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Water Quality and Movement in Agricultural Landscapes

Stephen K. Hamilton

Water quality refers to the physical, chemical, and biological characteristics of surface waters and groundwaters that determine their suitability for use by humans and aquatic life. Both natural and managed landscapes provide an important ecosystem service by maintaining water quality, which is key for water supply, recreational use, aesthetic values, and biodiversity, including fish and wildlife habitat. The upper U.S. Midwest is a region endowed with abundant groundwater, lakes, and wetlands as a result of a glacial topography and humid climate. Within this region lies the Kellogg Biological Station Long-Term Ecological Research site (KBS LTER) in southwest Michigan, situated in a heterogeneous, largely rural landscape (Fig. 11.1). The region in the vicinity of KBS is ideal for comparative study of how water quality changes as water moves through landscapes and how the transport of nutrients via water movement through watersheds is affected by land use and land cover, human activities, and biogeochemical transformations in surface water bodies. Agricultural influences on water quality are of particular interest in the U.S. Midwest, where nutrient export from farmland to groundwaters, lakes, and streams can lead to high nitrate in drinking water supplies and to surface water eutrophication (i.e., excessive algal and plant growth).

Water-quality work at the KBS LTER has two major goals. The first is to improve our understanding of how water quality changes as water flows across the landscape, including the effects of natural processes as well as changes ascribed to agricultural row-crop management. A second goal is to examine how the movement of water through streams and wetlands may lead to changes in water quality that include retention or removal of nutrients of concern for eutrophication, and to investigate the specific processes responsible for the changes. Although the information presented is largely from the KBS region, it is generally applicable to landscapes with intensive agriculture.

In this chapter, I discuss the main effects of row-crop agriculture on water quality, as illustrated by findings from the KBS LTER and from studies in the KBS

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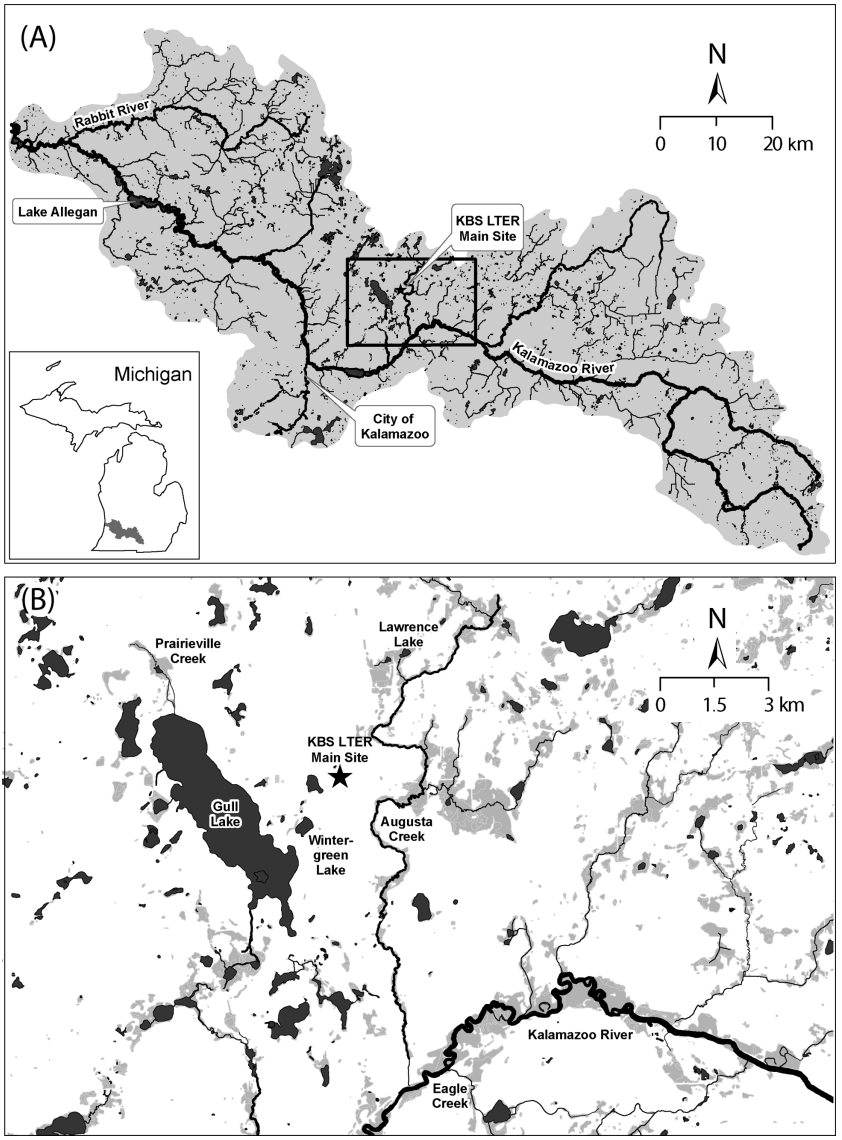

Figure 11.1. Location of the Kellogg Biological Station Long-term Ecological Research site (KBS LTER; within rectangle) in the (A) Kalamazoo River watershed, which includes Kalamazoo, the largest urban area. Enlargement of the rectangle area (B) shows lakes and streams in black and wetlands in gray. Surface-water features referred to in the text are labeled.

region that have shown how abiotic and biotic factors, including human activity, interact to determine water quality. I have organized the chapter by separating the landscape flow path into two distinct parts: (1) water movement from precipitation to soils and groundwater, and (2) receiving surface waters including streams, wetlands, and lakes. Unless noted otherwise, the data presented in this chapter are derived from water samples collected from 1996–2009 using consistent methods as detailed in Hamilton et al. (2001, 2007, 2009). Most of the water samples were collected in nonurban regions of Kalamazoo, Barry, and Allegan counties, within

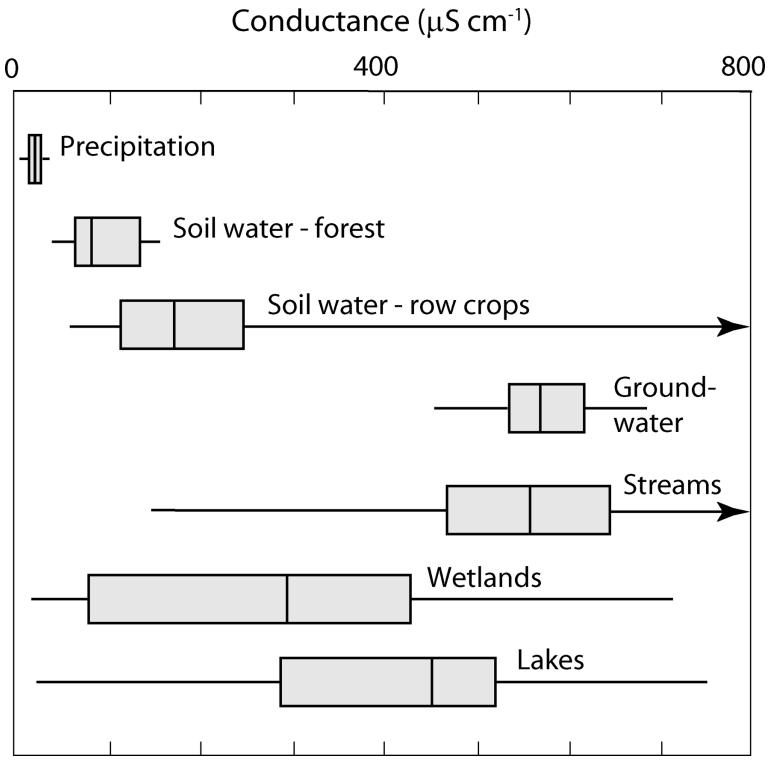

Figure 11.2. Distributions of specific conductance of precipitation, soil waters sampled at 1.2 m depth, groundwater pumped from residential wells, and surface waters. The conductance (corrected to 25°C) reflects the total ionic content. Boxes show the interquartile range and median, and lines show the range (arrows indicate outliers not shown here). Data sources: (i) Precipitation based on 30 years of year-round monitoring by NADP/NTN (2011) (volume-weighted means for 1979–2008; see Table 11.1); (ii) Soil water from forest based on 98 samples taken at three of the KBS LTER Main Cropping System Experiment (MCSE; Table 11.2) Deciduous Forest plots during Mar–Nov from 2000–2003 (Kurzman 2006); (iii) Soil water from row-crop fields based on 128 samples taken at three of the MCSE Conventional plots during Mar–Nov from 2000–2003 (Kurzman 2006); (iv) Groundwater based on 19 pumped well samples collected from 1996–2008; and (v) Streams, wetlands, and lakes based on means for sites (n = 245 streams, 174 wetlands, and 184 lakes), mainly from southwest Michigan except for lakes which were sampled across the Lower Peninsula of Michigan.

the Kalamazoo River watershed (Fig. 11.1) or just north of it in southern Barry County. A rich body of KBS research on the limnology and ecology of local lakes and streams that has been published since the 1970s aided in the interpretation of patterns and processes.

What can be learned from patterns of water chemistry across landscapes? By making simple measurements of specific conductance, we find that the total ion content of water changes dramatically across the landscape, and the patterns observed reflect biogeochemical processes along subsurface and surface flow paths (Fig. 11.2). Ion content increases greatly as water from precipitation passes through soils and the underlying unsaturated zone before reaching groundwater reservoirs. Streams largely reflect the chemistry of their groundwater sources. In contrast, lakes and particularly wetlands tend to have lower and more variable total ion contents, and hence specific conductances, mainly due to variable relative contributions of groundwater and direct precipitation. These changes in water chemistry have implications for the biological availability of nitrogen (N), phosphorus (P), and silicon (Si)—the nutrients that often limit aquatic primary production. Total ion content also affects mineral precipitation reactions—particularly those involving calcium carbonate—that, in turn, affect the transport and fate of pollutants. In this chapter, we evaluate landscape patterns in water quality, including both major ions and key nutrient forms, and consider how the effects of agricultural activities are superimposed on natural patterns and processes.

From Precipitation to Groundwater

Precipitation Amount and Variability

Southern Michigan's climate is continental and is significantly influenced by the Great Lakes. Mean air temperatures at KBS range from –3.8°C in January to 22.9°C in July (1981–2010; NCDC 2013). Mean seasonal cycles of precipitation and Thorthwaite potential evapotranspiration (PET) are typical for this part of North America (Crum et al. 1990, Fig. 11.3). From 1951 to 1980, the mean annual precipitation for KBS was 855 mm, and the difference between precipitation and PET was 124 mm. And during the next 30 years (1981–2010), the mean annual precipitation increased 17% (1005 mm). Total precipitation varies considerably from year to year; since 1996, water levels in a number of local wetlands and lakes near KBS site have varied over 1–2 m (for an example, see Robertson and Hamilton 2015, Chapter 1 in this volume), reflecting this interannual climate variability.

