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Nitrogen Transfers and Transformations in Row-Crop Ecosystems

Neville Millar and G. Philip Robertson

Nitrogen (N) is an essential constituent of both proteins and nucleic acids, crucial components of all living things. Humans depend on agricultural systems to provide most of their daily protein, prompting Liebig (1840) to note that agriculture's principal objective is the production of digestible N. Today's intensive agriculture is built on a foundation of N augmentation via the use of synthetic fertilizers and cultivation of N-fixing crops on a massive scale. Globally, the addition of this fixed N to cropping systems is now greater than natural terrestrial N fixation (Galloway et al. 2004, Vitousek et al. 2013) and is a pervasive and fundamental feature of modern crop management (Robertson and Vitousek 2009). The net benefit to humans of this additional N to agriculture is immense—it has enabled greater food production and unprecedented increases in human population (Smil 2002). At the same time, however, this anthropogenic acceleration of the global N cycle has caused serious environmental problems including contributing to climate change and stratospheric ozone depletion, eutrophication and harmful algal blooms, poor air quality, biodiversity loss, and degradation of drinking water supplies (Galloway et al. 2008).

Here, we summarize findings on the cycling of N in agricultural ecosystems of the Kellogg Biological Station Long-term Ecological Research site (KBS LTER). KBS LTER results illustrate a number of opportunities to manage agricultural N in ways that improve N conservation and reduce the escape of fixed N to the environment; they also reveal needs for future research to fill knowledge gaps and more fully document the complex cycling of N in cropping systems that range from conventional to organic and from annual to perennial.

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The Agricultural Nitrogen Cycle

A comprehensive understanding of the agricultural N cycle requires knowledge of the transfers (movement) of N into and out of the soil–plant system (e.g., precipitation, gas exchange, leaching) as well as the exchange of N between compartments within the system (e.g., biological assimilation and release). Transformations in the chemical form of N, often mediated by microbes, determine the availability and mobility of N in soils and water.

Nitrogen Inputs and Outputs

New N is added to cropping systems through biological N fixation, N deposition, and the application of compost, manure, and synthetic fertilizers (Fig. 9.1). In any cropping system, to remain sustainable, the amount of N added must replace the N removed in crop yield and in environmental losses. The amount of N removed with crop harvest varies widely, largely as a function of crop species and growing conditions. In high-yielding annual grain systems, 100–270 kg N ha^{-1} are typically removed during harvest (Robertson 1997).

In annual cropping systems of the KBS LTER Main Cropping System Experiment (MCSE; Table 9.1), average harvest N removals range from 34 kg N ha^{-1} yr^{-1} by winter wheat (*Triticum aestivum* L.) in the Biologically Based system to 163 kg N ha^{-1} yr^{-1} by soybean in the No-till system (Table 9.2). Among perennial crops, Poplar (*Populus* spp.) harvest removes only 107 kg N ha^{-1} after 10 years of growth, or an annualized average of 10.7 kg N ha^{-1} yr^{-1}, whereas alfalfa harvest removes 215 kg N ha^{-1} yr^{-1}. The Early Successional system is not harvested but with each annual burn loses

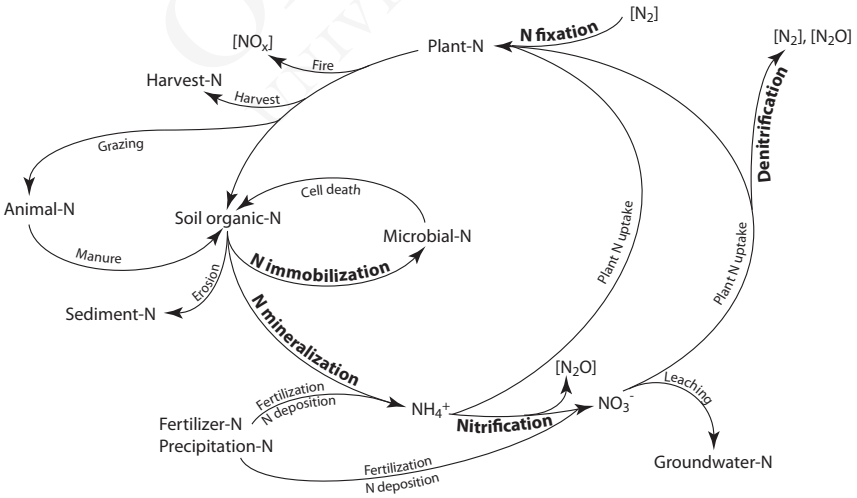

Figure 9.1. Schematic representation of the major elements of the terrestrial nitrogen (N) cycle. Processes mediated by soil microbes appear in bold, and gases appear in brackets. Redrawn from Robertson and Groffman (2015) with permission from Elsevier Limited.

Table 9.1. 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).

~41 kg N ha^{-1} to the atmosphere. These N removals represent the minimum amount of N that must be replaced annually to avoid N depletion—the minimum because not included are additional N losses by other pathways such as leaching and denitrification (Fig. 9.1). Although a small amount of N is added as deposition (see Nitrogen Deposition below), most N is replaced by either biological or industrial fixation of atmospheric N_2 or by application of organic N fertilizers such as compost or manure.

Table 9.2. Nitrogen (kg N ha^{-1} yr^{-1}) contained in crop components and removed in harvest of MCSE systems.[a]

Component	MCSE System						
	Annual Crops[b]				Perennial Crops		Successional
	Conventional	No-Till	Reduced Input	Biologically Based	Alfalfa[c]	Poplar[d]	Early Successional[e]
Corn							
Grain	84	88	80	61			
Stover	22[f]	26[f]	25[f]	18[f]			
Soybean							
Grain	138	163	151	148			
Stover	21[f]	21[f]	19[f]	18[f]			
Wheat							
Grain	61	66	57	34			
Straw	9	10	10[f]	6[f]			
Harvested N[g]	97	109	96	81	215	11	41

[a]Mean, $n = 6$ replicated plots.
[b]Crop N in different components calculated as biomass × N content. Values are the average annual N amount in each crop component over 18 years (1993–2010), covering six 3-year rotations of the annual cropping systems.
[c]Annual N in alfalfa calculated as the sum of N harvested annually and averaged over 1993–2010 (15 years with crop present).
[d]N removed in aboveground woody biomass at clear-cut harvest of 1999 (107 kg N ha-1) divided by the number of growth years (10; 1989–1998).
[e]N in aboveground biomass volatilized by burning and calculated from aggregated postfrost aboveground biomass and surface litter.
[f]Not harvested (left on soil surface).
[g]N removed at harvest of annual crops (corn–soybean–wheat) determined as the annual sums of N removed in grain (corn, soybean, and wheat) plus harvested straw for wheat as noted, averaged over 18 years (1993–2010) covering six 3-year rotations. N removed in wheat straw is based on the straw N content and the ratio of grain to aboveground biomass at peak biomass.

Nitrogen Fertilizers

In 1900 agriculture used very little inorganic N fertilizer, with less than 0.5 Tg of N applied to crops worldwide, mainly as nitrate from Chile and as ammonium sulfate derived from coke-oven gas. The Haber–Bosch process—the production of ammonia from its constituent elements N_2 and H_2—was industrialized by 1913 in Germany (Leigh 2004). Global ammonia production was ~2.4 Tg yr^{-1} N in 1946 and today is ~133 Tg yr^{-1}, most of which is used to make N fertilizers (Kramer 2004).

Synthetic or industrially fixed N differs from organic N sources in that most synthetic N is immediately available for plant uptake, whereas most organic N must first be mineralized to NH_4^+ and then nitrified to NO_3^- (see Internal Nitrogen Transformations below) before it is available to plants (Robertson and Vitousek 2009). In the United States, synthetic fertilizer accounts for ~60% of the total N added to agricultural land; legume N fixation and manure make up most of

the rest (IPNI 2012). In North America, most synthetic fertilizer N is applied as anhydrous ammonia (27% of inputs), urea ammonium nitrate (24%), or urea (23%) (IFA 2011).

Synthetic fertilizers used in the MCSE include different combinations of ammonium nitrate (applied in N–P–K formulations) and urea ammonium nitrate (UAN) (Table 9.3). Rates of N application in the Conventional and No-till systems have ranged from 112–163 kg N ha^{-1} yr^{-1} for corn (*Zea mays* L.) and from 56–90 kg N ha^{-1} yr^{-1} for winter wheat. The Reduced Input system receives ~one-third of the synthetic inputs of the Conventional system (Table 9.3). No synthetic N fertilizer is applied to the Biologically Based system or to soybean and Alfalfa (*Medicago sativa* L.), and no system receives manure or other organic N forms. Poplars receive between ~120 to 160 kg N ha^{-1} at or shortly after planting.

Decisions about N fertilizer rates in MCSE annual crops are guided by MSU Extension recommendations as well as past practice and best judgment. Prior to 2008, Extension recommendations for the Conventional and No-till corn and wheat rotations were based on the yield goal approach (Warncke et al. 2004), which calculates base rates from past yields and projected yield increases. Since 2008 recommendations for corn have been based on the Maximum Return to Nitrogen approach (MRTN; Warncke et al. 2009), now used by seven U.S. Corn Belt states including Michigan (ISU 2004). For MRTN, N is applied on the basis of statewide N response trials weighted by the price of fertilizer and corn to provide an economically optimized N rate. In 2011 we applied 156 kg N ha^{-1} to the Conventional and No-till corn in the MCSE. This is very close to the Economic Optimum Nitrogen Rate (EONR) of 155 kg N ha^{-1} based on 5-year average corn yields for different N-fertilizer levels in the adjacent Resource Gradient Experiment (Fig. 9.2; Robertson and Hamilton 2015, Chapter 1 in this volume). For wheat, a yield goal approach still guides N rate recommendations; in 2010 we applied 89 kg N ha^{-1} to wheat, which exceeded the EONR rate of 68 kg N ha^{-1} based on the average yields (2007 and 2010) for wheat in the Resource Gradient Experiment (Fig. 9.2). The EONR is always less than the agronomic maximum nitrogen rate, the rate at which agronomic yields are maximized (Fig 9.2), because at some point the cost of additional N fertilizer is greater than the income provided by more yield.

