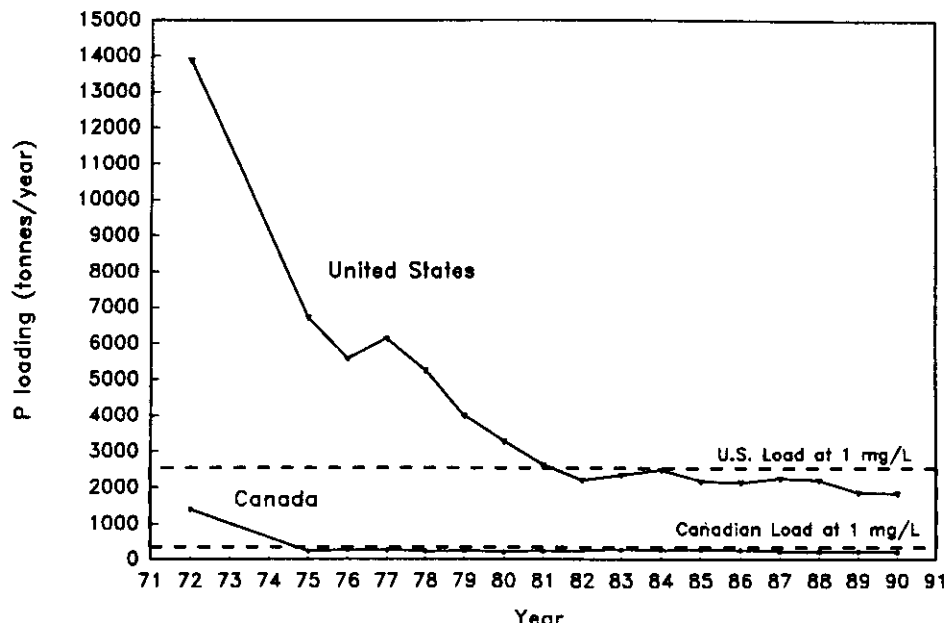


Figure 3. The decline in reported phosphorus municipal loadings to Lake Erie demonstrates the success of point source reductions as major waste-water treatment plants were limited to 1 mg/L total phosphorus in their effluent by the 1972 Great Lakes Water Quality Agreement. The horizontal dashed lines show expected loadings under full compliance. Continued improvements reflect better than target performance by larger plants as well as compliance by additional smaller plants. Further reductions in point source loadings is not considered practical. The target load of 11,000 metric tonnes per year for Lake Erie is met in dry but not wet years, because P runoff is greater in wet years. Of total loadings, municipal sources contribute approximately 2,000 to 2,500 tonnes, demonstrating that other (nonpoint) sources of P are of much greater importance. From Dolan (1993).