Hydrogeology and Landscape Flow Paths

Southwest Michigan's recently glaciated landscape is distinct because of its high degree of linkage between surface waters and groundwaters and the predominant influence of groundwater discharge on streams, rivers, most lakes, and many wetlands (Grannemann et al. 2008). The landscape geomorphology is largely a reflection of the most recent continental glaciation, when the Saginaw and Lake

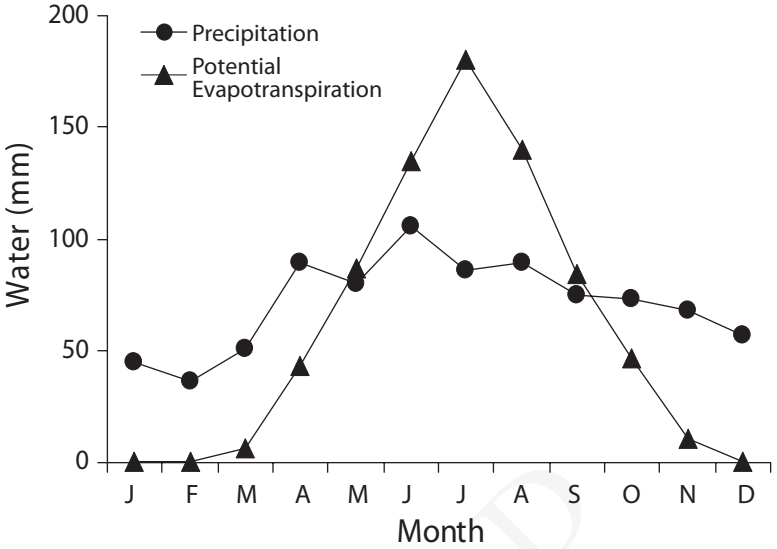

Figure 11.3. Monthly means of precipitation and potential evapotranspiration (Thornthwaite method) based on measurements at KBS from 1951–1980. Redrawn from Crum et al. (1990).

Michigan ice lobes converged in this area (Kincare and Larson 2009). As these lobes retreated beginning around 18,000 years ago, they left till plains and upland end moraines that contain sand and gravel mixed with finer materials. Outwash plains—with medium to coarse sand and gravel derived from the erosion of these moraines—were deposited by the general southward drainage of the glacial meltwaters (Rheaume 1990, Kehew et al. 1996). In the vicinity of KBS, the unconsolidated glacial till and outwash deposits extend to depths of 15–60 m, with the thinnest deposits found along the Kalamazoo River valley where elevations are lowest (Rheaume 1990). The bedrock lying beneath the glacial deposits is either the Coldwater Shale or, to the northeast, the Marshall Sandstone formation. The glacial deposits are so thick that bedrock outcrops are not found in the area.

Land around KBS drains southward toward the Kalamazoo River, a tributary to Lake Michigan with a drainage basin of 5260 km^2 (Fig. 11.1). The Kalamazoo River watershed is approximately 50% agricultural land (dominated by corn and soybean, with wheat and alfalfa as well), 33% unmanaged terrestrial uplands (mostly secondary deciduous forest and successional old fields), 7% lakes and wetlands, and 10% urban. Most agricultural land around KBS is naturally well drained and is neither tile drained nor ditched (Schaetzl 2009). Most of the area's abundant lakes and wetlands occupy depressions (kettles) formed by melting residual glacial ice, and many lack surface connections to other water bodies. The Kalamazoo River and its floodplain occupy an incised valley that formed from drainage of glacial meltwaters. Tributary streams reach the river through side valleys that dissect the outwash plains, and often originate in or pass through lakes and wetlands. A substantial fraction of the upland area contains undulating, hummocky terrain that is

difficult to assign to a particular stream watershed based on surface topography. Instead, analysis of groundwater levels in domestic water-supply wells can be used to reveal the direction and magnitude of underground flow and can provide a reasonable indication of watershed boundaries (Lusch 2009).

Hydrologic budgets for the Kalamazoo River watershed (Allen et al. 1972) show for a 34-year record (1933–1966) that of the period's 889 mm of annual precipitation, about 580 mm (65%) was returned to the atmosphere by evapotranspiration. Most of the remainder became river runoff, mainly via groundwater flow paths. The annual rate of groundwater recharge by precipitation in the area averaged 229 mm (26% of mean annual precipitation) and occurred mainly during the cooler months of November through May, when evapotranspiration rates are low (Fig. 11.3).

In general, surface runoff is low because glacial deposits in the watershed have high hydraulic conductivity, which facilitates infiltration. Thus, on a landscape scale most precipitation that is not evapotranspired readily infiltrates the soil and percolates to the water table, making groundwater flow paths especially important. Groundwater flow in turn supplies water to lakes, streams, and rivers. The hydrological linkages between ground and surface waters in the KBS LTER landscape resemble those well documented in the North Temperate Lakes LTER site in northern Wisconsin (Webster et al. 2006).

A hydrologic budget has been constructed for Augusta Creek (Fig. 11.1), the tributary of the Kalamazoo River draining ~90 km^2 of land including the eastern side of the KBS LTER sites (Rheaume 1990). For a year of average precipitation (1977: 950 mm), evapotranspiration returned 65% of the annual precipitation to the atmosphere (Fig. 11.4), the same percentage found by Allen et al. (1972) in earlier work on the entire Kalamazoo River watershed. The remaining 35% was discharged as stream runoff, of which an estimated 75% entered as groundwater flow, corresponding to an annual groundwater recharge rate of 248 mm (26% of precipitation in that year). Thus, the area around KBS, which includes the Main Cropping System Experiment (MCSE) of the KBS LTER (Robertson and Hamilton 2015, Chapter 1 in this volume), has a similar groundwater recharge rate to that of the overall landscape of the region.

While such hydrologic budgets provide a long-term water balance, they give no picture of the time scales of water movement through landscapes (Webster et al. 2006). Given the importance of groundwater flow paths and the large volume of groundwater reservoirs, transit times of water through these watersheds are undoubtedly long compared to watersheds in which overland flow is a more important route for water movement. Groundwater dating—using tracers such as industrial chlorofluorocarbon gases—shows that the mean age of groundwater sampled from water-supply wells in recently glaciated landscapes is often several decades (Saad 2008, Rupert 2008, Stewart et al. 2010, Hamilton 2012). Although the mean age of groundwater discharged into streams can be similar to that of water from groundwater wells, streams typically receive convergent groundwater flow paths of widely differing ages (Böhlke 2002). While groundwater dating based on tracers has not been conducted in the vicinity of KBS, a model for the Augusta Creek watershed shows the expected convergence of flow paths of widely varying distances and residence times to deliver water to the stream (Bartholic et al. 2007).

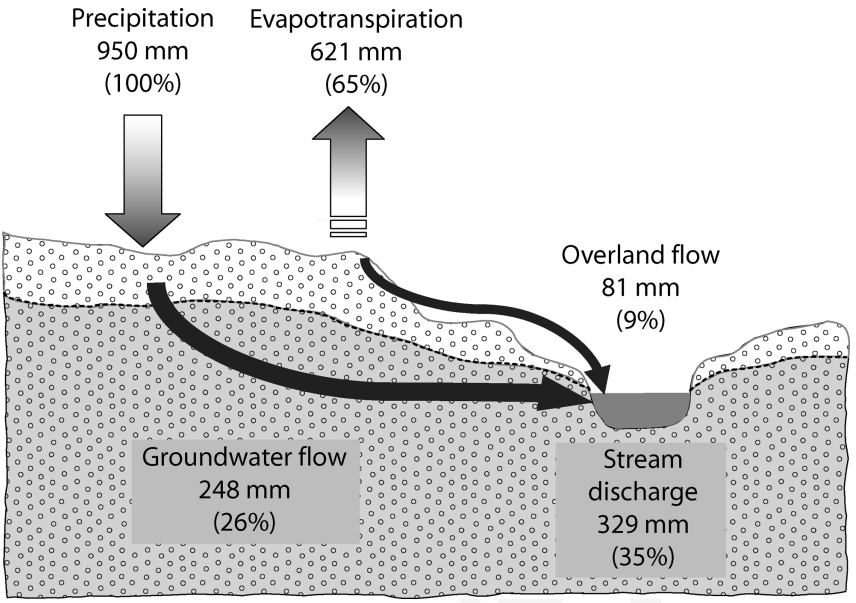

Figure 11.4. Water budget for the Augusta Creek watershed representing a year of average precipitation. Annual fluxes are expressed as equivalent depth of water over the watershed, and as a percentage of the annual precipitation. Shading represents the water table. Data from Rheaume (1990).

Precipitation Chemistry

On account of air pollution, precipitation at KBS is more acidic and enriched in nitrate (NO_3^-) and sulfate (SO_4^{2-}) than it would be otherwise (Table 11.1, Fig. 11.5), although concentrations of these anions and the accompanying acidity have been declining in recent years. Southwest Michigan is within a broad region of moderate to high acid deposition rates that extends across the midwestern and northeastern United States (Driscoll et al. 2001). High atmospheric deposition rates of NO_3^- and SO_4^{2-} in industrialized regions result from anthropogenic N and sulfur (S) oxide emissions, originating primarily from fossil fuel combustion. In addition, anthropogenic activities—particularly those dealing with livestock and fertilized crops—likely increase ammonium (NH_4^+) deposition (Konarik and Aneja 2008). From 1979 to 2010, the mean wet deposition rates of NH_4^+-N, NO_3^--N, and SO_4^{2-} at KBS were 3.09, 3.44, and 20.2 kg ha^{-1} yr^{-1}, respectively. Sources and fluxes of organic N and P in atmospheric deposition have not often been measured and are not well understood. Total (wet + dry, or bulk) deposition rates of N and P were determined by Rheaume (1990) by combining data from two National Oceanic and Atmospheric Administration stations and two U.S. Geological Survey stations in Kalamazoo County. Rheaume estimated total annual bulk deposition rates, which are mostly due to wet deposition, as 14.8 kg N ha^{-1} yr^{-1} for total nitrogen (NO_3^- + NH_4^+ + organic N) and 0.34 kg P ha^{-1} yr^{-1} for total phosphorus (PO_4^{3-} + organic P). Tague (1977) reported a similar atmospheric deposition rate for total P (0.33 kg ha^{-1} yr^{-1}) at KBS during 1974.

Table 11.1. Hydrochemistry of precipitation and groundwater in the vicinity of Kellogg Biological Station.

Measurement*	Precipitation		Groundwater		
	USGS[a]	NADP/NTN[b]	Hamilton[c]	USGS -Kalamazoo[d]	WMU-Barry[e]
# dates or sites	14 dates	1240 dates	18 sites	46 sites	170–179 sites
Conductance (μS cm^{-1}; 25°C)	34.0	21.7	556	587	403
pH	4.3	4.47	7.48	7.34	NA
ANC* (mg HCO_3^- L^{-1})	~0	~0	318	259	240
Ca^{2+} (mg L^{-1})	0.19	0.21	80.6	81.0	70.0
Mg^{2+} (mg L^{-1})	<0.01	0.04	25.0	25.0	23.0
Na^+ (mg L^{-1})	<0.2	0.08	6.40	5.1	9.30
K^+ (mg L^{-1})	<0.1	0.02	1.54	1.0	1.60
Cl^- (mg L^{-1})	0.25	0.13	11.0	11.0	0
SO_4^{2-} (mg L^{-1})	3.5	2.25	36.7	32.0	35.00
NO_3^- (mg N L^{-1})	0.61	0.39	1.85	0.19	0
NH_4^+ (mg N L^{-1})	0.56	0.35	0.035	0.04	0.06
Si (mg Si L^{-1})	0.0	NA	6.96	1.69	3.04
DOC* (mg L^{-1})	NA	NA	1.65	NA	NA
TDN* (mg L^{-1})	1.6	NA	NA	0.46	NA
TDP* (mg L^{-1})	0.03	NA	0.011	0.01	NA

*DOC = dissolved organic carbon. ANC = acid-neutralizing capacity (also known as total alkalinity). TDN = total dissolved N. TDP = total dissolved P.