Over the 1993 to 2010 period, corn in the Conventional and No-till systems received 141 kg N ha^{-1} yr^{-1}, on average. This value is close to the statewide and national averages of 134 and 149 kg N ha^{-1} yr^{-1} for the same period (NASS 2014). For wheat over this period, we added 76 kg N ha^{-1} yr^{-1}, on average, ~29% lower than the average N rate applied to wheat in Michigan (107 kg N ha^{-1} yr^{-1}) between 2004 and 2009, but very close to the national average (75 kg N ha^{-1} yr^{-1}) for the same period (NASS 2014).

Nitrogen Fixation

Approximately 78% of the atmosphere is composed of dinitrogen gas (N_2), which is unusable by most organisms because of the strong triple bond between two

Table 9.3. Nitrogen fertilizer application rates (kg N ha^{-1} yr^{-1}) and cover crops in the MCSE annual cropping systems (1989–2010).

Year	Crop(s)[a]	Conventional	No-till	Reduced Input	Biologically Based
		Rate (Formulation; Timing)[b]		Rate (Formulation; Timing)[b] + Cover Crop[c]	Cover Crop[c]
1989	Corn[1] or wheat[2]	123 (34-0-0; Sd)	123 (34-0-0; Sd)	28 (34-0-0) + RC	RC
1990	Soybean[1] or corn[2]	0	0	28 (34-0-0) + CC	CC
1991	Corn[1] or soybean[2]	123 (34-0-0; Sd)	123 (34-0-0; Sd)	0	0
1992	Soybean[1] or wheat[2]	0	0	28 (34-0-0) + RC	RC
1993	Corn	28 (UAN; Pl) 84 (34-0-0; Sd)	28 (UAN; Pl) 84 (34-0-0; Sd)	28 (UAN; Pl) + CC	CC
1994	Soybean	0	0	0	0
1995	Wheat	56 (34-0-0)	56 (34-0-0)	28 (34-0-0) + RC	RC
1996	Corn	28 (UAN; Pl) 135 (34-0-0; Sd)	28 (UAN; Pl) 135 (34-0-0; Sd)	28 (UAN; Pl) + CC	CC
1997	Soybean	0	0	0	0
1998	Wheat	56/(34-0-0)	56 (34-0-0)	28 (34-0-0) + RC	RC
1999	Corn	28 (UAN; Pl) 87 (34-0-0; Sd)	28 (UAN; Pl) 87 (34-0-0; Sd)	28 (UAN; Pl) + CC	CC
2000	Soybean	0	0	0	0
2001	Wheat	78 (UAN; split)	78 (UAN; split)	47 (UAN) + RC	RC
2002	Corn	30 (19-17-0; Pl) 125 (UAN; Sd)	30 (19-17-0; Pl) 125 (UAN; Sd)	30 (19-17-0; Pl) + RC	RC
2003	Soybean	0	0	0	0
2004	Wheat	36 (19-19-19; Pl) 54 (UAN; Sd)	36 (19-19-19; Pl) 54 (UAN; Sd)	54 (UAN; Sd) + RC	RC
2005	Corn	34 (19-17-0)[Pl] 123 (UAN)[Sd]	34 (19-17-0)[Pl] 123 (UAN)[Sd]	34 (19-17-0; Pl) + RC	RC
2006	Soybean	0	0	0	0
2007	Wheat	35 (19-19-19; Pl) 54 (UAN; Sd)	35 (19-17-0; Pl) 54 (UAN; Sd)	54 (UAN; Sd) + RC	RC
2008	Corn	33 (19-17-0; Pl) 113 (UAN; Sd)	33 (19-17-0; Pl) 113 (UAN; Sd)	33 (19-17-0; Pl) + RC	RC
2009	Soybean	0	0	0	0
2010	Wheat	89 (UAN; split)	89 (UAN; split)	50 (UAN) + RC	RC

[a]From 1989 to 1992, different crops were grown in the Conventional and No-till systems (denoted as superscript 1) than in the Reduced Input and Biologically Based systems (denoted as superscript 2).
[b]Nitrogen was applied as ammonium nitrate (N–P–K content: 34-0-0, or 19-17-0, or 19-19-19) and urea ammonium nitrate (UAN; 28% N) at planting (Pl) and/or as a side-dressing (Sd). For wheat, a split application of UAN was applied in some years.
[c]Cover crops were red clover (RC, *Trifolium pratense* L.) and crimson clover (CC, *Trifolium incarnatum* L.) which are grown prior to corn and plowed under before planting in spring. Wilke (2010; Table 14) estimated aboveground N in red clover at spring harvest as 67 and 59 kg N ha^{-1} in the Reduced Input and Biologically Based systems, respectively. No data available for crimson clover.

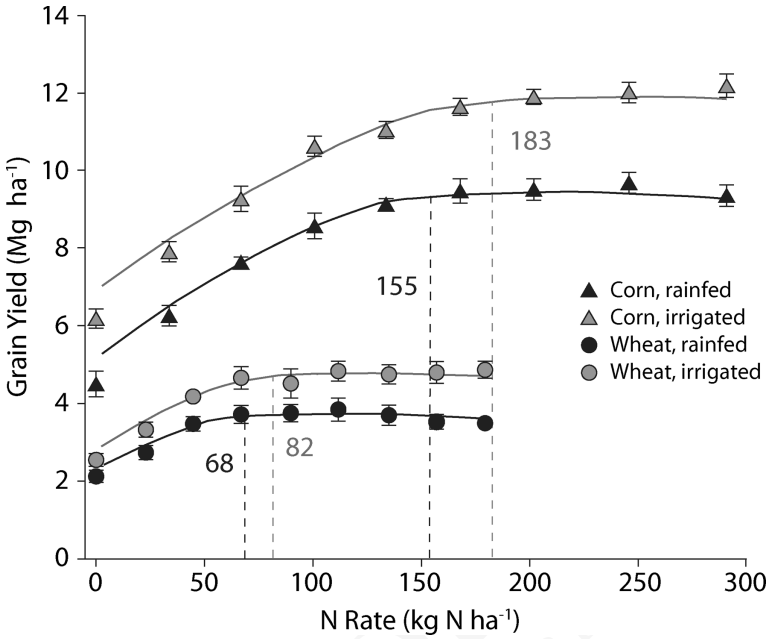

Figure 9.2. Yield responses to incremental increases in synthetic N fertilization rate in corn and winter wheat at the KBS LTER Resource Gradient Experiment. Economic Optimum Nitrogen Rates (EONR; dashed lines) were calculated as the weighted mean of four yield response curves (quadratic, quadratic-plateau, linear-plateau, and spherical) using the International Plant Nutrition Institute Crop Nutrient Response Tool (CNRT) v4.5; http://nane.ipni.net/article/NANE-3068). The EONRs for rainfed and irrigated corn are based on average yields for the 2003, 2004, 2005, 2008, and 2011 crop years, and EONRs for rainfed and irrigated wheat are based on average yields for the 2007 and 2010 crop years. The agronomic optimum nitrogen rates (AONR) were 191 and 198 kg N ha^{-1} for rainfed and irrigated corn, respectively, and for rainfed and irrigated wheat, 94 and 108 kg ha^{-1}, respectively (not shown for clarity).

N atoms. Biological N fixation (BNF) is the dominant process by which this N becomes reactive:

$$N_2 + 8\ H^+ + 6\ e^- \rightarrow 2\ NH_3 + H_2$$

Most BNF is carried out by bacteria possessing the nitrogenase enzyme, and in terrestrial ecosystems most BNF is plant-associated (Vitousek et al. 2013).

Plant-mediated N fixation is largely facultative: where soil N is readily available, plants allocate less fixed carbon (C) to BNF bacteria and less N is fixed. Thus, fixation rates can vary widely even within the same crop species. Soybeans when N-fertilized, for example, fix very little N, but when grown in infertile soil without added N, they can fix 98% of a 200 kg ha^{-1} N requirement (Ruschel et al. 1979). In the MCSE Conventional system, soybeans fix 56–58% of their aboveground N needs based on ^{15}N natural abundance experiments (Gelfand and Robertson, in

press), or 92 kg N ha^{-1} yr^{-1} (Table 9.4). This percentage agrees closely with recent reviews (Herridge et al. 2008, Salvagiotti et al. 2008).

Cover crops are a second major source of BNF in the MCSE Reduced Input and Biologically Based systems (Table 9.4). Wilke (2010), based on ^{15}N natural abundance, estimated that BNF in red clover accounted for 55 and 72% of its total aboveground N in these respective systems. BNF in the successional communities of the MCSE has not been measured but based on legume biomass, and N content is likely ~10 kg N ha^{-1} yr^{-1} in the Early Successional community and negligible in the Mid-successional system. No more than 7 kg N ha^{-1} yr^{-1} is likely fixed in the mature Deciduous Forest system (Cleveland et al. 1999).