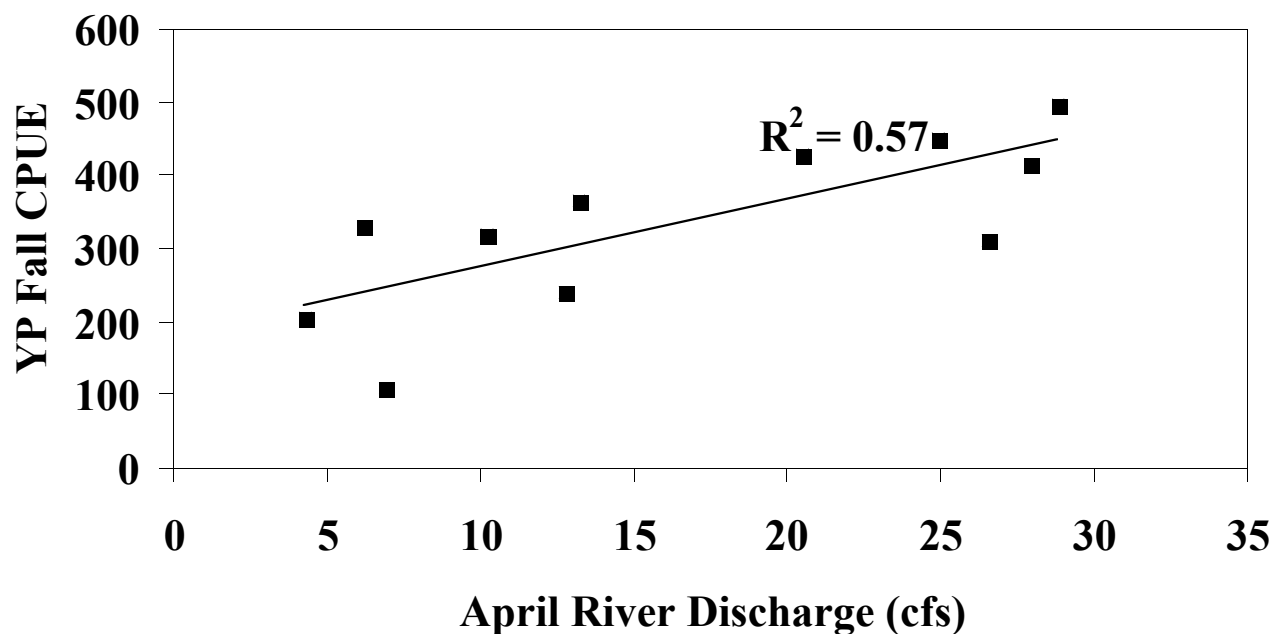


Figure 4. Relationship between cumulative discharge (cfs) of the Maumee and Sandusky Rivers, and fall catch per unit effort of age 2 yellow perch (recruits) in survey trawls in western Lake Erie, 1987-present. Unpublished data from Stuart A. Ludsin, University of Windsor. Reproduction without the express written permission of the author is prohibited.

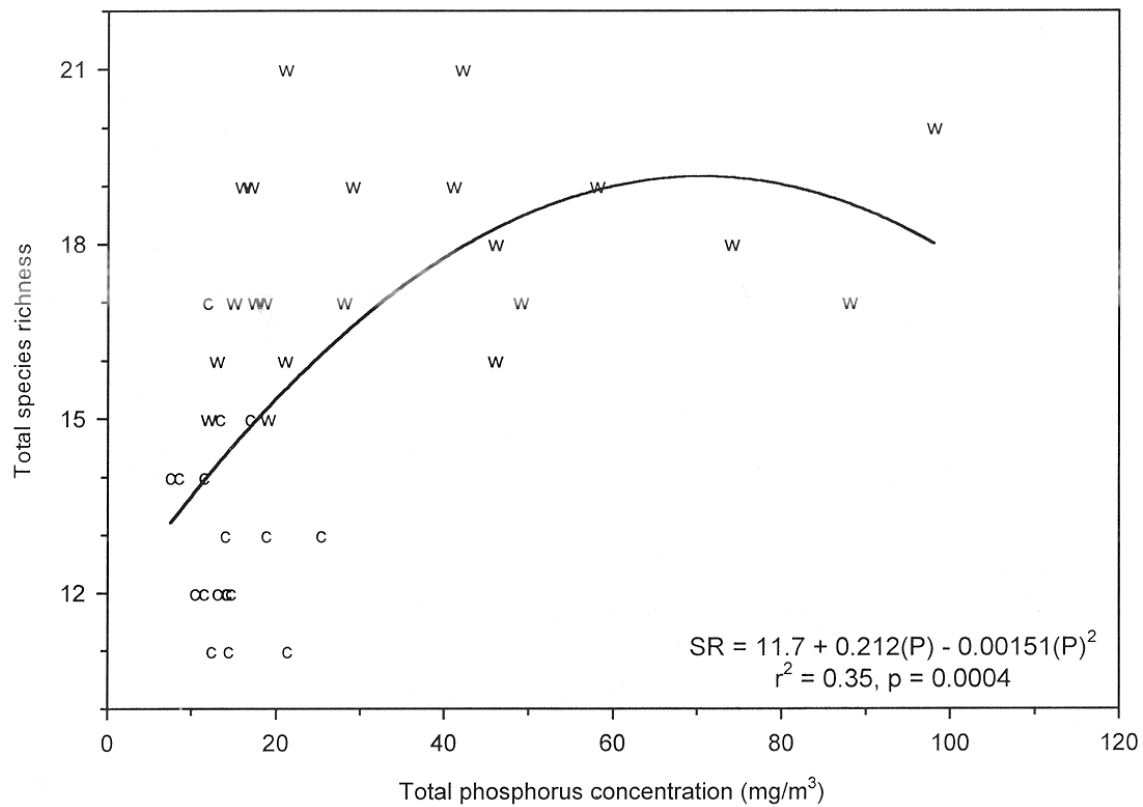


Figure 5. Relationship between phosphorus loadings and fish species richness in the western (w) and central (c) basins of Lake Erie. From Ludsin et al. 2001.