[a]Rheaume (1990: Tables 7 and 8 in that report); data are means of wet deposition for a precipitation station near the mouth of Gull Creek, sampled for most variables 14 times between November 1986 and September 1987.

[b]National Atmospheric Deposition Program (NRSP-3)/National Trends Network means of annual volume-weighted means in wet deposition for 1979–2010 from the KBS station (MI26), downloaded August 14, 2011. NADP/NTN Coordination Office, Illinois State Water Survey, Champaign, IL.

[c]Mostly residential water-supply wells at homes on KBS property and most were sampled once; Hamilton lab database queried December 2009.

[d]Rheaume (1990: Table 20); data are medians for 46 observation wells located throughout Kalamazoo County. The mean concentration of NO_3^- was 3.64 mg N L^{-1}.

[e]Kehew and Brewer (1992: Table 2); data are medians for 170–179 domestic wells located throughout Barry County (excludes wells judged to be contaminated by anthropogenic NO_3^-, NH_4^+, or Cl^-).

Notably, long-term monitoring of precipitation chemistry at KBS has shown a marked reduction of SO_4^{2-} and NO_3^- wet deposition since the 1980s and a consequent increase in the pH of precipitation (NADP/NTN 2011). Wet deposition of SO_4^{2-} has fallen from a mean annual rate of 28.8 kg ha^{-1} yr^{-1} in the 1980s to a mean annual rate of 12.2 kg ha^{-1} yr^{-1} in recent years (2006–2010). A less marked but significant decrease in NO_3^- wet deposition is also apparent, falling from a mean annual rate of 4.23 kg N ha^{-1} yr^{-1} in the 1980s to 2.51 kg N ha^{-1} yr^{-1} from 2006 to 2010. There is no apparent trend for NH_4^+ over this period. Precipitation acidity has decreased greatly in conjunction with SO_4^{2-} and NO_3^- decreases; precipitation pH

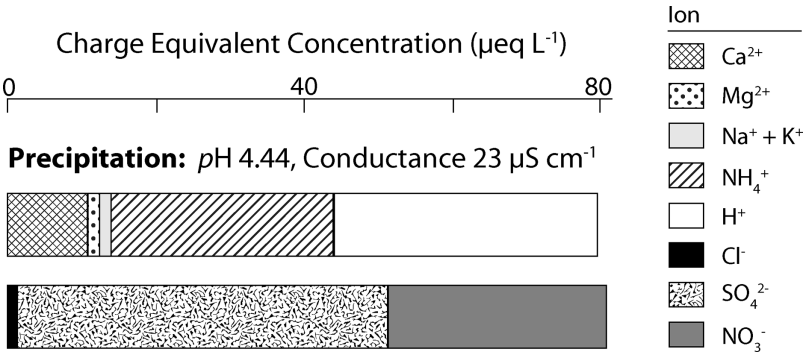

Figure 11.5. Ionic composition of precipitation at KBS, expressed as charge equivalents. Data are volume-weighted means for the 30-year monitoring record (1979–2008; see Table 11.1 for sources).

has increased from a mean of 4.34 in the 1980s to 4.83 from 2006 to 2010, and total acid deposition has fallen from 0.44 to 0.14 kg H^+ ha^{-1} yr^{-1} in the same time frame. Similar trends have been observed throughout the midwestern and eastern United States and likely reflect reduced emissions of S and N oxides due to tighter environmental controls on anthropogenic sources (Driscoll et al. 2001, Kahl et al. 2004).

Natural Chemical Changes as Water Moves through Soils

Water from precipitation changes greatly in chemical composition as it percolates through soils. Some of these changes reflect dissolution of materials at or near the soil surface, but as water percolates through the upper few meters of the soil profile, mineral weathering changes its chemistry further. Because the soils and underlying glacial deposits in the vicinity of KBS are recently formed, they still contain an abundance of readily weathered minerals. Groundwater at KBS begins to acquire its chemical signature within a few meters of the soil surface.

Upland soils in the KBS landscape are generally well-drained loams that developed under deciduous forest (Robertson and Hamilton 2015, Chapter 1 in this volume). The forest was interspersed with smaller areas of oak openings, prairie, and savanna before most areas were converted to agriculture during European settlement in the mid-1800s (Chapman and Brewer 2008). In recent decades, row-crop agriculture has continued on the relatively level outwash plains, while secondary forest has developed on much of the less productive land that was abandoned from agriculture during the 1900s. The most common soil formations are alfisols that cover most of the upland areas, with histosols, mollisols, and entisols occupying lower-lying areas around lakes, wetlands, and streams (Schaetzl 2009). Soil mineralogy on upland soils at KBS is dominated by quartz, K-feldspar, plagioclase, and amphibole (Jin et al. 2008a).

Carbonate minerals (calcite and dolomite) are abundant in the glacial deposits from which KBS soils are derived. Acid precipitation has little effect on most surface water bodies in the region because the acidity is neutralized as water passes

through these carbonate-rich soils on its way to groundwater, and because most surface waters receive groundwater inputs that are alkaline. However, in surface soils (0.5–2 m, or deeper in the coarsest soils) where carbonate minerals have been leached since deglaciation and their acid neutralization capacity diminished, acid precipitation could cause various biotic stresses including aluminum toxicity and leaching of calcium to the point where plant growth may experience calcium deficiency (Driscoll et al. 2001). In cropped soils, substantial acidity is generated by nitrification stimulated by N fertilizers and by removal of base cations in harvest, but much of this acidity is counteracted by the application of agricultural lime (calcium carbonate or dolomite) at several year intervals (see below).

As indicated earlier, the hydrochemical changes that occur as water percolates through the first few meters of soil are dramatic (Fig. 11.6). For example, as precipitation percolates through unfertilized soils at KBS, soil solute concentrations increase considerably, primarily due to mineral dissolution (Kurzman 2006). In the upper 1.2 m—the carbonate-leached zone in these soils—silicate mineral weathering produces modest increases in solutes including base cations (calcium [Ca^{2+}], magnesium [Mg^{2+}], sodium [Na^{+}]), dissolved Si, and carbonate alkalinity (Jin et al. 2008a, b). However, a much larger and abrupt increase in total solutes occurs beneath about 1.5 m as percolating water contacts carbonate minerals. Within the carbonate mineral zone, the soil water reacts with calcite and dolomite to substantially increase concentrations of dissolved Ca^{2+}, Mg^{2+}, and acid neutralizing capacity (ANC, almost entirely due to bicarbonate at these pH values), with a concomitant increase in pH and specific conductance (Hamilton et al. 2007, Jin et al. 2008a). Nitrate also contributes significantly to the total anion composition in the soil waters depicted in Fig. 11.6.

Effects of Agricultural Management on Water Quality

Land management practices—particularly fertilization and cultivation of N-fixing crops—can profoundly influence the chemical composition of percolating waters (Böhlke 2002, Chen and Driscoll 2009). Nitrogen often readily moves as NO_3^- from cropping systems into groundwater, and in well-drained soils groundwater NO_3^- leaching rates beneath fertilized crops are commonly 10–50% of fertilizer N application rates (Böhlke 2002, Raymond et al. 2012). In contrast, P and other contaminants such as metals and pesticides that are less mobile tend to be retained in upland soils, with some notable exceptions such as the herbicide atrazine and its derivatives (Unterreiner and Kehew 2005, Bexfield 2008, Saad 2008). However, P binding by soils eventually becomes saturated with high rates of application, increasing the mobility of P in soils and potentially leading to its export into surface waters (Domagalski and Johnson 2011, Kleinman et al. 2011, Sharpley et al. 2013).

The KBS Main Cropping System Experiment (MCSE; Table 11.2; Robertson and Hamilton 2015, Chapter 1 in this volume) provides an opportunity to investigate how conventional and alternative management of row crops affects the quality of water percolating through soils in comparison with unmanaged (nonagricultural) vegetation at various stages of ecological succession. Such investigations commonly use tension samplers to collect soil water samples (using a vacuum)

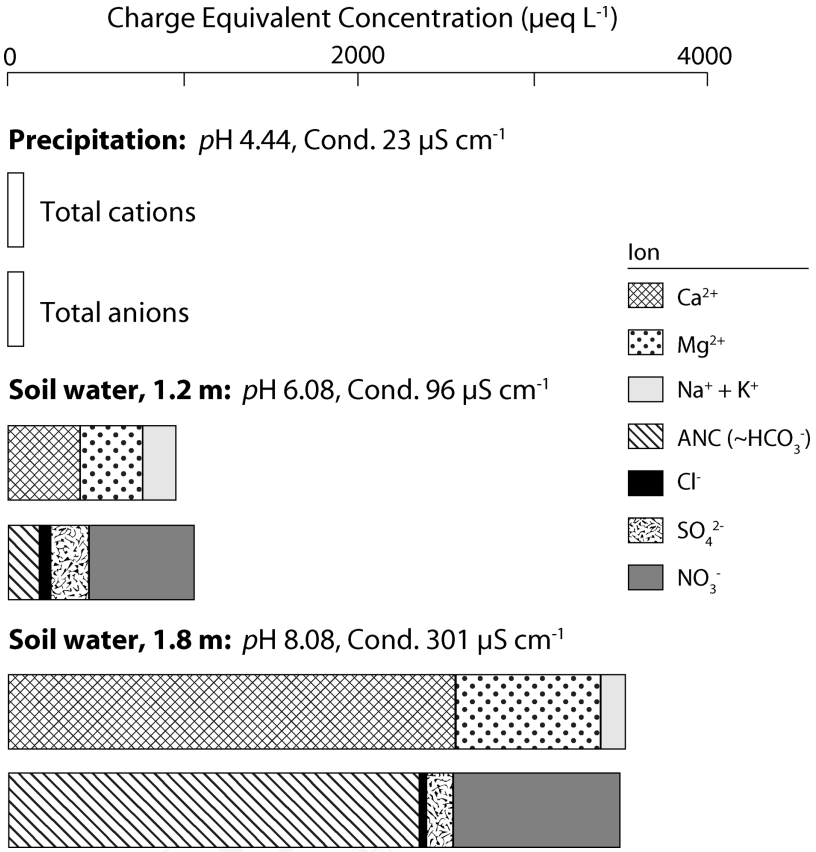

Figure 11.6. Ionic composition, expressed as charge equivalents, of soil water collected with tension samplers at 1.2 and 1.8 m depths, and of precipitation (data from Fig. 11.5). The soil water samples represent hydrochemical changes in precipitation as it percolates through soils without added fertilizer, lime, and organic wastes. Soils at the 1.2-m depth had no detectable carbonate minerals at the three MCSE Deciduous Forest sites, whereas those collected from 1.8-m depth contained abundant carbonate minerals (8 wt % calcite and 9 wt % dolomite: Jin et al. 2008a). Cond. = specific conductance; ANC = acid neutralizing capacity, due almost entirely to bicarbonate (HCO_3^-) alkalinity in these waters. Soil water at 1.2 m based on 98 samples taken at three of the KBS Deciduous Forest sites during Mar–Nov from 2000–2003 (data from Kurzman 2006). Soil water at 1.8 m based on 35 samples from a monolith lysimeter located near the MCSE, within the 3BC2 horizon, collected during Mar–May from 2003–2004 (data from Jin et al. 2008a).