Nitrogen Deposition

Nitrogen oxides (NO and NO_2, referred to as NO_x) are emitted from industrial combustion and other sources, including agricultural soils. Oxidation of NO_x results in increased atmospheric N deposition to ecosystems, which in turn causes higher regional watershed N fluxes (e.g., Jaworski et al. 1997), increased soil N_2O

Table 9.4. Biological N fixation (BNF) by legumes, aboveground N, and percentage of aboveground N derived from BNF in annually harvested MCSE systems.[a]

Variable	Annual Crops				Perennial Crops[d]
	Conventional	No-Till	Reduced Input	Biologically Based	Alfalfa
Legume aboveground N (kg N ha^{-1} yr^{-1})[b]					
Soybean	159	184	170	166	
Red clover			56	63	
Alfalfa					215
Total aboveground N (kg N ha^{-1})[c]	342	383	398	341	215
BNF (kg N ha^{-1} yr^{-1})[b]					
Soybean[e]	92	107	99	96	
Red clover[f]			31	45	
Alfalfa[g]					157
Aboveground N met by BNF (%)	27	28	33	41	73

[a]Mean, $n = 6$ replicated plots (SE not shown).
[b]N in legume aboveground biomass and N from BNF per year (de facto per 3-year rotation for soybean and red clover) for each N-fixing crop (as described below) averaged over six rotations (1993–2010).
[c]N in grain and stover/straw of corn, soybean, and wheat plus N in harvests of the cover crops red clover (1995–2008) and cereal rye (2006–2009) per 3-year rotation averaged over six rotations (1993–2010).
[d]For alfalfa, legume aboveground N, total aboveground N, and N from BNF determined per year averaged over 1993–2010 (15 years with crop present).
[e]BNF of soybean estimated as 58% of the total aboveground N uptake (Gelfand and Robertson, in press; Salvagiotti et al. 2008).
[f]BNF of red clover estimated from the percentage of BNF-derived N (55 and 72% for Reduced Input and Biologically Based systems, respectively; average of fall 2007 and spring 2008 harvest data from Wilke 2010; Figure 9).
[g]BNF of alfalfa estimated as 73% of the total aboveground N uptake (Yang et al. 2010).

emissions (Butterbach-Bahl et al. 2002, Ambus and Robertson 2006), and changes in species composition (Bobbink et al. 1998, 2010). Chronic increases in atmospheric N deposition have been shown to decrease plant species diversity even at moderate levels (e.g., 10 kg N ha^{-1} yr^{-1}; Stevens et al. 2004, Clark and Tilman 2008). In agricultural systems, N deposition could be considered a free fertilizer input and, in locations where deposition is high, may need to be considered when making fertilizer N recommendations.

Between 1989 and 2010, KBS received, on average, 6.3 ± 1.3 kg N ha^{-1} yr^{-1} via wet precipitation (NH_4 + NO_3; NADP/NTN 2011). At sites in Michigan, dry deposition of N (HNO_3 + NO_3 + NH_4) between 1989 and 2010 was ~one-third that of wet N deposition (CASTNET 2011). Using this ratio, an annual average total N deposition (wet and dry) at KBS during this period was ~8.4 kg N ha^{-1} yr^{-1}. This estimate is lower than the earlier estimate of 14.2 kg N ha^{-1} yr^{-1} by Rheaume (1990) for Kalamazoo County between 1986–1987. The declining trend for wet deposition of NO_3^- at KBS (Fig. 9.3) is likely due to the drop in NO_x emissions following adoption of air-quality regulations and emission-control technologies (Greaver et al. 2012; Hamilton 2015, Chapter 11 in this volume).

Nitrogen fertilizer rates for wheat and corn at the MCSE are ~10 to 15 times higher than atmospheric N deposition levels, so N deposition has little impact in these systems. In the successional and forested systems, however, the present rate of atmospheric N deposition represents a 2- to 3-fold increase over preindustrial levels and likely has profound ecological effects in these N-limited ecosystems (Galloway et al. 2004, Dentener et al. 2006).

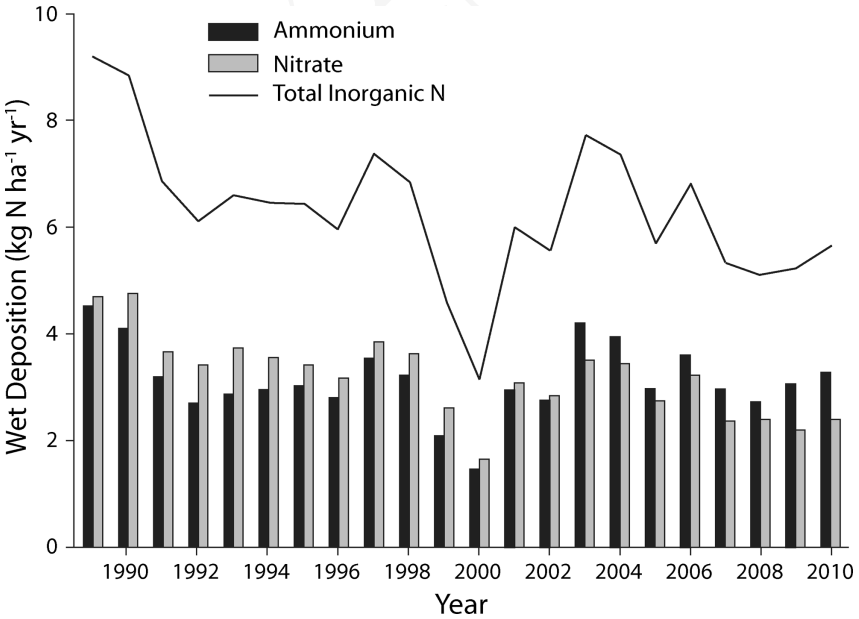

Figure 9.3. Wet nitrogen (NH_4^-N, NO_3^-N) and total wet nitrogen ($[NH_4 + NO_3]^-N$) deposition (kg N ha^{-1} yr^{-1}) at KBS for 1989–2010. Data from NADP/NTN (2011).

Internal Nitrogen Transformations

Microbial activity mediates the major N transformations within the ecosystem, including mineralization, immobilization, nitrification, and denitrification (Fig. 9.1).

Mineralization and Immobilization

Nitrogen mineralization is the conversion of organic N to soluble inorganic forms that can be taken up by plants and other microbes (Robertson and Groffman 2015). If plant residues are rich in N, microbes release inorganic N in excess of their needs to the soil solution. Nitrogen immobilization is the uptake of N by soil microbes—the reverse of mineralization. If plant residues are low in N, microbes scavenge additional soluble N from their surroundings, immobilizing it in microbial biomass. In soil, both processes occur simultaneously, and the balance is known as net mineralization. When net mineralization is positive, inorganic N is added to the soil solution; when net mineralization is negative, inorganic N is removed from the soil solution.

At the MCSE, net N mineralization over the growing season (April to October) is greater in the Reduced Input and Biologically Based systems (178 and 163 kg N ha^{-1}) than in the Conventional and No-till systems (99 and 113 kg N ha^{-1}), respectively (Table 9.5; Robertson et al. 2000). Higher rates reflect the build-up of mineralizable N and soil organic matter (Syswerda et al. 2011) in these cover-cropped systems and, in particular, the importance of leguminous cover crops in providing inorganic N to the subsequent primary crop (Sánchez et al. 2001). The cover crop effect is also seen in the N content of soils—inorganic N concentrations are about as high in the Reduced Input and Biologically Based systems as they are in the fully fertilized Conventional and No-till systems (Fig. 9.4). Moreover, N appears to be more available, especially as nitrate, from June through August (Fig. 9.5), the portion of the growing season when plant uptake is greatest.

Among the perennial crops, net N mineralization between April and October (Table 9.5) is slightly higher in Alfalfa (192 kg N ha^{-1}) than in the annual cropping systems with legume cover crops, but considerably lower in Poplar (62 kg N ha^{-1}). Low N mineralization in Poplar may reflect this system's lower quality (higher C:N ratio) leaf litter, and is associated with low soil inorganic N pools (Figs. 9.4 and 9.5). Among the successional systems, net N mineralization generally followed the pattern Deciduous Forest > Mid-successional > Early Successional > Mown Grassland (never tilled) (Table 9.5). Net N immobilization appears to only occur in the Mown Grassland (never tilled) system and only during July and August (Fig. 9.6).

Total soil N contents of the A/Ap horizon of the Mown Grassland (never tilled) system (5.95 Mg N ha^{-1}) and the late successional Deciduous Forest (5.33 Mg N ha^{-1}) represent indigenous (precultivation) soil N, and are about 50–65% higher than total soil N in the annual cropping systems (~3.6 Mg N ha^{-1}; Table 9.5). This difference reflects the loss of soil organic N due to a century or more of cultivation, which accelerated the mineralization of soil organic matter (Paul et al. 2015, Chapter 5 in this volume) and subsequent N loss by various pathways—including

Table 9.5. Mean total soil N content, relative nitrification rate, and net N mineralization rate during the growing season in the A/Ap horizon of MCSE soils.[a]

System	Total N[b]		Relative Nitrification[c] (%)	Net N Mineralization Rate[d] (kg ha^{-1} season^{-1})
	(g kg soil^{-1})	(Mg ha^{-1})		
Annual Cropping Systems				
Conventional	1.12	3.58	79	99
No-till	1.21	3.63	76	113
Reduced Input	1.24	3.72	80	178
Biologically Based	1.17	3.51	79	163
Perennial Cropping Systems				
Poplar	1.17	3.28	32	62
Alfalfa	1.35	4.05	75	192
Coniferous Forest	Na	na	60	na
Successional and Reference Communities				
Early	1.30	3.90	42	90
Mown Grassland	2.48	5.95	28	27
Mid-successional	1.36	4.08	31	113
Deciduous Forest	2.05	5.33	72	137

[a]n = 6 plots for all systems, except Mown Grassland (n = 4) and the Mid-successional, Coniferous, and Deciduous Forest systems (n = 3). na = not available.
[b]Calculated from Syswerda et al. (2011).
[c]Percentage of net mineralizable N as nitrate at the end of *in situ* incubations averaged over 18 years (1993–2010), covering six 3-year rotations of the annual cropping systems (Robertson et al. 1999).
[d]Determined by extrapolation of daily net N mineralization rates (modified from Robertson et al. 2000, Table 1) over the growing season (April to October, 1989–1995).

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harvest, which removes ~0.1 Mg ha^{-1} yr^{-1} from cropped systems (Table 9.2). The proportion of total N in the A/Ap horizon that is mineralized each year ranges from 0.5% (Mown Grassland never tilled system) to 4.8% (Reduced Input system; calculated from Table 9.5), which is consistent with values reported for cropping systems elsewhere in the U.S. North Central Region (Cassman et al. 2002).