for measuring the concentration of solutes in percolating water leaving the rooting zone, and when combined with water budget estimates of drainage, they provide an estimate of total hydrologic solute loss. A comprehensive analysis of major solute hydrochemistry in soil water collected from tension samplers located just beneath the rooting zone of MCSE systems (Kurzman 2006) shows that the hydrologic loss of solutes varies with vegetation and agronomic management. The total ionic

Table 11.2. Description of the KBS LTER Main Cropping System Experiment (MCSE).[a]

Cropping System/Community	Dominant Growth Form	Management
Annual Cropping Systems		
Conventional (T1)	Herbaceous annual	Prevailing norm for tilled corn–soybean–winter wheat (c–s–w) rotation; standard chemical inputs, chisel-plowed, no cover crops, no manure or compost
No-till (T2)	Herbaceous annual	Prevailing norm for no-till c–s–w rotation; standard chemical inputs, permanent no-till, no cover crops, no manure or compost
Reduced Input (T3)	Herbaceous annual	Biologically based c–s–w rotation managed to reduce synthetic chemical inputs; chisel-plowed, winter cover crop of red clover or annual rye, no manure or compost
Biologically Based (T4)	Herbaceous annual	Biologically based c–s–w rotation managed without synthetic chemical inputs; chisel-plowed, mechanical weed control, winter cover crop of red clover or annual rye, no manure or compost; certified organic
Perennial Cropping Systems		
Alfalfa (T6)	Herbaceous perennial	5- to 6-year rotation with winter wheat as a 1-year break crop
Poplar (T5)	Woody perennial	Hybrid poplar trees on a ca. 10-year harvest cycle, either replanted or coppiced after harvest
Coniferous Forest (CF)	Woody perennial	Planted conifers periodically thinned
Successional and Reference Communities		
Early Successional (T7)	Herbaceous perennial	Historically tilled cropland abandoned in 1988; unmanaged but for annual spring burn to control woody species
Mown Grassland (never tilled) (T8)	Herbaceous perennial	Cleared woodlot (late 1950s) never tilled, unmanaged but for annual fall mowing to control woody species
Mid-successional (SF)	Herbaceous annual + woody perennial	Historically tilled cropland abandoned ca. 1955; unmanaged, with regrowth in transition to forest
Deciduous Forest (DF)	Woody perennial	Late successional native forest never cleared (two sites) or logged once ca. 1900 (one site); unmanaged

[a]Site codes that have been used throughout the project's history are given in parentheses. Systems T1–T7 are replicated within the LTER main site; others are replicated in the surrounding landscape. For further details, see Robertson and Hamilton (2015, Chapter 1 in this volume).

content, as indicated by the conductance of soil solutions, ranged widely across the various systems with the lowest levels beneath the Deciduous Forest and the highest levels beneath the Conventional agriculture systems. Nitrate concentrations were correlated with total dissolved phosphorus (TDP) concentrations in soil water, and higher concentrations of both NO_3^- and TDP were associated with fertilization or cultivation of alfalfa, an N-fixing crop (Fig. 11.7).

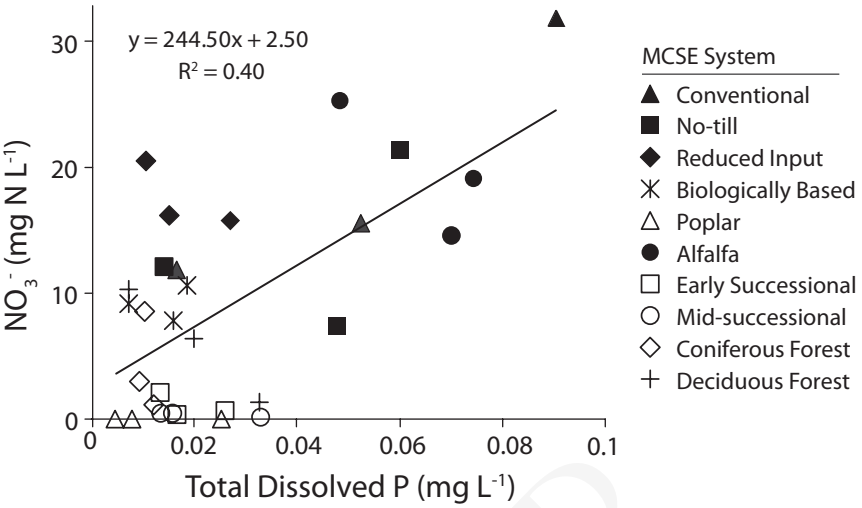

Figure 11.7. Total dissolved phosphorus (TDP) and nitrate (NO_3^-) in soil waters collected with tension samplers at 1.2 m depth from MCSE systems. Row-crop systems receiving fertilizer are shown with solid symbols. Each symbol represents the mean of 100–150 samples collected at a particular site from 2000–2003; n = 3 replicate sites for each system. The regression line is fit to all points and is highly significant ($P < 0.001$). Data from Kurzman (2006).

Although soil water NO_3^- and TDP concentrations are correlated across MCSE systems, these two ions are differentially retained by surface soils, as illustrated by following changes in N:P ratios. The molar N:P ratio of $NO_3^- + NH_4^+$ to TDP in precipitation is ~70–86, based on the NADP/NTN or USGS N data, respectively, assuming TDP is ~0.03 mg L^{-1} (Table 11.1). Soils tend to retain P but lose N by NO_3^- leaching. The molar N:P ratio in soil water beneath the root zone, averaged across all MCSE cropping systems, was 749 based on the ratio of $NO_3^- + NH_4^+$ to TDP concentrations (Kurzman 2006). Thus, the water percolating out of the root zone is enriched in N, largely in the form of NO_3^-, relative to P. This increase in dissolved N:P ratios as precipitation infiltrates the soil reflects not only gains in N but also the tendency for P to be retained in the soil. As a result, soils in the root zone of the MCSE contain much more P relative to N; Robertson et al. (1997) reported a molar N:P in the upper 15 cm of MCSE soils of 0.3, based on extractable inorganic N ($NO_3^- + NH_4^+$) and total P. Given the considerable depth of the unsaturated zone below the root zone (and the depth of soil water sampling), and the predominance of inorganic phosphate in the soil water (>90% of TDP, on average: Kurzman 2006), it is possible that much of the P that is transported downward in percolating water becomes sequestered with minerals below the depth of sampling, but possibly within the reach of deeply rooted plants. This is consistent with the lower TDP concentrations typical of groundwater pumped from water-supply wells (means, 0.011 mg L^{-1} in well waters vs. 0.027 mg L^{-1} in soil waters). This selective retention of P in soils helps to explain why N is the most frequently limiting nutrient

in terrestrial ecosystems despite the high N inputs, while P tends to be limiting in groundwater-fed surface waters.

Estimates of NO_3^- leaching under MCSE systems clearly show the contrast between annual row crops and unmanaged perennial vegetation and the role of fertilization and N-fixing crops as sources of NO_3^- (Fig. 11.8). Syswerda et al. (2012) combined measured NO_3^- concentrations in soil water beneath the root zone with modeled soil water export to provide estimates of NO_3^- leached from the root zone over 11 years. Soil water export (drainage) is markedly higher in the Conventional, No-till, and Deciduous Forest systems (Fig. 11.8A) than in the Reduced Input, Biologically Based, Alfalfa, Poplar, and Early and Mid-successional systems, indicating differences in evapotranspiration losses among these systems.

Nitrate leaching fluxes ranged from less than 1 kg N ha^{-1} yr^{-1} in unfertilized Poplar to 62 kg N ha^{-1} yr^{-1} in the Conventional corn–soybean–wheat rotation (Fig. 11.8B). Over 75% of the fertilizer added to the Conventional system was lost as NO_3^- over the 11-year period. Mean annual leaching losses were also high in the No-till, Reduced Input, and Biologically Based annual cropping systems, but progressively and significantly lower in each; the Biologically Based system leached only 19 kg N ha^{-1} yr^{-1}, on average. Alfalfa leached even less N over this period, and most of this occurred during a normal break year when a small unfertilized grain crop was grown prior to reestablishing the alfalfa stand. The lowest rates of NO_3^- leaching were observed in the Early and Mid-successional systems, and in Poplars, none of which were regularly fertilized (the Poplar system received 60 kg N ha^{-1} in its first year). The relatively mature Deciduous Forest leached more NO_3^- than these systems, presumably reflecting low nutrient demand by the forests' steady-state biomass in combination with high drainage rates. Over the 11-year period, volume-weighted mean NO_3^- concentrations in drainage water (Fig. 11.8C) were highest in the Conventional system—above the threshold for acceptable drinking water quality of 10 mg L^{-1} as N, established by the U.S. Environmental Protection Agency—and they approached this threshold in the No-till and Reduced Input systems. Dissolved organic N and NH_4^+ were measured in these soil water samples in earlier work and were found to be relatively minor constituents compared to NO_3^- (Syswerda et al. 2012). These findings corroborate results from other studies (Power et al. 2001), although few studies have included such a diversity of land cover and management regimes at a single location nor for this long a period.

Carbonate mineral dissolution and precipitation in soils can contribute to soil-atmosphere carbon dioxide (CO_2) exchanges (Hamilton et al. 2007). Dissolution of carbonate minerals occurs in reaction with acidity, and can be either a source or a sink for CO_2 depending on whether the reaction occurs with strong acids (e.g., nitric acid) or carbonic acid, respectively. Acidity in agricultural soils is mostly produced by two processes: (1) carbonic acid formed by CO_2 produced when roots and microbes respire, and (2) nitric acid produced during nitrification of NH_4^+ to NO_3^-. Acidification can reduce soil fertility through several mechanisms; therefore, typically farmers of land free of native carbonate minerals periodically add carbonate minerals (agricultural lime) to the soil to counteract acidifying processes.

Hamilton et al. (2007) analyzed the pathways by which carbonate minerals dissolve in soils and groundwater of the KBS region. In particular, they investigated

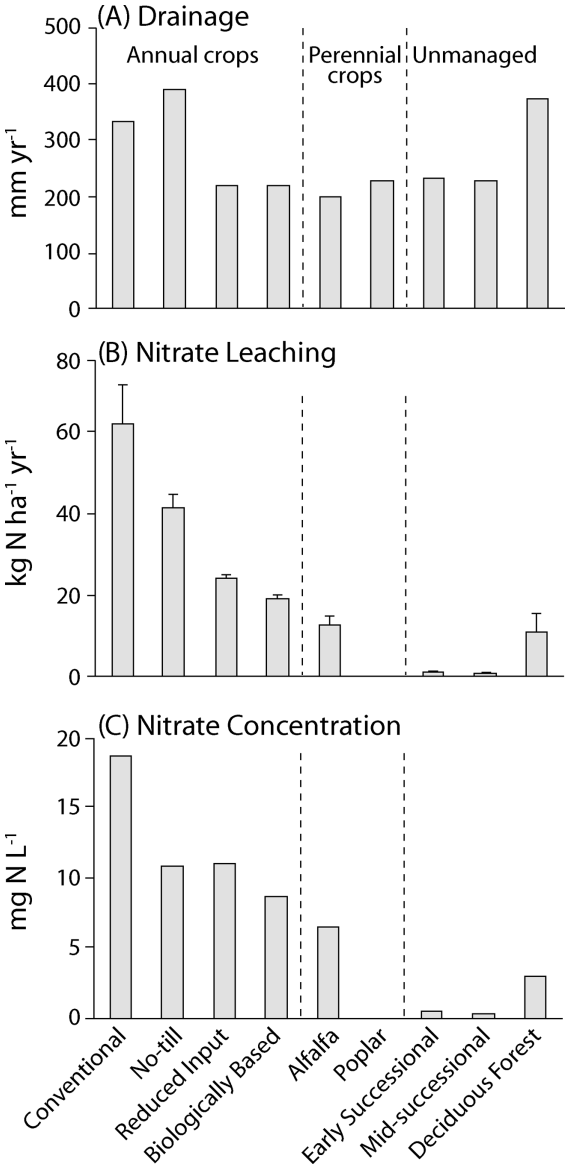

Figure 11.8. Determination of nitrate (NO_3^-) leaching losses from MCSE systems. Modeled water drainage (A) was combined with NO_3^- concentrations measured at 1.2 m during periods of drainage to estimate mean annual NO_3^- leaching losses (B) over an 11-year period. Volume-weighted mean NO_3^- concentrations in drainage water (C) were calculated from the total fluxes and drainage over the 11 years. Means of 100-150 water samples from three replicate plots in each system. The 11-year period from 1995–2006 spanned 3.5 full rotations (corn-soybean-wheat) of the annual cropping systems. Data from Syswerda et al. (2012).

how soil microbial processes influence the fate of the carbon in carbonate, dissolved from either native carbonate minerals or from agricultural liming materials. The degree to which percolating water can dissolve carbonate minerals and accumulate Ca^{2+} and Mg^{2+} is controlled by temperature and pH. The pH of soil water is inversely proportional to dissolved free CO_2 from root and microbial respiration and to mineral acidity from precipitation and from internal soil processes. Nitrification of fertilizer-derived N by soil bacteria is an important source of nitric acid in the fertilized systems, and reaction of nitric acid with carbonate minerals can cause their dissolution to switch from a net CO_2 sink to a source as NO_3^- concentrations increase in infiltrating waters. Whether carbonate minerals dissolve in reaction with dissolved free CO_2 or with nitric acid, either reaction yields dissolved Ca^{2+} and Mg^{2+}. In glacial landscapes such as southern Michigan, carbonate mineral dissolution is an important source of these cations when the sum of Ca^{2+} and Mg^{2+} concentrations exceeds ~2 meq L^{-1} (Hamilton et al. 2007); dissolution of other minerals (e.g., silicates) does not generate such high concentrations, although soils elsewhere can contain other significant sources of these cations.

The charge equivalents of Ca^{2+}, Mg^{2+}, HCO_3^-, and NO_3^- in soil solutions yield clues about the relative importance of carbonate mineral dissolution by reaction with carbonic acid vs. nitric acid (Hamilton et al. 2007). Concentrations of Ca^{2+} and Mg^{2+} were significantly and positively correlated with NO_3^- ($r = 0.9$ and 0.8, respectively) across all MCSE systems (Kurzman 2006), reflecting the importance of nitric acid reaction with carbonate minerals, as discussed above. And positive correlations of Ca^{2+} and Mg^{2+} with NO_3^- in soil water have also been observed in other agricultural systems (Böhlke 2002). High NO_3^- concentrations in soil water beneath or emerging from fertilized agricultural fields are associated with unnaturally high concentrations of Ca^{2+} and Mg^{2+} (i.e., well above the charge equivalent of HCO_3^-), likely as a result of the additional dissolution capacity of nitric acid (and possibly sulfuric acid in some cases) compared with carbonic acid (Böhlke 2002, Hamilton et al. 2007).

Groundwater Quality

Groundwater in the vicinity of KBS occurs in unconsolidated glacial deposits as an upper unconfined aquifer, with an underlying semi-confined aquifer in some areas (Allen et al. 1972). The depth of the unsaturated zone (i.e., from the land surface to the water table) is generally <15 m. Groundwater surface gradients tend to follow the land surface, but as noted above, the direction of groundwater flow is not always apparent from surface topography. Nonetheless, groundwater is generally recharged in the upland areas and discharged to the lower-lying lakes, streams, and wetlands. Lateral flow toward streams and rivers is likely to be more important in the outwash plains, while the morainal systems are more likely to be dominated by localized vertical flow systems (Kehew and Brewer 1992). Wetlands and lakes can receive groundwater through-flow, in which groundwater inputs may enter on one end and exit back to the groundwater on the other end (Kehew et al. 1998).

Groundwater flow paths can be complex in glacial deposits because of the presence of interbedded layers of coarse and fine materials, as shown by a detailed

study of flow patterns in an outwash plain located ~35 km southwest of KBS (Kehew et al. 1996). For the Augusta Creek watershed near KBS, spatial patterns of groundwater flow have been inferred from maps of the water table in unconfined aquifers, as derived from water-supply well records (Bartholic et al. 2007). In the land surrounding Gull Lake (Fig. 11.1B), the elevation of the water table varies only about 40 m; the water table around the MCSE lies about 30 m higher than the lowest land-surface elevation in the area (along the Kalamazoo River).

Hydrochemical information on local groundwaters is available mainly from analyses of domestic wells and is summarized in Table 11.1 (Allen et al. 1972, Rheaume 1990, Kehew and Brewer 1992). Most domestic wells in the area pump groundwater from relatively shallow depths of <25 m, so the analysis of well water samples provides an indication of the hydrochemistry of groundwaters that would be discharged to lakes and streams. The major ion composition of a well close to the KBS LTER main site is depicted in Fig. 11.9. As discussed above, the dissolution of carbonate minerals is largely responsible for the high ionic strength of groundwater around KBS (Kehew et al. 1996), as it is throughout the lower peninsula of Michigan (Wahrer et al. 1996, Jin et al. 2008b). Compared to the water sampled from the soil profile at a depth of 1.8 m (Fig. 11.6), which is just into the carbonate mineral zone, groundwater has higher concentrations of Ca^{2+}, Mg^{2+} and HCO_3^-, and higher ratios of Mg^{2+} to Ca^{2+} (Jin et al. 2008b, 2009). Groundwater also often has higher SO_4^{2-} concentrations than the soil waters measured at KBS; SO_4^{2-} in groundwater can originate from gypsum ($CaSO_4$) dissolution or from oxidation of sulfide minerals (e.g., pyrite FeS_2) in the glacial deposits (Böhlke 2002).

Local groundwaters can generally be classified as the calcium–magnesium–bicarbonate type due to the dissolution of carbonate minerals. Ferrous iron concentrations may be elevated in groundwaters with little or no dissolved oxygen. These concentrations likely increase during the passage of recharge waters through zones of low redox potential such as lake and wetland sediments (Kehew et al. 1996) or when there is very high organic loading at the soil surface.

In agricultural landscapes, NO_3^- concentrations in domestic wells commonly exceed the drinking-water standard of 10 mg N L^{-1} (Rupert 2008, Puckett et al. 2011), although the KBS well water shown in Fig. 11.9 had a particularly low NO_3^- concentration (13 μg N L^{-1} = 1 μeq L^{-1}) compared to other wells in the area. Chowdhury et al. (2003) analyzed data for 8733 wells in Kalamazoo County (where KBS is located) and found that NO_3^- concentrations exceeded 5 and 10 mg N L^{-1} in 28% and 3% of the wells, respectively; concentrations >5 mg N L^{-1} were considered indicative of surface contamination sources. Rheaume (1990) presented evidence that NO_3^- concentrations in the area have increased substantially over the past few decades, documented the spatial patterns in NO_3^- contamination as of the late 1980s, and formulated an N budget that implicates agricultural fertilizers as the primary cause of the increased contamination of local aquifers. As mentioned above, atmospheric deposition is a substantial source of N loading as well. Groundwater in the deeper layers of the glacial deposits still tends to be lower in NO_3^- (Rheaume 1990, Kehew et al. 1996), which likely reflects its longer turnover time and the relatively recent history of fertilizer use in the region as well as reactions that consume NO_3^- in the groundwater system (Böhlke 2002).

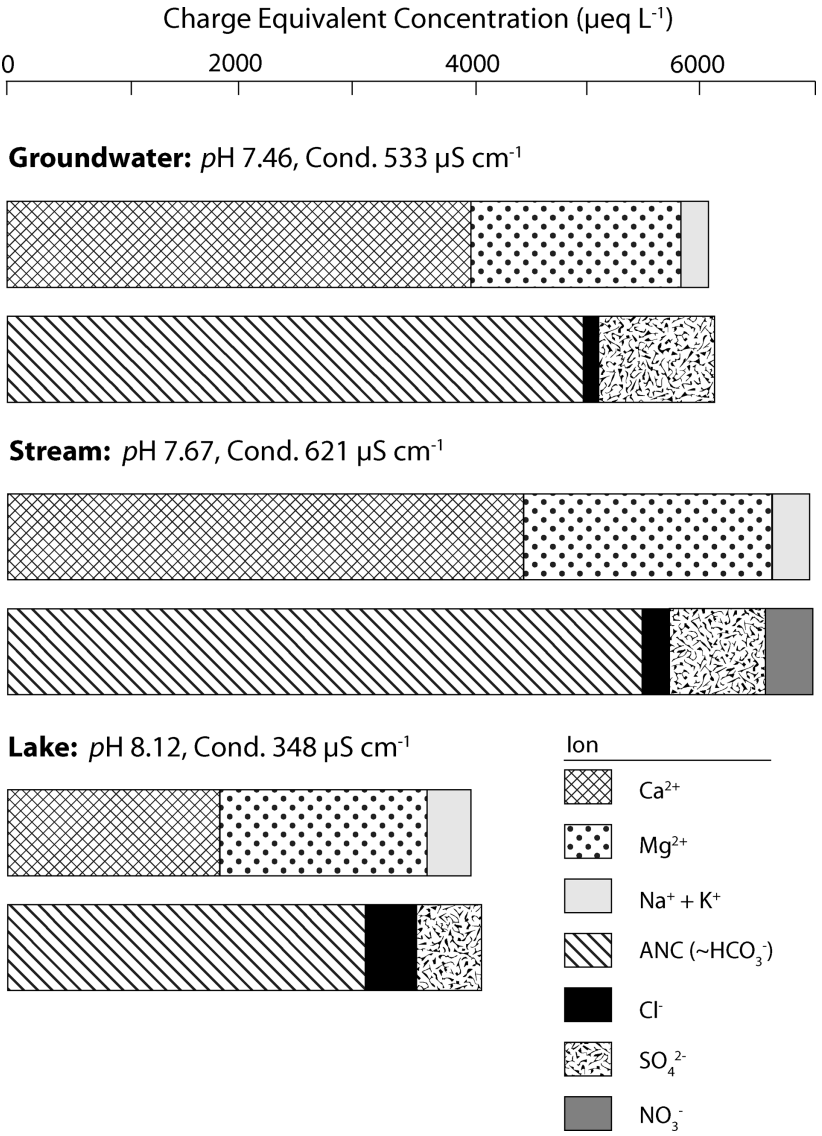

Figure 11.9. Ionic composition, expressed as charge equivalents, of groundwater from KBS wells, a groundwater-fed stream (Prairieville Creek) draining outwash plains northwest of KBS, and the large inland lake (Gull Lake) into which that stream flows. Note the increased scale from Figure 11.6. Cond. = specific conductance; NO_3^- concentrations in groundwater and the lake water were too low to depict. Data are means for 19 groundwater wells with variable sampling dates, 41 sampling dates for the creek, and 86 sampling dates for the lake.