Temporal and spatial patterns in rates of net N mineralization with respect to crop N requirements largely determine the degree of N synchrony within the system (Robertson 1997). Where N mineralization is asynchronous with plant growth—as might happen, for example, when N mineralization occurs largely in the spring prior to crop growth or in the fall after plant senescence—the mineralized N will be susceptible to loss. Such asynchrony is unfortunately a normal situation for annual row-crop production in temperate climates. Managing the system to maximize synchrony is an important strategy for conserving N in cropping systems (e.g., McSwiney et al. 2010). Synthetic fertilizers owe their effectiveness to adding a large pulse of available N to soil just as crops enter their prime growth phase. Reproducing this pulse with biological management is an extraordinary challenge, although evidence from the Reduced Input and

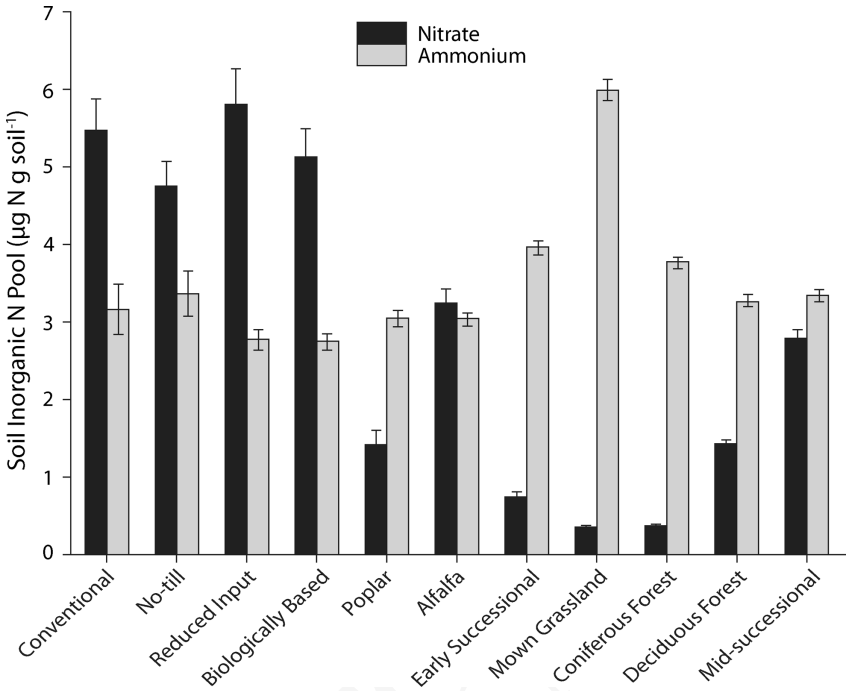

Figure 9.4. Soil inorganic N pools of nitrate and ammonium (µg N g soil^{-1}) in MCSE systems for 1993–2010. Mean ± SE for all measurements during the period.

Biologically Based systems suggests that the leguminous cover crop may provide much of this timely input (Fig. 9.5). Residue placement can also better ensure the timely mineralization of N from soil organic matter (Loecke and Robertson 2009).

Manipulating N mineralization offers a primary opportunity to improve N synchrony. Particulate organic matter (POM) measurements could be used to estimate N mineralization if combined with information about the previous year's crop and cover crop production (Willson et al. 2001). Permanganate Oxidizable Carbon (POXC) has also been shown to be a quick and inexpensive assay for assessing management changes associated with changes in the labile C pool, which can reflect key processes such as N mineralization (Culman et al. 2012).

Nitrification

Autotrophic nitrification is the microbial oxidation of NH_4^+ to nitrite (NO_2^-) by ammonia oxidizers and then to nitrate (NO_3^-) by nitrite oxidizers (Robertson and Groffman 2015). In most soils, the NO_2^- produced rarely accumulates as it is quickly oxidized to NO_3^-. Nitrification can also produce the gas nitric oxide (NO) as a by-product of the chemical breakdown of hydroxylamine (NH_2OH) during NH_3 oxidation, and, when oxygen (O_2) is limiting, produce both NO and N_2O

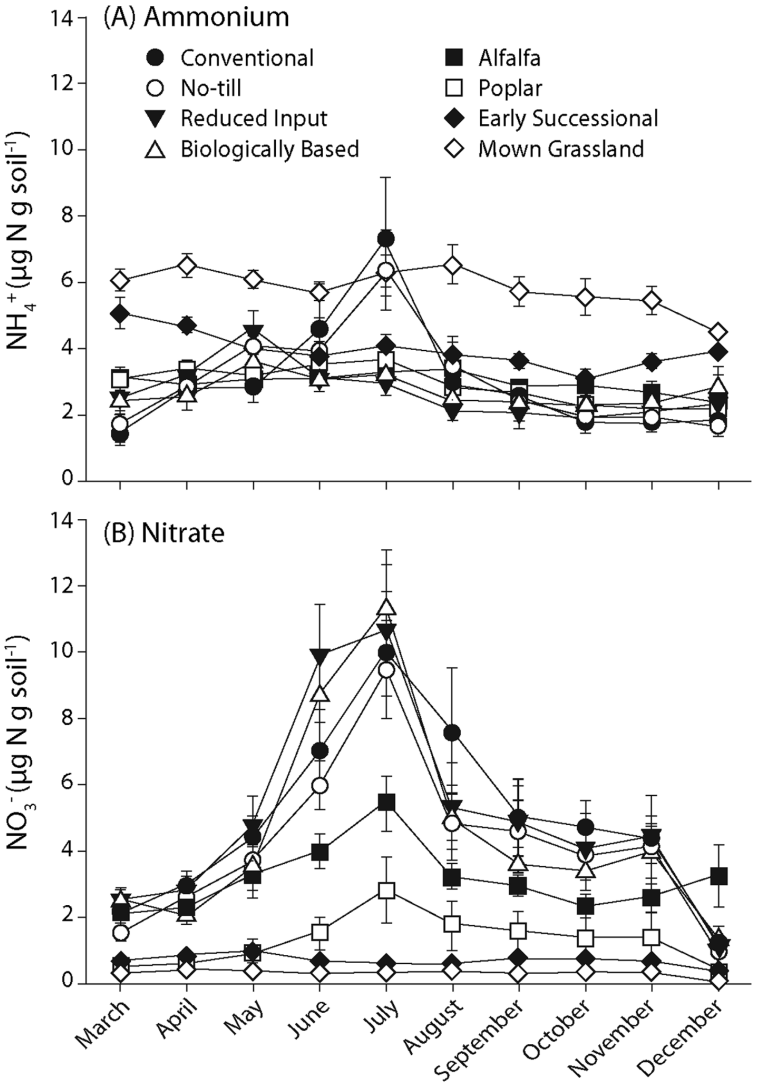

Figure 9.5. Monthly A) ammonium and B) nitrate concentrations (µg N g soil^{-1}) in MCSE systems for 1989–1995. Mean ± SE for all measurements within each month.

via NO_2^- reduction—effectively becoming denitrifying nitrifiers (Zhu et al. 2013, Robertson and Groffman 2015).

Phillips et al. (2000a) found larger populations of nitrifiers in the MCSE Conventional and No-till systems than in the Poplar and Early Successional systems, likely due to N fertilizer addition. However, nitrifier abundance, even when high, still constitutes a relatively small proportion of the total microbial population. Phillips et al. (2000b) found no detectable differences in the species composition of ammonia oxidizers in these systems—all were dominated by members of

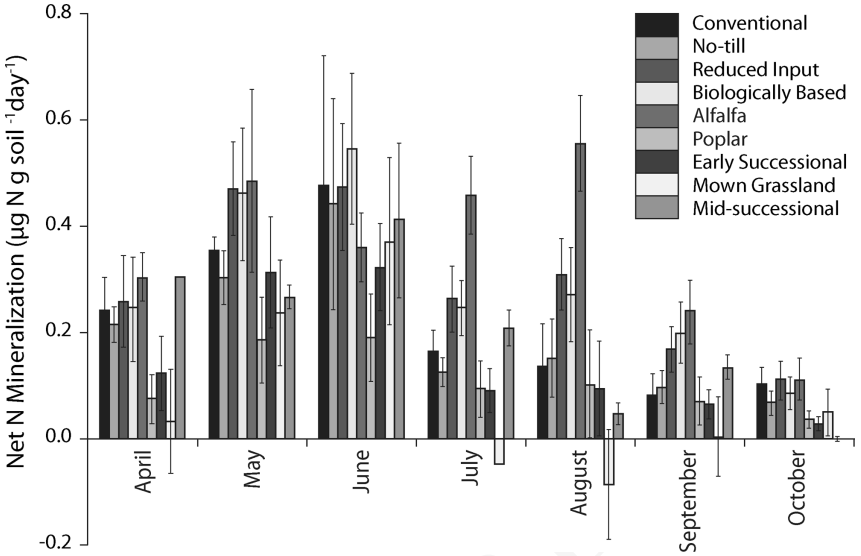

Figure 9.6. Net N mineralization rates (µg N g soil^{-1} day^{-1}) during the growing season (April to October) in the MCSE systems for 1989–1995 (except no data 1991). Mean ± SE for all measurements within each month.

Nitrosospira cluster 3. On the other hand, Bruns et al. (1999) did find more, but less diverse, culturable ammonia oxidizers (also *Nitrosospira*) in Conventional system soils than in Early Successional or Mown Grassland (never tilled) systems. The recent discovery of Archaeal nitrifiers and their likely prevalence in many soils promises to transform our community-level understanding of nitrifiers at the KBS LTER as elsewhere (Robertson and Groffman 2015).

In most aerated soils, nitrification is controlled primarily by factors that affect NH_4^+ availability and rates can be inferred by measuring changes in NH_4^+ and NO_3^- in soil incubations. In most soil incubations, where plant uptake and leaching losses are excluded, much of the mineralized N typically ends up as NO_3^- rather than NH_4^+ (Robertson and Groffman 2015). In all annual cropping systems as well as the Alfalfa and Deciduous Forest systems, the proportion of net mineralized N that exists as NO_3^- at the end of the incubation—here called relative nitrification (Robertson et al. 1999)—is high (70–80%, Table 9.5), indicating rapid nitrification of NH_4^+ as it is formed during mineralization. In contrast, relative nitrification is low (28–42%) in the Poplar, Early Successional, Mid-successional, and Mown Grassland (never tilled) systems. Low relative nitrification may reflect edaphic, plant, or other conditions that affect nitrifier communities or otherwise delay nitrification.

Nitrification is typically rapid in cultivated soils and may be regarded as a gateway to N loss (Robertson 1982); only after NH_4^+ is transformed into NO_3^- is N readily lost from most ecosystems. Nitrate can be quickly leached from soils and also serves as the substrate for denitrification, which produces the gases N_2 and N_2O.