Surface-derived contaminants other than NO_3^- do not yet appear to be an extensive problem in local groundwaters around KBS, and a survey of a wide suite of organic contaminants and trace elements in wells and streams throughout Kalamazoo County revealed little contamination in the rural areas (Rheaume 1990). Hydrogeological characteristics indicate, however, that most of the area surrounding KBS is moderately to highly susceptible to groundwater contamination from surface sources (Rheaume 1990). In the glacial deposits of Barry County, a rural area just north of KBS, Kehew and Brewer (1992) did find evidence of surface-derived contamination from human activity in water samples collected from domestic water-supply wells. About 25% of those wells had not only elevated concentrations of NO_3^- (>1 mg N L^{-1}) but also NH_4^+ (>0.5 mg N L^{-1}) and/or chloride (≥10 mg L^{-1}), the latter likely originating from the use of de-icing salts on roads and probably also the addition of potash (most commonly composed of KCl) to agricultural fields.

Arsenic is a common health concern in well water, including wells around KBS. In Michigan its origin is thought to be largely from native minerals, but mobilization of arsenic could be related to human activities, including increased loading of soluble cations (e.g., Ca^{2+} and Mg^{2+} associated with NO_3^- leaching, as discussed above). Anthropogenic increases in cation loading can cause arsenic to be released from ion exchange sites in soils, potentially resulting in arsenic accumulation downstream in groundwater flow paths (Böhlke 2002).

Surface Waters

Streams and Rivers

Streams and rivers are important in the transformation and retention of nutrients, often reducing the nutrient load in water passing through them (Alexander et al. 2009, Mulholland et al. 2008). Alterations in surface flow paths—by draining wetlands and straightening streams—prevent water from passing through soil and wetland filters that naturally retain nutrients and sediments, and result in degraded water quality downstream (NRC 1995). There has been less wetland drainage in the immediate vicinity of KBS than in most other parts of southern Michigan and the rest of the upper Midwest (Prince 1997) because it is difficult to drain the abundant isolated depression wetlands.

Streams around KBS resemble the groundwater in their total ionic content because they derive most of their annual discharge from groundwater (Fig. 11.2). The stream example depicted in Fig, 11.9 is for Prairieville Creek (Fig. 11.1), a tributary to Gull Lake that originates from a complex of groundwater springs and drains a largely agricultural watershed. Streams with lower conductance than groundwater tend to be outflows from larger lakes and wetlands that capture more direct precipitation that dilutes groundwater inflows. The few streams in the region around KBS that have significantly higher conductance than groundwater tend to be in urban areas and likely receive pollution, particularly Na^+ and Cl^-. Overland flow from storm runoff or snow melt also tends to dilute the total ion content. When

groundwater emerges at the surface, it loses dissolved CO_2 by diffusion to the atmosphere. This, as well as warmer summertime temperatures, often causes calcium carbonate to precipitate on underwater surfaces and sediments. Carbonate precipitates are frequently visible in local springs and streams as well as in wetlands and lakes where groundwater inflow rates are high. The influence of carbonate precipitation on streamwater concentrations of Ca^{2+} and acid neutralizing capacity (carbonate alkalinity) is small unless the water resides in a lake or reservoir along the stream network (Szramek and Walter 2004, Reid and Hamilton 2007, Baas 2009).

Most local streams receive considerable groundwater inputs as their valleys cut downward through the glacial outwash plains, with groundwater entering via diffuse seepage and occasional discrete springs along their channels. Stream riparian zones with high rates of groundwater discharge are known to be hotspots of biogeochemical activity due to high biological productivity and the constant delivery of reactive solutes by groundwater flow (McClain et al. 2003). Hedin et al. (1998) analyzed biogeochemical processes at the soil–stream interface in a small tributary of Augusta Creek (Fig. 11.1) to show the changing importance of aerobic and anaerobic microbial processes across a gradient of decreasing oxygen availability. Denitrification, sulfate reduction, and methanogenesis occurred within the anaerobic zones.

The Lotic Intersite Nitrogen Experiment (LINX) investigated N cycling in headwater streams across the United States, including streams in the vicinity of KBS. This experiment used a coordinated set of whole-stream stable isotope additions to reveal how streams act as N processors (Peterson et al. 2001; Webster et al. 2003; Mulholland et al. 2008, 2009; Hall et al. 2009). The first set of LINX studies examined N cycling through food webs and included a stable isotope addition of ^{15}N in NH_4^+ for 6 weeks. Using ^{15}N as a tracer enables the flow of N to be traced through the stream ecosystem. This is because the minute amount of ^{15}N added has little effect on N availability and ^{15}N behaves the same in the N cycle as does ^{14}N, the much more abundant isotope in nature. Results for Eagle Creek, a second-order tributary of the Kalamazoo River southeast of KBS (Fig. 11.1), showed a rapid turnover of dissolved NH_4^+ and NO_3^- in spite of relatively stable concentrations. The distribution of the ^{15}N tracer in stream organic matter and organisms revealed the importance of assimilative uptake of N by heterotrophic bacteria and fungi as well as benthic algae (algae dwelling on submersed stream surfaces) for N uptake into food webs (Hamilton et al. 2001, 2004; Raikow and Hamilton 2001).

A second set of LINX experiments focused on NO_3^- dynamics in headwater streams across the United States and included whole-stream ^{15}N tracer additions in three predominant land-cover types: forest or other natural vegetation, agriculture, and urban/suburban. The Rabbit River, a tributary of the Kalamazoo River (Fig. 11.1), was included in the study. A survey of streams in the Rabbit River watershed showed the highest NO_3^- concentrations in watersheds with the most agriculture (Arango and Tank 2008). And nationally, streams in agricultural watersheds tended to have the highest NO_3^- concentrations, followed by urban/suburban ones. Among the 72 experiments conducted across eight biomes, there were positive relationships between NO_3^- concentrations and the rates of biotic N uptake and of denitrification. However, at high NO_3^- loading, stream N removal did not increase proportionately

with increasing NO_3^- loads, suggesting that the capacity of streams to remove NO_3^- can become saturated, which then allows more NO_3^- to move downstream. High NO_3^- loading was correlated with increased stream primary production (mainly by algae), and NO_3^- removal by denitrification was correlated with increased stream respiration (which, in turn, is driven by organic matter supply). The role of stream denitrification as a source of atmospheric nitrous oxide, a potent greenhouse gas, was also elucidated from these ^{15}N tracer experiments, providing evidence that streams and rivers are more important to global nitrous oxide emissions than previously thought (Beaulieu et al. 2008, 2011). These cross-site studies show how stream channels and riparian zones could be better managed to promote higher rates of N removal by denitrification and thereby reduce eutrophication of downstream waters, but with the undesirable side effect of enhanced nitrous oxide emission to the atmosphere.

For Augusta Creek, like many streams in this glacial landscape, the large groundwater inflow and the presence of lakes and wetlands along the stream system result in a stable physicochemical environment compared to streams in other kinds of landscapes (Allen et al. 1972, Fongers 2008). The water level of Augusta Creek has been monitored since October 1964 by the U.S. Geological Survey (Station 04105700), and the long-term mean discharge (1964–1994) near its mouth is 1.28 $m^3\ s^{-1}$. Because of the relatively slow movement of groundwater across the local landscape, the water discharged by the creek is likely to reflect the recharge from upland parts of the watershed over the past several decades (Stewart et al. 2010, Tesoriero et al. 2013). Given this time lag, the stream water of Augusta Creek may not be in equilibrium with or reflect changes in the current recharge of upland areas. Bartholic et al. (2007) presented a groundwater flow model that estimates spatial patterns of groundwater inflow and water temperature in Augusta Creek; this model is used to show how large-scale groundwater withdrawals might affect stream discharge and habitat for cool-water fishes. Augusta Creek and most other local streams carry little inorganic material in suspension, but transport significant quantities of bed load, mainly as sand, which may be affected by changes in stream discharge.

Monitoring of NO_3^- concentrations in Augusta Creek by the KBS LTER since 1997 has shown increasing concentrations (Fig. 11.10A). However, when corrected for discharge variation using the concentration–discharge relationship (Fig. 11.10B) and daily discharge records from the USGS station, NO_3^- fluxes appear consistent and stable across 13 years of observation (Fig. 11.10C). Thus, the temporal increase in concentrations is explained by changes in stream discharge rather than by increasing amounts of NO_3^- exported from the watershed. This tendency for little short-term change in stream NO_3^- export is not uncommon and likely reflects the time lags and attenuation associated with groundwater movement through the watershed (Basu et al. 2011, Sprague et al. 2011, Hamilton 2012) and possibly also the delayed release of nitrogen from fertilized soils (Sebilo et al. 2013).

Total P concentrations are low and NO_3^- concentrations can be high in many headwater streams, reflecting the importance of groundwater inflows and the high mobility of NO_3^- relative to P in the soil–groundwater system, as discussed earlier. When N-enriched groundwaters are discharged to surface waters, PO_4^{-3} is further

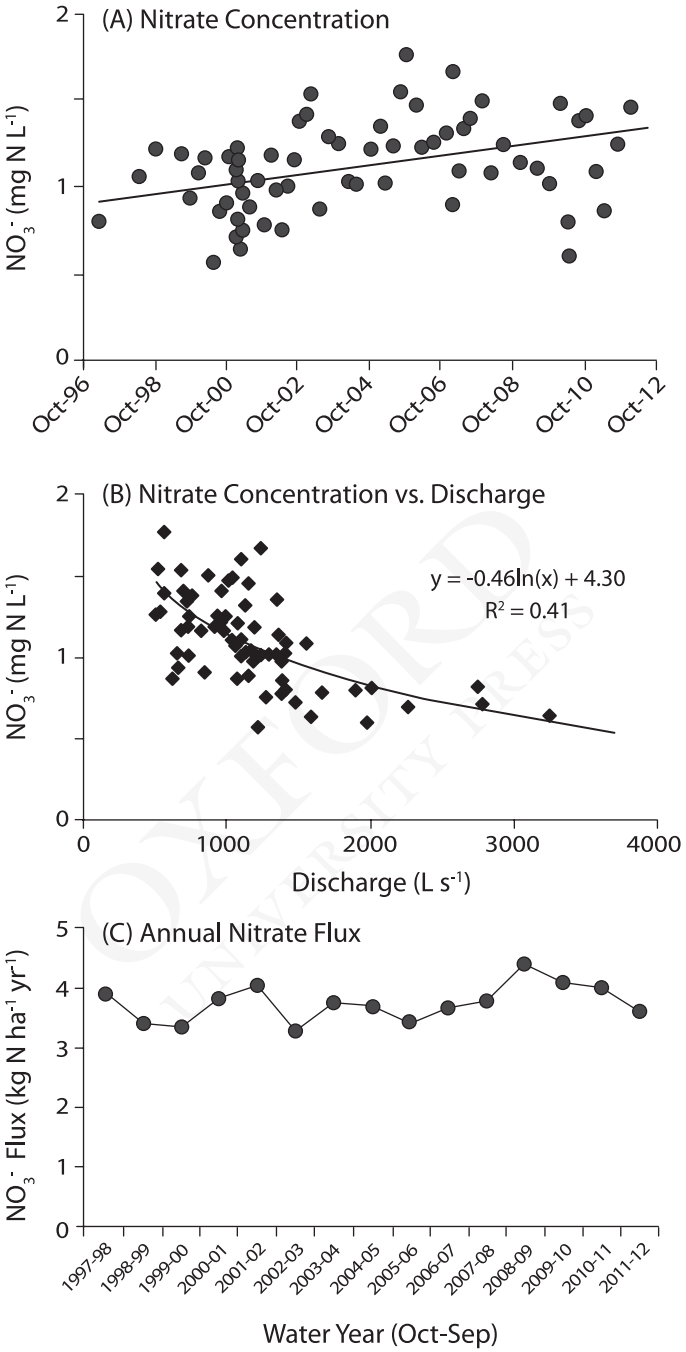

Figure 11.10. Nitrate export in stream water from Augusta Creek: (A) concentrations, (B) NO_3^- concentration-discharge relation, and (C) annual NO_3^- fluxes in the lower reaches of Augusta Creek, which drains land east of and including part of the KBS LTER main site. Annual fluxes are based on the concentration-discharge relation (64 sampling dates) and daily discharge measured by the U.S. Geological Survey.

removed by co-precipitation with calcite and sedimentation. As a result, primary production in local streams and other groundwater-fed surface waters tends to be strongly limited by the availability of P (Wetzel 1989, Hamilton et al. 2009).

Augusta Creek discharges into the Kalamazoo River, and further downstream in the Kalamazoo River system nutrient concentrations increase considerably. This river system has several reservoirs, and the largest and most downstream reservoir (Lake Allegan; Fig. 11.1) has a history of poor water quality ascribed mainly to eutrophication by high P loading. Reid and Hamilton (2007) presented evidence for shifting patterns of nutrient limitation in these reservoirs, with N, P and Si all potentially important as limiting factors for algal growth, but only at times of low river discharge and reservoir flushing. Phosphorus contributions from the various subwatersheds of the Kalamazoo River and the transport and transformation of P and other elements through the river system were subsequently quantified in greater detail through intensive monitoring and modeling (Baas 2009). This work documented the importance of nonpoint (diffuse) sources of P loading to the river system, including the release of sediment P from a reservoir (Morrow Lake) upstream of the City of Kalamazoo to river water, possibly reflecting a legacy of high sediment loading rates.

Wetlands

Wetlands are generally recognized for their positive effects on water quality, for example, nutrient removal and sediment trapping (NRC 1995). Wetlands are abundant in the landscape around KBS, covering 10% of the four townships in the vicinity (Fig. 11.1). The National Wetland Inventory (U.S. Fish and Wildlife Service) provides maps and information on the general types of wetlands and their spatial patterns (http://www.fws.gov/wetlands/Data/index.html). The present vegetation and, to some extent, the hydrology of local wetlands has been strongly influenced by the history of land use since settlement in the 1830s (Rich 1970). Logging, grazing, farming, construction of ponds and drainage channels, and mining of peat and calcium carbonate were common practices in local wetlands. And the effects of these activities on the geomorphology, hydrology, and vegetation still persist today.

The abundance and diversity of wetlands near KBS make this landscape ideal for comparative studies. The wide range in specific conductance of wetland waters shows that they are the most hydrochemically variable surface waters in the landscape (Fig. 11.2). This is because wetlands have highly variable hydraulic connectivity with groundwater: they span the range from receiving negligible groundwater inputs to having their water budgets dominated by groundwater through-flow (Kehew et al. 1998).

Thobaben and Hamilton (2014) surveyed wetland hydrology across a diverse set of 24 wetlands around KBS. They estimated the relative importance of groundwater as a source of water to the wetlands by comparing solute composition and found—consistent with previous studies in lakes—that dissolved Mg^{2+} is the best tracer of groundwater in this landscape (Wetzel and Otsuki 1974, Stauffer 1985). This is because (1) concentrations are negligible in precipitation but consistently high in groundwater in contact with dolomite minerals in the glacial deposits, (2) biological activity has no detectable effect on Mg^{2+} concentrations, and (3) Mg^{2+}

does not tend to precipitate from solution in wetlands or other surface waters. The study found that the relative importance of groundwater varied from near zero to near 100% of the water supplied to the wetlands, and that this explained much of the variation in plant species composition across wetland sites. Statistical analyses revealed seven wetland plant communities across the 24 wetlands: leatherleaf bogs, bogs, a poor fen, fens, sedge meadow fens, wet swamps, and dry swamps. The environmental variables most strongly related to these community classes were water pH, fraction of groundwater, soil nutrient availability, hydrochemical variables that covaried with pH and fraction of groundwater, and shading by tall woody species. Water levels were of secondary importance.

Biogeochemical processes in aquatic sediments of wetlands and other shallow waters have been studied in detail in connection with the KBS LTER as well as in earlier work focused mainly on lakes (see below). Whitmire and Hamilton (2008) compared rates of anaerobic metabolism (denitrification, iron reduction, sulfate reduction, and methanogenesis) in three groundwater- and three precipitation-fed wetlands. Denitrification was not measurable in these wetlands, all of which had low NO_3^- concentrations. Iron reduction was measurable mainly in precipitation-fed wetlands, while sulfate reduction was only measurable in the groundwater-fed wetlands (groundwater supplies SO_4^{2-}; see Fig. 11.9). Methanogenesis was measurable in all wetlands, with no differences between wetlands with contrasting water sources. In terms of total carbon mineralization by anaerobic metabolism, sulfate reduction and methanogenesis were the most important processes in groundwater- and precipitation-fed sites, respectively.

Whitmire and Hamilton (2005) examined NO_3^- removal in wetland sediments around KBS and found that N removal was linked to S cycling in many of the study sites. Further research in the Hamilton lab revealed that the linkage is biologically mediated and consistent with NO_3^- utilization by S-oxidizing bacteria (Burgin and Hamilton 2008, Payne et al. 2009). While NO_3^- evidently can either be denitrified or reduced to NH_4^+ during S oxidation, only denitrification represents a permanent loss of reactive N from the ecosystem. The factors governing the relative importance of these two reactions remain incompletely understood (Burgin and Hamilton 2007), but we can conclude that there is enough reduced S in these environments for S-oxidizing bacteria to play a significant role in NO_3^- removal via a form of chemolithoautotrophic denitrification. This stands in contrast to what has long been thought (Robertson and Groffman 2015): heterotrophic denitrification (i.e., denitrification coupled to the oxidation of organic matter) is not the only process that can permanently remove N in fresh waters.

Lakes

Lakes are abundant and diverse in the landscape around KBS, and they are an important ecological, aesthetic, and recreational resource. Larger, deeper lakes have been the subject of much study because of their importance to people (Wetzel 2001). Notably, most lakes in the area are shallow (i.e., <2 m deep) and become entirely filled with emergent and floating-leaf aquatic vegetation during the summer; therefore, they would be considered wetlands in the National Wetlands Inventory (Cowardin et al. 1979). Most local lakes are hydraulically connected to

adjacent groundwater (Allen et al. 1972, Tague 1977, Rheaume 1990, Kehew et al. 1996), although the relative importance of groundwater and precipitation varies. Lakes fed primarily by groundwater (commonly known as "spring-fed lakes") are the most common, as evident from the distribution of their conductances (Fig. 11.2). As noted earlier, lakes around KBS are similar in their spatial and temporal hydrologic variation to lakes in the vicinity of the North Temperate Lakes (NTL) LTER site (Webster et al. 2006). However, in contrast to lakes at NTL, lakes around KBS contain more alkaline, ion-rich water, reflecting the influence of the abundant carbonate minerals in glacial deposits.

Groundwater-fed lakes around KBS commonly exhibit high rates of calcite precipitation during the summer, when water temperatures warm and aquatic primary production increases the pH through assimilation of CO_2 (Hamilton et al. 2009). Carbonate precipitates often build up in the sediments of such lakes. The effect of calcite precipitation on lake Ca^{2+} concentrations is significant: up to half of the Ca^{2+} in groundwater inputs may precipitate out during the summer (Fig. 11.11).

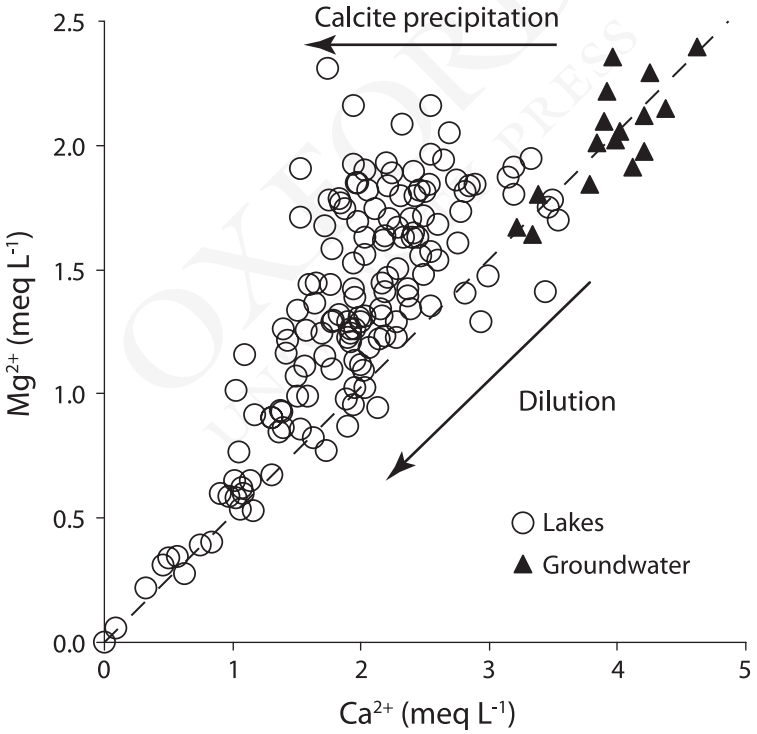

Figure 11.11. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations in southern Michigan lakes during the summer, and in groundwater from wells at KBS. Assuming similar groundwater composition across the Lower Peninsula, precipitation water inputs would dilute the ion concentrations along the dashed line, whereas calcite precipitation would lower the ratio of Ca^{2+} to Mg^{2+}. Data based on 152 lakes across southern Michigan, most sampled once in the summer from 1996–2008, and 16 groundwater wells with variable sampling dates.