Nitrogen Loss from Cropping Systems

Hydrologic Losses and Fate

A significant amount of the N fertilizer applied to cultivated crops is lost in agricultural drainage waters, primarily as highly mobile NO_3^-. Other forms of reactive N in the soil solution (e.g., NH_4^+, dissolved organic nitrogen [DON]) are typically present in such small quantities that they are unimportant sources of N loss, even in fertilized soils (Hamilton 2015, Chapter 11 in this volume; cf. van Kessel et al. 2009).

Syswerda et al. (2012) estimated NO_3^- leaching losses from MCSE systems by combining measured NO_3^- concentrations in water draining the root zone (sampled at 1.2-m depth) with modeled rates of water loss. Nitrate losses varied with tillage and the intensity of management inputs. Among the annual cropping systems, average annual losses followed the order Conventional (62.3 ± 9.5 kg N ha^{-1} yr^{-1}) > No-till (41.3 ± 3.0) > Reduced Input (24.3 ± 0.7) > Biologically Based (19.0 ± 0.8) management. Among the perennial and unmanaged ecosystems, NO_3^- losses followed the order Alfalfa (12.8 ± 1.8 kg N ha^{-1} yr^{-1}) = Deciduous Forest (11.0 ± 4.2) >> Early Successional (1.1 ± 0.4) = Mid-successional (0.9 ± 0.4) > Poplar (<0.01 ± 0.007 kg N ha^{-1} yr^{-1}) systems (Fig. 9.7).

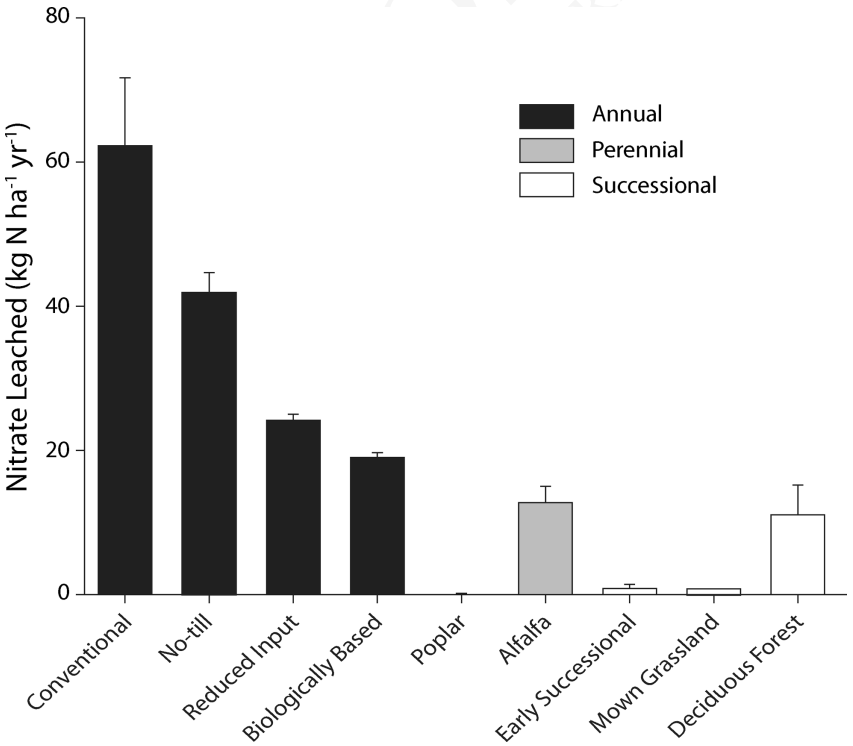

Figure 9.7. Nitrate leaching losses (kg NO_3^-–N ha^{-1} yr^{-1}) in MCSE systems for 1995–2006. Mean ± SE (n = 3 replicate locations). Modified from Syswerda et al. (2012).

These patterns suggest the potential for management intervention to significantly reduce NO_3^- leaching from cropping systems: (1) compared to conventional management, no-till cultivation reduced NO_3^- losses by 33%; (2) the incorporation of cover crops as a substitute for N fertilizer reduced losses by 60–70%; and (3) substituting perennial crops (alfalfa and hybrid poplars) for annual crops reduced losses by 80–100%. In annual crops, most NO_3^- loss takes place during periods when plants are absent—the fall and spring for those systems without cover crops (e.g., Syswerda et al. 2012). Management to conserve NO_3^- might thus be best focused on reducing losses during these periods.

Nitrate lost to groundwater is later discharged from seeps, springs, and drains into streams and rivers (Mueller and Helsel 1996, Crumpton et al. 2008), where it can be further transformed or transported to lakes, estuaries, and marine systems (Howarth et al. 1996, Alexander et al. 2000). In the U.S. Corn Belt, NO_3^- concentrations in ground and surface waters often exceed the 10 mg N L^{-1} maximum contaminant level for drinking water set by the U.S. Environmental Protection Agency (Jaynes et al. 1999, Mitchell et al. 2000).

Much of the NO_3^- entering wetlands and small headwater streams is likely to be transformed to the inert N_2 form (Hamilton 2015, Chapter 11 in this volume), albeit with some production and emission of N_2O (Paludan and Blicher-Mathiesen 1996, Stadmark and Leonardson 2005, Beaulieu et al. 2011). Nitrate concentrations in headwater streams often limit denitrification (Inwood et al. 2005) and are the best predictor of N_2O emissions rates from streams around KBS (Beaulieu et al. 2008). On an areal basis, these streams have higher N_2O emission rates (on average, 35.2 μg N_2O-N m^{-2} hr^{-1}; Beaulieu et al. 2008) than annual crops of the MCSE (on average, 14.5 μg N_2O-N m^{-2} hr^{-1}; Robertson et al. 2000), though their regional contribution is small because of a much smaller areal extent.

Losses via denitrification can be extremely high at the interface where emerging groundwater enters surface water bodies (e.g., Cooper 1990, Whitmire and Hamilton 2005) as well as along subsurface flow paths (e.g., Pinay et al. 1995). In a headwater stream at KBS, Hedin et al. (1998) and Ostrom et al. (2002) showed that substantial amounts of NO_3^- are removed from flow paths prior to stream entry when sufficient dissolved organic carbon (DOC) is available to support denitrification. Subsurface N chemistry and $\delta^{15}N$ natural abundance analyses suggest that a narrow near-stream region is functionally the most important location for denitrifier NO_3^- consumption. These studies suggest that managing these areas to provide sufficient DOC—for example, by planting perennial vegetation streamside—could be an effective mitigation strategy for reducing the impact of leached NO_3^- on aquatic systems.

Denitrification

Denitrification is the stepwise reduction of soil NO_3^- to the N gases NO, N_2O, and N_2. Four denitrification enzymes—nitrate reductase (Nar), nitrite reductase (Nir), nitric oxide reductase (Nor), and nitrous oxide reductase (Nos)—are usually induced sequentially under anaerobic conditions (Tiedje 1994, Robertson 2000). A wide variety of mostly heterotrophic bacteria can denitrify (Schmidt and Waldron

2015, Chapter 6 in this volume), using NO_3^- rather than O_2 as a terminal electron acceptor during respiration when O_2 is in short supply.

In well-aerated soils, denitrification mainly occurs within soil aggregates and particles of organic matter, where O_2 is depleted because its consumption by microbial activity is faster than its replacement by diffusion (Sexstone et al. 1985). Other factors can also be important, including denitrifier community composition (Schmidt and Waldron 2015, Chapter 6 in this volume). Cavigelli and Robertson (2000, 2001), for example, found numerically dominant denitrifying taxa in MCSE Conventional system soils that were absent in Mown Grassland (never tilled) soils, and vice versa. They also found that taxa differed in the sensitivities of their Nos enzymes to O_2, and thus in their abilities to reduce N_2O to N_2 under identical C, NO_3^-, and O_2 conditions (Fig. 9.8). This study provided an early example of the importance of microbial diversity for ecosystem function, which has subsequently become an important research topic (Schmidt and Waldron 2015, Chapter 6 in this volume).

Denitrification in normally unsaturated soils is highly episodic, occurring primarily after wetting events that create anoxic microsites in soil layers where NO_3^- and labile C are abundant. Because denitrifying enzymes are induced sequentially, there can be a lag period just after wetting when N_2O is a dominant end product (Robertson 2000). Bergsma et al. (2002), for example, used ^{15}N tracers at KBS to show that in soils from the Conventional system, the N_2O mole fraction (($N_2O/[N_2O + N_2]$) after a wetting event depended on whether or not the soils had been wetted

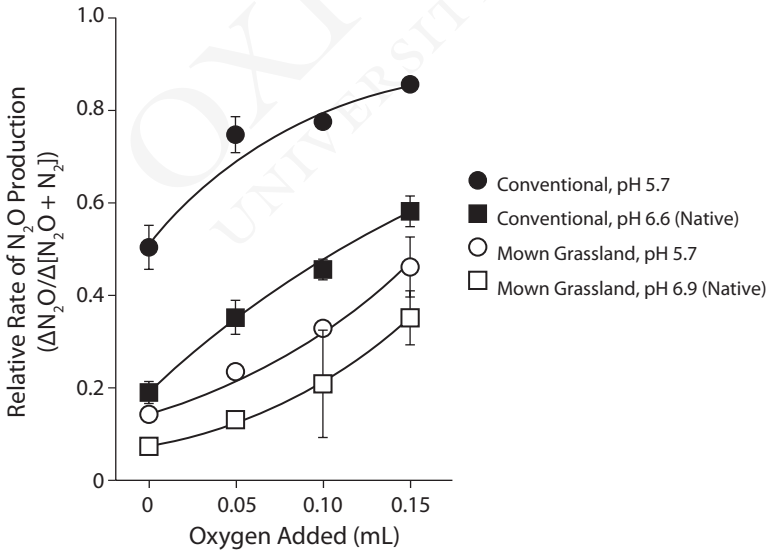

Figure 9.8. N_2O as a proportion of total N gas production (N_2O / [$N_2O + N_2$]) at four oxygen and two pH levels (native and adjusted) for soil from the Conventional and Mown Grassland (never tilled) MCSE systems. Mean ± SE (n = 3 for Conventional; n = 2 for Mown Grassland systems). Redrawn from Cavigelli et al. (2000) with permission of the Ecological Society of America; permission conveyed through Copyright Clearance Center, Inc.