Algal and plant growth in such lakes tends to be strongly limited by P availability (Wetzel 2001, Schindler 2012). Above a pH of ~9, the co-precipitation of phosphate with calcite contributes to the limited availability of P. Sedimentation of this co-precipitated P serves as a negative feedback mechanism for aquatic primary production, potentially ameliorating P-driven eutrophication (Koschel et al. 1983, Hamilton et al. 2009). Calcite precipitation can also act as a negative feedback to aquatic primary production by attenuating light in the water column and by flocculation and consequent sedimentation of algal cells (Koschel et al. 1983). Calcite precipitation and deposition on underwater surfaces impact the ecology and biogeochemistry of lakes in many other ways, for example, by binding trace metals and dissolved organic matter and by smothering biofilms and underwater plant leaves (Kelts and Hsü 1978, Wetzel 2001).

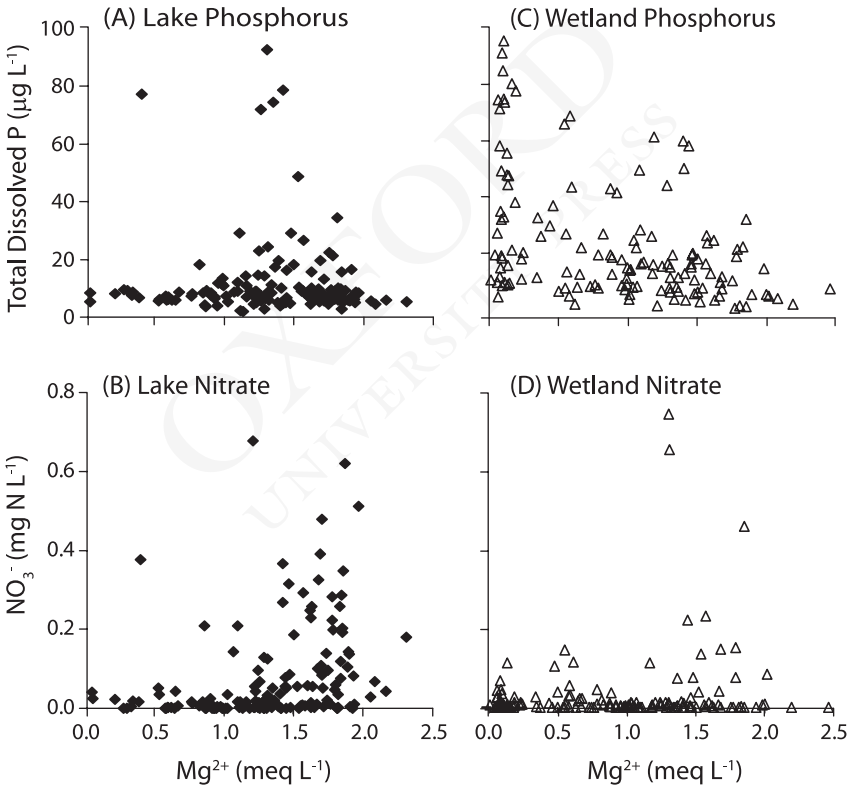

Figure 11.12. Concentrations of total dissolved phosphorus (P) and nitrate (NO_3^-) in lakes (A, B) and wetlands (C, D), in relation to the importance of groundwater as indicated by magnesium (Mg^{2+}) concentrations. Groundwater at equilibrium with dolomite tends to contain ~2 meq L^{-1} of Mg^{2+} whereas the concentration of Mg^{2+} in precipitation is negligible (Fig. 11.11). Data based on 152 lakes across southern Michigan, most sampled once in the summer, and 17 wetland sites in the KBS area, many sampled multiple years in May and Oct; sampling was conducted from 1996–2008.

The influence of groundwater inputs on nutrient availability differs between lakes and wetlands in southern Michigan, as can be seen in Fig. 11.12, although the sample set given is biased by the prevalence of groundwater-fed lakes in the area (i.e., those with Mg^{2+} concentrations exceeding about 1.0 meq L^{-1}). Both TDP and NO_3^- are often, but not always, higher in groundwater-fed lakes (Fig. 11.12). Wetlands, especially those fed by precipitation (as indicated by Mg^{2+} < 1 meq L^{-1}), often have TDP concentrations that are high by lake standards, for reasons that are not well understood. In contrast, NO_3^- concentrations tend to be lower in wetlands even where groundwater with high NO_3^- concentrations is an important water source, likely reflecting the high capacity of wetlands for both

Table 11.3. Hydrochemistry of surface waters in the vicinity of Kellogg Biological Station.

Measurement*	Surface waters				
	Augusta Creek[a]	Gull Lake[b]	Wintergreen Lake[c]	Lawrence Lake[d]	Lower Crooked Lake[e]
# of dates	34	42	16	7	18
Conductance (μS cm^{-1}; 25°C)	481	348	343	441	205
pH	8.06	8.12	8.09	7.94	8.53
ANC* (mg HCO_3^- L^{-1})	286	189	182	266	100
Ca^{2+} (mg L^{-1})	70.6	36.8	38.9	63.0	21.0
Mg^{2+} (mg L^{-1})	21.3	21.7	18.6	22.7	9.33
Na^+ (mg L^{-1})	6.45	6.30	6.54	5.54	6.98
K^+ (mg L^{-1})	1.21	1.24	6.10	2.43	0.47
Cl^- (mg L^{-1})	11.1	11.8	14.2	6.40	17.6
SO_4^{2-} (mg L^{-1})	19.8	23.3	8.74	18.1	4.16
NO_3^- (mg N L^{-1})	1.10	0.20	0.06	0.62	0.02
NH_4^+ (mg N L^{-1})	0.019	0.090	0.150	0.183	0.014
Si (mg Si L^{-1})	5.55	3.37	0.84	5.91	0.14
DOC* (mg L^{-1})	4.92	5.65	11.44	4.30	9.24
TDN* (mg L^{-1})	NA	NA	NA	NA	NA
TDP* (mg L^{-1})	0.008	0.007	0.049	0.009	0.007

*DOC = dissolved organic carbon, ANC = acid-neutralizing capacity (also known as total alkalinity), TDN = total dissolved N, TDP = total dissolved P.

[a]Augusta Creek was sampled near its mouth at the Village of Augusta; Hamilton lab database queried December 2009.

[b]Gull Lake data are means of integrated samples of the epilimnion and point samples from the middle of the hypolimnion (Raikow et al. 2004); Hamilton lab database queried December 2009.

[c]Wintergreen Lake data are means of samples taken mostly at its outflow stream, representing the epilimnion when it was stratified; Hamilton lab database queried December 2009.

[d]Lawrence Lake data are means of samples taken at several depths when it was stratified; Hamilton lab database queried December 2009.

[e]Lower Crooked Lake data are means of samples taken near the surface, mostly in May and October when it was not stratified; Hamilton lab database queried December 2009.

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denitrification and NO_3^- assimilation by plants and algae (Whitmire and Hamilton 2005). Denitrification can also be an important sink for NO_3^- in groundwater-fed lakes, even though concentrations remain quite high (Bruesewitz et al. 2012, Finlay et al. 2013).

The limnology of three local lakes—Gull, Wintergreen, and Lawrence (Fig. 11.1B)—was widely studied during the 1970s and 1980s, and these lakes remain among the most studied inland water bodies in the world. Table 11.3 presents data on the hydrochemistry of these lakes based on a recent survey; detailed information on the spatial and temporal variability of some of the variables can be found in the earlier studies. These three lakes represent contrasts in morphometry, hydrology, hydrochemistry, and ecology, but all are "hardwater" lakes that mix vertically in the spring and fall and develop thermal stratification during the summer and in ice-forming winters. The hardness of their water reflects the high Ca^{2+} and Mg^{2+} concentrations in groundwater inflows.

Recent studies on Gull Lake include work on invasive zebra mussels (*Dreissena polymorpha*), which thrive in alkaline waters and could potentially colonize most of the lakes in the region. These mussels tend to promote dominance by *Microcystis aeruginosa*, a phytoplanktonic cyanobacterium that often produces a potent toxin (Raikow et al. 2004; Knoll et al. 2008; Bruesewitz et al. 2009; Sarnelle et al. 2005, 2012). This is of particular interest because Gull Lake is only moderately productive (i.e., mesotrophic) and harmful cyanobacterial blooms, often produced by this species, are traditionally associated with eutrophic lakes that have greater levels of P enrichment.

Summary

Landscape-level patterns in water quality in recently glaciated landscapes can be ascribed to a combination of natural and anthropogenic influences. Weathering of minerals—particularly the carbonate minerals calcite and dolomite—produces marked changes in water quality as water from precipitation percolates through the upper 1–2 m of the soil profile, and these changes influence underlying groundwater and all downstream groundwaters and surface waters. Nitrate pollution of infiltrating water is particularly apparent beneath conventionally N-fertilized annual row crops, whereas perennial crops, poplar plantations, and natural successional vegetation leach comparatively little N. In contrast, P tends to be retained in most upland soils, and hence groundwater N:P ratios are high, contributing to the importance of P for limiting aquatic primary production in most groundwater-fed surface waters.

Hydrologic exchanges between surface and groundwater systems are particularly important in the KBS landscape and have numerous ecological ramifications. In nonurban areas, most water is delivered to streams and rivers by groundwater flow. Many lakes also receive a large fraction of their water from groundwater and thus their chemistry resembles that of groundwater, although calcium carbonate precipitation and biotic uptake in surface waters can reduce concentrations of Ca^{2+}, acid-neutralizing capacity, and labile nutrients (N, P, and Si). Elevated concentrations of NO_3^- present a water-quality issue in this

region, particularly where groundwater serves as a water supply for people, but passage of water through streams, wetlands, and lakes can remove much of the NO_3^-.

Landscapes similar to KBS are common across the upper U.S. Midwest, as well as in northern Europe. Agricultural row crops, in particular, annual crops that are heavily fertilized, produce notable effects on water quality that extend through water flow paths to groundwater, streams, rivers, wetlands, and lakes. The groundwater flow path introduces a protracted time lag for the movement of contaminants from the land surface to streams and lakes (Hamilton 2012). Urban and residential development further alters water quality in myriad ways, and those effects are superimposed on the water-quality patterns described here. The long-term, landscape-level research described here provides the foundation for understanding natural patterns in water quality and the influence of agricultural activities on groundwater and surface waters; such an understanding is essential for better management of water and water quality for human and ecological benefits.

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