2 days prior to the measurement period, which considerably reduced the proportion of N_2O emitted, vs. immediately prior to measurement. In contrast, prior wetting had no effect on the mole fraction in the Early Successional system—further illustrating presumed differences in denitrifier communities.

Measuring denitrification rates in the field is difficult (Groffman et al. 2006). Fluxes of N_2 cannot be assessed directly because the comparatively small amount of N_2 produced by denitrification cannot be readily differentiated from the very large atmospheric background. Consequently, we must rely on inference from laboratory incubations (e.g., Robertson and Tiedje 1985, Weier et al. 1993) or mass balance techniques where denitrification rates are assumed to be the difference between total N inputs (e.g., N fixation, fertilization, and deposition) and measurable outputs (e.g., leaching, harvest, and erosion).

In a novel approach to directly measure denitrification *in situ*, Bergsma et al. (2001) used an ^{15}N-gas nonequilibrium technique to measure simultaneous fluxes of N_2O and N_2 from an MCSE soil planted to winter wheat. The N_2O mole fraction ranged from <0.004 to 0.14, with an average of 0.008 ± 0.004 when both gases were above the detection limit, showing that N_2O production is only a small fraction of total N gas production ($N_2O + N_2$). If generalizable, this suggests that N_2 emissions from U.S. Midwest row crops may, on average, be substantially greater than N_2O emissions. If so, then extrapolation suggests that total losses of N from denitrification in these systems are of similar importance to the hydrologic losses discussed earlier (Fig. 9.7). Although similar findings have been estimated from mass balance approaches elsewhere (e.g., Gentry et al. 2009), N losses from denitrification in KBS LTER soils remain highly uncertain.

Nitrous Oxide (N_2O) Emissions

Nitrous oxide is produced primarily by denitrifying and nitrifying bacteria; other sources appear unimportant in agricultural soils (e.g., Robertson and Tiedje 1987, Crenshaw et al. 2008). The extent to which N_2O is produced by denitrifiers vs. nitrifiers in agronomic systems is a source of controversy; knowing this could be valuable for designing N_2O mitigation strategies. Nitrous oxide isotopomer analysis (the intramolecular distribution of the ^{14}N and ^{15}N isotopes; Ostrom and Ostrom 2011) is the only current field-based technique that can unambiguously differentiate between these two processes without significantly altering microbial activity. Ostrom et al. (2010a) measured isotopomer site preference to show that denitrification is the dominant source of N_2O in the Mown Grassland (never tilled) community following tillage of a subplot; in that experiment, denitrification accounted for 53–100% of the N_2O produced over a diurnal cycle. Using the same approach in no-till wheat of the Resource Gradient Experiment, Ostrom et al. (2010b) showed that denitrification dominated regardless of N fertilizer rate (0, 134, and 246 kg N ha^{-1}).

Nitrogen availability, on the other hand, is the single best predictor of overall N_2O emissions across both unmanaged and cropped ecosystems at KBS LTER (Gelfand and Robertson 2015, Chapter 12 in this volume) as elsewhere (Matson and Vitousek 1987; Bouwman et al. 2002a, b). In cropped systems, paired comparisons

of N_2O production in fertilized vs. unfertilized soils suggest that ~1% of added N is converted to N_2O, and this is the factor currently used by most national greenhouse gas (GHG) inventories to estimate N_2O production (IPCC 2006; Gelfand and Robertson 2015, Chapter 12 in this volume). However, the response curves of N_2O emission vs. N fertilizer rate are beginning to illustrate a more nonlinear relationship that suggests N_2O fluxes increase disproportionately as fertilizer rates exceed the crop's capacity to utilize added N (Shcherbak et al. 2014).

McSwiney and Robertson (2005), for example, reported a nonlinear, exponentially increasing N_2O fertilizer response along the nine N fertilizer rates in corn at the KBS LTER Resource Gradient Experiment. They found that N_2O emissions more than doubled at N fertilizer rates greater than the level at which yield was maximized. Likewise, across six N fertilizer rates in winter wheat, Millar et al. (2014) also found an exponential increase in N_2O emissions with an increasing N rate. Hoben et al. (2011) confirmed this relationship in commercial corn fields across Michigan (Fig. 9.9), and Grace et al. (2011) used this relationship to revise estimates for N_2O emissions from corn in the U.S. North Central Region for 1964–2005 from 35% to 59% of all GHG emissions associated with corn, and the revised N_2O emission was equivalent to 1.75% of N fertilizer

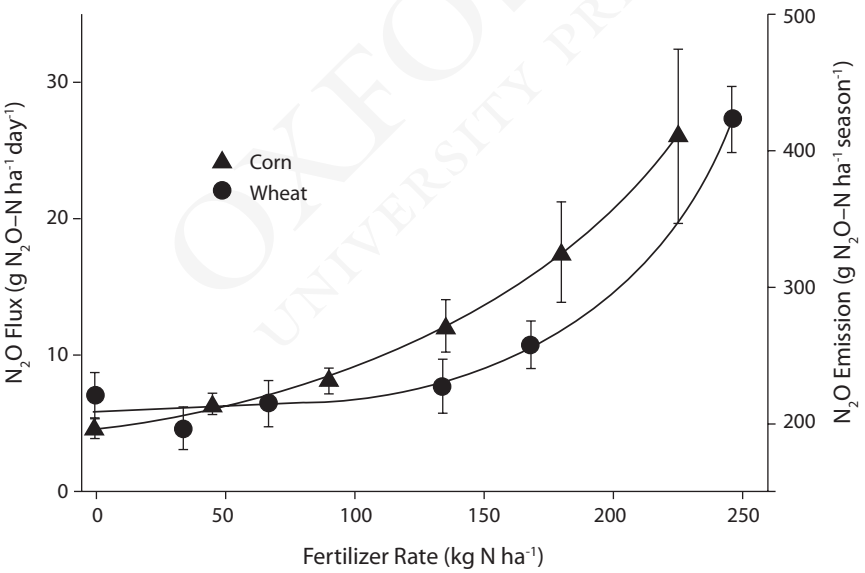

Figure 9.9. Nitrous oxide (N_2O) response to increasing N fertilizer rates for wheat (g N_2O-N ha^{-1} $season^{-1}$) at the KBS LTER Resource Gradient Experiment (adapted from Millar et al. 2014), and for corn (g N_2O-N ha^{-1} day^{-1}) in five commercial corn fields in Michigan (redrawn from data presented in Hoben et al. 2011). For wheat, emissions were measured using automated sampling chambers; values are means determined from sub-daily fluxes over 47 days (right axis) ± SE (n = 159 – 230, repeated measures). For corn, emissions were measured using manual sampling chambers; values are means (left axis) ± SE (n = 32, 8 site years × 4 replicate blocks).

inputs. This agrees well with the estimate by Griffis et al. (2013) of 1.8% based on tall tower measurements of atmospheric N_2O at an agricultural landscape in central Minnesota (USA). Millar et al. (2010, 2012) used this relationship to develop a methodology for C markets to better incentivize N_2O mitigation via improved N fertilizer management.

Temporal variability severely challenges accurate estimates of annual N_2O fluxes from agricultural systems. As for denitrification, N_2O emissions are often stimulated by episodic agronomic and environmental events, including fertilization, tillage, rainfall, and freeze-thaw cycles (e.g., Wagner-Riddle et al. 2007, Halvorson et al. 2008). Episodic N_2O fluxes can constitute a substantial portion of long-term total N_2O emissions (Parkin and Kaspar 2006), questioning the validity of annual emission estimates based on infrequent sampling (Smith and Dobbie 2001). Automated chamber methods where fluxes are measured several times a day address the issue of the temporal variability, and at KBS as elsewhere, such measurements reveal a substantial amount of diel and day-to-day variation (Ambus and Robertson 1998).

Agronomic Nitrogen Balances in Annual MCSE Ecosystems

Although we do not have sufficient knowledge of all N fluxes in the MCSE to construct complete N budgets for each system, we can construct simple agronomic budgets (e.g., Vitousek et al. 2009) for the annual cropping systems that are informative. Estimates of N in agronomic inputs (from fertilizer additions and BNF) less outputs (in harvest) provide a first-order measure of surplus N. The balance (Table 9.6) is instructive: the Conventional system has an overall balance of +7 kg N ha^{-1} yr^{-1}, followed by No-till (0 kg N ha^{-1} yr^{-1}), Reduced Input (–28 kg N ha^{-1} yr^{-1}), and Biologically Based (–34 kg N ha^{-1} yr^{-1}). The Conventional system closely compares to the balance of +10 kg N ha^{-1} yr^{-1} (Table 9.6) for a generalized U.S. Midwest (Illinois) corn–soybean rotation determined by Vitousek et al. (2009).

That the Conventional System is in near balance (only ~7% of estimated inputs are not removed by harvest) and the No-till is in exact balance suggests conservative N management in these systems (Table 9.6). As noted earlier, N fertilizer for corn is applied at rates recommended by university extension based on an EONR approach. The negative surpluses in the Reduced Input and Biologically Based systems are striking, and likely indicate cover crop scavenging of N that would otherwise be lost to the environment by leaching and denitrification. Alternative explanations are that soil organic matter could be providing additional N or that BNF by the cover crops could be underestimated. However, soil organic matter is accreting in these systems rather than declining (Syswerda et al. 2011), and thus is a sink not a source of N. And while rates of BNF in the Reduced Input and Biologically Based systems are only 12–16 kg N ha^{-1} yr^{-1} greater than in the Conventional system, which seems low, recall that leguminous cover crops are grown during only one of the MCSE's three rotation phases (preceding wheat). For this phase, rates of BNF for red clover are 31 and 45 kg N ha^{-1} yr^{-1} for the Reduced Input and Biologically Based systems, respectively (Table 9.4), which is a reasonable range for red clover (Schipanski and Drinkwater 2011) and for winter cover crops in general (Parr et al. 2011).

Table 9.6. Agronomic N inputs, N outputs and surplus (difference) for corn–soybean–wheat rotations in the U.S. Midwest[a] and the annual MCSE systems.[b]

Agronomic N Inputs, Outputs, and Balance	U.S. Midwest	MCSE System			
		Conventional	No-Till	Reduced Input	Biologically Based
Agronomic Inputs (kg N ha^{-1} yr^{-1})					
Fertilizer	93	73	73	25	0
BNF	62	31	36	43	47
Total	*155*	*104*	*109*	*68*	*47*
Agronomic Outputs (kg N ha^{-1} yr^{-1})					
Harvest	145	97	109	96	81
Total	*145*	*97*	*109*	*96*	*81*
Surplus	**+10**	**+7**	**0**	**–28**	**–34**

[a]Values for the U.S. Midwest from Vitousek et al. (2009) for a tile-drained corn–soybean rotation in Illinois.
[b]Values for MCSE systems from Tables 9.2, 9.3, and 9.4, annualized to crop rotation cycle.

Worth noting is that the overall balance for each system is the sum of balances for individual crops within each 3-year rotation, and that year-to-year balances differ by crop. In the Conventional and No-till systems, for example, only wheat has an agronomic N budget in approximate balance; corn has a significant N surplus, and soybean a significant N deficit. On average for 1993–2010, wheat in these systems had a 3 kg N excess (76 kg N fertilizer less 73 kg N harvest), corn had a 55 kg N ha^{-1} yr^{-1} excess (141 kg N from fertilizer inputs less 86 kg N harvested), and soybean had a 51 kg N deficit (100 kg N from BNF less 151 kg N harvested). N balance over the entire rotation, then, is the result of soybean's deficit being made up by corn's excess.

That leaching and presumably denitrification losses are significant in all systems, but especially in the annual cropping systems (see the prior section above), suggests that overall N budgets are substantially out of balance: in the annual cropping systems, more N appears to be lost via harvest, leaching, and denitrification than is being gained via N deposition, BNF, and N fertilizer. This suggests either that BNF has been underestimated, and that (1) more N is being mineralized from soil organic matter than is being immobilized annually; (2) N leaching losses have been overestimated; or (3) there is an unrecognized N source such as atmospheric NH_3 adsorption. This apparent imbalance is a major knowledge gap that deserves future attention.

Mitigation of Excess Nitrogen

The main management challenge for mitigating reactive N in the environment is to maximize the efficiency with which N is used in agricultural systems (CAST 2011)—for field crops, this means implementing practices that minimize fertilizer

use and maximize N conservation. Robertson and Vitousek (2009) organized practices to improve the N Use Efficiency (NUE) of high-productivity cropping systems into four strategies: (1) provide farmers with decision support to better match fertilizer N rates to crop N requirements; (2) adjust the rotation to add crops and cover crops that will improve uptake of added N; (3) better manage the timing, placement, and formulation of N fertilizers—including organic—to better synchronize N additions with plant N needs; and (4) manage hydrologic flow paths to capture and process the N leached from farm fields. Tillage management provides a fifth option for some soils. KBS LTER results inform all strategies and as well the degree to which farmers are likely to adopt various strategies (Swinton et al. 2015, Chapter 13 in this volume).

Nitrogen Fertilizer Rate

As noted earlier, a direct relationship exists between crop yield and N fertilizer rate up to the point at which crop N needs are met. In recent years, hundreds of N-response trials conducted throughout the U.S. Midwest (e.g., Vanotti and Bundy 1994) have contributed to a database sufficient to support the new MRTN approach based on the EONR (ISU 2004, Sawyer et al. 2006).

At KBS LTER, the difference between the traditional Agronomic Optimum N Rate (AONR) and the EONR approach illustrates potential fertilizer savings. Results from the Resource Gradient Experiment (Fig. 9.2) suggest that applying N fertilizer at economic optimum rates could result in a potential savings of 23% on N fertilizer costs for corn and 36% for wheat, assuming a typical fertilizer to crop price ratio of 0.10. That NO_3^- leaching also increases substantially at N fertilizer rates in excess of crop N demand (e.g., Andraski et al. 2000, Gehl et al. 2006) suggests that the EONR approach could mitigate other forms of N in the environment in addition to N_2O.

Cover Crops

Winter cover crops can capture N that would otherwise be available for loss following annual crop harvest. During active growth in the fall and spring, winter cover crops take up mineralized N and/or residual N fertilizer, which can then become available to the next crop upon remineralization (Rasse et al. 2000, Strock et al. 2004). Much of the N immobilized by the cover crop presumably would be otherwise lost as leached NO_3^- (Feyereisen et al. 2006) or as N_2O and N_2 via denitrification (Baggs et al. 2000a).

In the KBS LTER Living Field Lab Experiment (Snapp et al. 2015, Chapter 15 in this volume), McSwiney et al. (2010) found that the inclusion of cereal rye as a winter cover crop in a conventional corn system maintained corn yield, while significantly reducing N_2O and NO_3^- losses, particularly at N fertilizer rates in excess of corn N requirements. They calculated apparent N recoveries of >80% for N fertilizer rates up to 101 kg N ha^{-1} when cover crops were included; typical estimates for row crops without cover crops range from 30% to 60% (e.g., Cassman et al. 2002). Cover crops also significantly reduced NO_3^- leaching compared to

systems without cover crops (Syswerda et al. 2012). This reduction could be linked to increased evapotranspiration and soil nitrogen scavenging in cover crop systems.

When legumes are included as cover crops, as in the MCSE Reduced Input and Biologically Based systems, there is the potential benefit of N input by BNF. Although BNF will be low when adequate soil N is available, winter legumes can provide the same degree of soil inorganic N scavenging as their nonleguminous counterparts and have the additional advantage of a low C:N biomass that decomposes rapidly after spring killing, making more N available earlier for the growth of the summer crop (Fig. 9.5; Corak et al. 1991, Crandall et al. 2005). Crop residue quality (e.g., C:N ratio, lignin content) has also been shown to affect denitrification rates and N_2O emissions (Baggs et al. 2000b; Millar and Baggs 2004, 2005). Cost savings from avoided N fertilizer use could be put toward cover crop seed and planting expenses.

Fertilizer Formulation, Placement, and Timing

Applying an appropriate form of N when and where the crop can best use it can readily improve ecosystem NUE. Fertilizer N should ideally be applied in several doses to match the timing of crop N demand—this ensures the greatest synchrony between fertilizer addition and crop need. However, except where N might be applied continuously in irrigation water, weather and the availability of equipment and labor typically limit N applications to no more than two per season—in corn, a starter rate at planting and the remainder just before the rapid growth stage. Worse, for about one-third of U.S. cropland, fertilizer N is applied once in the fall—months before active crop growth (Randall and Sawyer 2008, Ribaudo et al. 2011). Long-term paired comparisons show lower corn yields and 15–40% greater NO_3^- losses with fall vs. spring fertilizer applications (e.g., Randall and Mulla 2001, Randall and Vetsch 2005). Bundy (1986) concluded that fall-applied N is usually 10–15% less effective for crop utilization than spring-applied N.

Fertilizer placement also affects NUE. The spatial arrangement of available N vis-à-vis the distribution of plants and their roots (e.g., Van Noordwijk et al. 1993) affects the likelihood of N uptake vs. N loss. Placing synthetic fertilizers in a concentrated band within or very close to crop rows, rather than between them as is more common, can increase NUE and reduce surface N loss (Malhi and Nyborg 1985, CAST 2011). Injecting anhydrous ammonia into soil near rows rather than broadcasting over the soil surface can decrease N leaching and volatilization by as much as 35% (Achorn and Broder 1984). And broadcasting it has been shown to double N_2O emissions (Venterea et al. 2010) when compared to broadcast urea.

The location and particle size of plant residue also have an impact on its N release and uptake. Loecke and Robertson (2009) found that N in red clover residue is more likely to be taken up by corn if the residue is sufficiently aggregated to concentrate mineralized N in small patches, but not so large as to inhibit decomposition by creating anoxic microsites.

Fertilizer placement at the field scale can also greatly influence NUE. That soil nitrogen availability is spatially variable in predictable patterns (Fig. 9.10) is well known from studies at the KBS LTER (Robertson et al. 1993, 1997; Senthilkumar

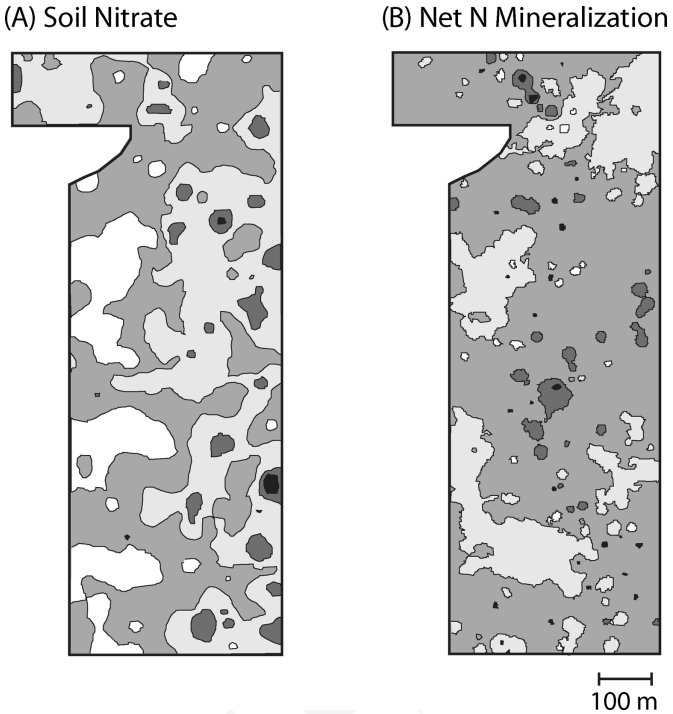

Figure 9.10. Isopleths for A) soil nitrate (5.7-15.1 mg N g soil^{-1}) and B) net N mineralization (0.30-0.70 mg N g^{-1} d^{-1}) across the 48-ha MCSE prior to plot establishment. Shading patterns denote five equal increments in levels for each variable across its range. Distance unit in meters. Redrawn from Robertson et al. (1997) with permission of the Ecological Society of America; permission conveyed through Copyright Clearance Center, Inc.

et al. 2009) and elsewhere, and yield patterns are concomitantly related to nutrient availability (Robertson 1997, Kravchenko and Bullock 2000, Kravchenko et al. 2006, Kravchenko and Robertson 2007). Applying fertilizer in a spatially targeted manner that recognizes this variability can concentrate N on those areas of a field with the highest yield potential and avoid adding N to those areas not likely to be N responsive. For most fields, less fertilizer N will be added using this approach than applying a generally recommended rate to the entire field. (e.g., Mamo et al. 2003, Scharf et al. 2005). On-the-go fertilizer placement, which uses spectral reflectance of the canopy to spatially judge real-time crop N needs (Raun et al. 2002, Li et al. 2009, Scharf and Lory 2009), is a promising technology for improving NUE.

Better management of crop residues can undergird, supplement, and even replace synthetic fertilizers. The quality of organic residues plays an especially important role and can influence N availability by (1) adding N to soils, (2) affecting N mineralization–immobilization patterns, (3) serving as an energy source for microbial activities, and (4) acting as precursors to N sequestration in soil organic matter (Palm and Rowland 1997; Paul et al. 2015, Chapter 5 in this volume).

Decomposition of crop residues and resultant N release are governed by climatic, edaphic, and resource quality factors (Swift et al. 1979).

Of these factors, resource quality is likely the easiest for farmers to manage, but its impact is often difficult to assess. Farmers use a variety of organic inputs, ranging from crop residues to manures, which vary widely in N content. And only a minority of the N from a winter cover crop may be available for the following summer crop (e.g., 4–35%; Ranells and Wagger 1997). Knowing how the quality of applied organic materials (e.g., C:N ratio, mineralizable C and N content, and lignin content) affects N mineralization and immobilization rates (Aulakh et al. 1991, Wagger et al. 1998) is critical for predicting the effect of organic residues on N availability for annual crops.

Due to its effect on available N, residue quality has also been shown to affect denitrification rates and N_2O emissions (Aulakh et al. 2001, Baggs et al. 2000a, Millar et al. 2004). In laboratory incubations using KBS soils, Ambus et al. (2001) found that high-quality (1.88% N) pea residues resulted in greater N_2O emissions than low-quality (0.63% N) barley residues, when both were separately incorporated into soil, either as ground or coarsely cut residues. That study also showed how residue particle size and placement affected both N_2O emissions and NO_3^- leaching potentials.

Managing Hydrologic Flow Paths to Retain or Remove Reactive N

Hydrologic export of reactive N from agricultural systems to ground and surface waters causes well-documented problems, including the degradation of drinking water by excessively high concentrations of NO_3^-, eutrophication of downstream surface waters including marine coastal zones, and additional emission of N_2O to the atmosphere (Galloway et al. 2008; Hamilton 2015, Chapter 11 in this volume). These problems have motivated research to understand how we can manage landscapes to retain or remove reactive N from hydrologic flow paths. Three strategies that specifically apply to agricultural watersheds are discussed in this section (Robertson et al. 2007, Robertson and Vitousek 2009).

First, riparian and other downslope conservation plantings can be managed to keep NO_3^- leached from cropped fields from entering local waterways (Liebman et al. 2013). Native or planted perennial vegetation in stream riparian (buffer) zones can immobilize N in growing biomass and soil organic matter (Lowrance 1998). It is well established that waterway grass (filter) strips can also trap soil particles that would otherwise erode organic N into surface waters. Such measures offer the additional benefits of mitigating sediment and phosphorus losses to surface waters.

Second, restoring stream channels and small wetlands in agricultural watersheds can promote denitrification and other microbial processes that convert NO_3^- to inert or less mobile forms of N (Mitsch et al. 2001). Denitrification is the main process through which streams can permanently remove N (Mulholland et al. 2009). The effectiveness of wetlands in reducing N export from agricultural fields is largely dependent on the magnitude and timing of NO_3^- inputs and the capacity of the system to denitrify or accumulate N in plant biomass and organic detritus. Channelization effectively turns headwater streams and wetlands into pipes that

are less conducive to N retention (Opdyke et al. 2006) because water moves out faster and its N has less contact with stream edges and sediments, particularly during periods of high flow (Peterson et al. 2001, Royer et al. 2006, Alexander et al. 2009). Restoring stream channels and small wetlands to intercept leached N has the potential to significantly reduce downstream NO_3^- loadings.

Additionally, the third strategy involves targeting landscape positions that contribute disproportionately to watershed N fluxes (Robertson et al. 2007; Robertson and Vitousek 2009; Hamilton 2015, Chapter 11 in this volume). It is increasingly clear that much nonpoint source pollution from agriculture arises from relatively small fractions of the landscape (Giburek et al. 2002). Planting forage or other perennial crops such as cellulosic biofuels in these areas (Robertson et al. 2011) could reduce landscape-level N outputs. Restoring or expanding wetlands in low-lying areas could even convert these areas from N sources to N sinks.

Tillage Management to Mitigate N Loss

Tillage affects a number of factors that influence N conservation: physical factors such as soil bulk density, water-holding capacity, drainage, aeration, and aggregate stability; chemical factors such as C and N stores and availability; and biological factors such as microbial activity, rates of decomposition, the presence of earthworms and other invertebrates, and plant root distributions. Few other management practices have such far-reaching effects on cropping system N cycling.

Historically, tillage is responsible for most soil organic matter loss in cultivated ecosystems (Paul et al. 2015, Chapter 5 in this volume) and thereby the loss of most soil organic N stores. On conversion from native vegetation or long-term fallow, most of the N initially harvested in subsequent crops is derived from decomposition (Robertson 1997). Once soil organic N pools are depleted—typically, a few decades in temperate regions, more quickly in the tropics (Robertson and Grandy 2006)—legumes and fertilizers are required to replace the soil's lost capacity to supply N. Because herbicides can now provide weed control as effectively as tillage, conservation tillage (including no-till) can be practiced to conserve organic C and N in soil and thereby restore many of the fertility benefits of less disturbed soils (e.g., Franzluebbers and Arshad 1997, Lal 2004).

Although the many benefits of no-till are well known (e.g., Blevins et al. 1977, Phillips et al. 1980), benefits related to NO_3^- and N_2O conservation are less clear. Comparisons of no-till vs. conventional tillage systems have shown no significant difference in NO_3^- leaching (e.g., Cabrera et al. 1999, Mitsch et al. 1999, Smith et al. 1990), or have demonstrated that no-till leaches either more (Tyler and Thomas 1977, Chichester 1977) or less (Rasse and Smucker 1999, Ogden et al. 1999) NO_3^-. Syswerda et al. (2012) argue that much of this ambiguity is due to experiment duration. They note that most studies last only 2–3 years and begin shortly after no-till establishment. Short-term studies may mask long-term effects that emerge only over periods with both higher and lower rainfall levels (e.g., Cabrera et al. 1999). And studies conducted too soon after a change in management can misrepresent the long-term effects that emerge after equilibration (Rasmussen et al. 1998). In addition to short duration, many studies are performed in small plots, which cannot

readily account for the effects of spatial variation at realistic field scales (Robertson et al. 2007).

Syswerda et al. (2012) made similar comparisons of no-till vs. conventional tillage, but examined NO_3^- losses over an 11-year period that began 6 years after no-till establishment. On average, they found NO_3^- leaching losses from the MCSE No-till and Conventional systems represented 50 and 76%, respectively, of the total N applied to these systems. NUE was higher in the No-till system despite 16% higher drainage losses (388 vs. 334 mm H_2O yr^{-1}, respectively), suggesting that channelized flow in the better-structured no-till soils allows water to leave the profile before it has equilibrated with NO_3^- in small pores (Rasse and Smucker 1999). Higher plant demand for NO_3^- may also have contributed to lower no-till fluxes as the No-till system had somewhat higher average yields (Grandy et al. 2006; Smith et al. 2007; Robertson et al. 2015, Chapter 2 in this volume) and therefore more N uptake.

No-till management can also affect N_2O emissions from soil, although such effects are not consistent. Comparisons of N_2O emissions in the MCSE Conventional and No-till systems have shown no consistently significant differences (e.g., Robertson et al. 2000, Grandy et al. 2006, Gelfand et al. 2013). This is in agreement with other (Parkin and Kaspar 2006, Dusenbury et al. 2008, Sey et al. 2008, Gregorich et al. 2008) but not all (e.g., Liu et al. 2006, Omonode et al. 2011) similar studies. Van Kessel et al. (2013) concluded through meta-analysis that it typically takes at least 10 years before no-till soils exhibit lower N_2O fluxes, in which case we can expect the MCSE No-till system to emit less N_2O in coming years.

Summary

Nitrogen is an essential nutrient for crop growth and the N demands of today's intensive cropping systems are met primarily by synthetic N fertilizer application. Direct consequences of over-applying N fertilizer are substantial losses of reactive N to the environment in the form of NO_3^- leached to ground and surface waters and N_2O emitted to the atmosphere. The environmental costs of excess N loading include coastal zone eutrophication, compromised drinking water and air quality, climate warming, stratospheric ozone depletion, and biodiversity loss. However, cropping systems can acquire N through legume N fixation, manure addition, and crop residue return—offering many options for N management at the farm scale.

Results from KBS LTER research underscore the value of practical agronomic practices that improve N retention in row crops. Potential interventions include increasing rotational complexity with different primary and cover crops; using no-till management; and improving N synchrony with better rate, timing, placement, and formulation of N fertilizers, so crop N needs are met more precisely. Residue management can also contribute to N conservation. Improved landscape management can partially mitigate N leaching losses from the farm field through measures such as maintaining or planting riparian vegetation, restoring stream channels and small wetlands, and the targeted planting of forage or other perennial crops such as cellulosic biofuels. The most poorly known N cycle fluxes at

the KBS LTER are emissions of N_2 and NO_x, both from denitrification. Providing farmers with strategies or incentives that reduce N fertilizer use while maintaining high agronomic yield is a logical first step in mitigating agriculture's impact on the environment.

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