Ecosystems (2001) 4: 582–602
DOI: 10.1007/s10021-001-0031-2

ECOSYSTEMS

Nitrogen Balance for the Central Arizona–Phoenix (CAP) Ecosystem

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Abstract

A detailed fixed nitrogen (N) mass balance was constructed for the Central Arizona–Phoenix (CAP) ecosystem. Input of fixed N input to the ecosystem was 98 Gg y^{-1}. Of this, humans deliberately imported or mediated the fixation of 51 Gg N y^{-1}; combustion processes added another 36 Gg y^{-1}. Fixation by desert plants, wet deposition, and surface water input accounted for 11% of total N input. Total fixed N output was 78 Gg N y^{-1}, a large component of which was gaseous N products of combustion and denitrification. Computed accumulation of N was 21 Gg y^{-1} (total input minus total output) or alternatively, 17 Gg y^{-1} (summing individual accumulation fluxes). Key uncertainties include dry deposition of atmospheric N and changes in soil storage. Inputs to the urban and agricultural components of the ecosystem were an order of magnitude higher than inputs to the desert. Human hydrologic modifications in this ecosystem promote the accumulation and volatilization of N while keeping riverine export low (3% of input). Interplay among the form and amount of N inputs, edaphic and climatic characteristics of the system, hydrologic modifications, and deliberate efforts to reduce N pollution controls the fate of N in human-dominated ecosystems.

Key words: nitrogen cycling; nitrogen budget; denitrification; groundwater; wastewater; fertilizer; dairy manure; vadose zone; nitrate; urban ecosystem.

Introduction

Nitrogen (N) is a key element in the functioning of many ecosystems (Schlesinger 1997). Human activities have profoundly altered the cycling of N over large regions, typically increasing inputs, availability, storage, and transport (Vitousek and others 1997a). Modification of the N cycle is likely to be particularly marked in and around urban areas (see, for example, Riggan and others 1985; Padgett and others 1999; Bytnerowicz and Fenn 1996) because cities constitute hugely heterotrophic patches or "hot spots" for nutrient transformation within the larger landscape (Grimm and others forthcoming).

N cycling in relatively undisturbed terrestrial ecosystems is typically dominated by internal transfers between plants and various soil pools (Schlesinger 1997). Major inputs and outputs are largely biotically controlled via fixation and denitrification; net physical transfers via atmospheric deposition and transport in surface runoff and to groundwater are usually less important (Schlesinger 1997). The N cycle in semi-arid and arid environments is largely similar to that of mesic terrestrial biomes, although a lack of moisture often supersedes the importance of N supply in terms of limitations to primary productivity. The relative importance of dry deposition (the deposition of particles and adsorption of gases) vs wet deposition increases in drier climates. Desert ecosystems usually have large stable N soil pools in which most N is fixed to clays and thus only partly available to plants (West and Skujins 1977).

In human-dominated ecosystems, particularly

Received 24 September 1999; accepted 7 March 2001.
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agricultural systems, N fixation by agricultural crops and the deliberate application of fertilizer are major N inputs (Schlesinger 1997; Vitousek and others 1997a). In urban ecosystems, additional N inputs occur primarily via the importation of foodstuffs for humans, as well as by inadvertent "fertilization" through the production and subsequent deposition of NO_x derived from the combustion of fossil fuels. In the United States, major sources of anthropogenic N include commercial fertilizers (9.2–10.3 Tg), crop fixation (6.6 Tg), and atmospheric deposition (2.6–2.9 Tg), which is largely derived from combustion processes (Jordan and Weller 1996; Puckett 1995). N transfers in human-dominated ecosystems are inherently inefficient; there is leakage of N at each point in the food chain from fertilization through human excretion. These leaks lead to increased storage in soil and groundwater pools and increased losses in rivers (Bleken and Bakken 1997; Puckett and others 1999; Vitousek and others 1997a).

The production of excess N in human ecosystems has serious deleterious effects. Groundwater in many areas in the United States has been so polluted by nitrate that it is no longer safe for human consumption (Neilsen and Lee 1987). High-ammonium wastes discharged to rivers may cause ammonia toxicity or deplete oxygen as ammonium is consumed by nitrification (Chapra 1994). Nitrogen enrichment also causes the eutrophication of lakes and estuaries and is a major component of acid rain (Vitousek and others 1997a). Finally, NO_x emissions cause undesirable ground-level ozone formation in urban environments (Masters 1996). Although many pollutants have been reasonably controlled by treating the point sources of waste water (for example, biodegradable municipal wastes) or by reducing or eliminating their uses (for instance, lead and chlorinated hydrocarbon pesticides), nitrogen remains a ubiquitous, poorly controlled pollutant (Baker 1992; Smith and others 1994; Howarth and others 1996; Vitousek and others 1997a).

A starting point for understanding the nitrogen cycle in agro-urban ecosystems is a detailed nitrogen mass balance. Fairly complete N mass balances for a number of watersheds with substantial human activity (mostly agriculture) have now been compiled (Messer and Brezonik 1983; Correll and others 1992; Jaworksi and others 1992; Barry and others 1993; Freifelder and others 1998; Puckett and others 1999), but there have been no detailed studies of N balances in watersheds that include major urban areas.

The objective of this study was to create a detailed N mass balance for an arid ecosystem that includes a major city (Phoenix) and the surrounding agricultural land and desert. The N balance was then examined to answer the following questions: What is the magnitude of major fluxes across the ecosystem boundary and among subsystems? How does N cycling vary among ecosystem components (desert, urban areas, agriculture)? What effect do dramatic modifications to the hydrological pathways have on N pools and fluxes? Which budget terms are most amenable to management efforts to reduce N pollution to recipient systems?

Study Area

For the purpose of this study, the Central Arizona Project (CAP) ecosystem is defined as the 12,384 km^2 watershed that includes the Phoenix metropolitan area and the surrounding agricultural land and desert (Figure 1). The upstream boundary is formed by the lower water supply reservoirs on the Salt and Verde rivers to the east and northeast, the Central Arizona Project Canal to the north, and the Gila River below its confluence with the Santa Cruz River to the south. Water exits the watershed via the Gila River at Gila Bend, Arizona (Figure 1).

In the vertical direction, the ecosystem extends below the surface to bedrock. This definition was adopted because there are significant vertical fluxes of N between the surface and underlying aquifers, and there is significant belowground storage of N in soils, the vadose zone, and aquifers. The upper boundary of the ecosystem is defined as a few hundred meters above the land surface. The ecosystem therefore includes combustion sources (automobiles, power plants, and so on).

Most (77%) of the ecosystem is undeveloped and sparsely populated. From the early part of the twentieth century through the 1950s, there was far more agricultural than urban land. In recent years, rapid population growth has led to a conversion of agricultural land and desert to urban uses. The human population of the ecosystem increased 40% in the 10 years prior to 1995, reaching 2.53 million inhabitants in 1995. The vast majority of the population lives in the urbanized area, which comprises about 13% of the ecosystem. About 10% of the land area is used to grow crops—mainly cotton, winter wheat, alfalfa, and citrus. Dairy is the main livestock industry; there are about 100 dairies and 150,000 cows within the CAP ecosystem.

The average rainfall is only 18 cm y^{-1}, which is insufficient to support the needs of the city and surrounding agriculture. To develop an agricultural system, dams were constructed to impound about

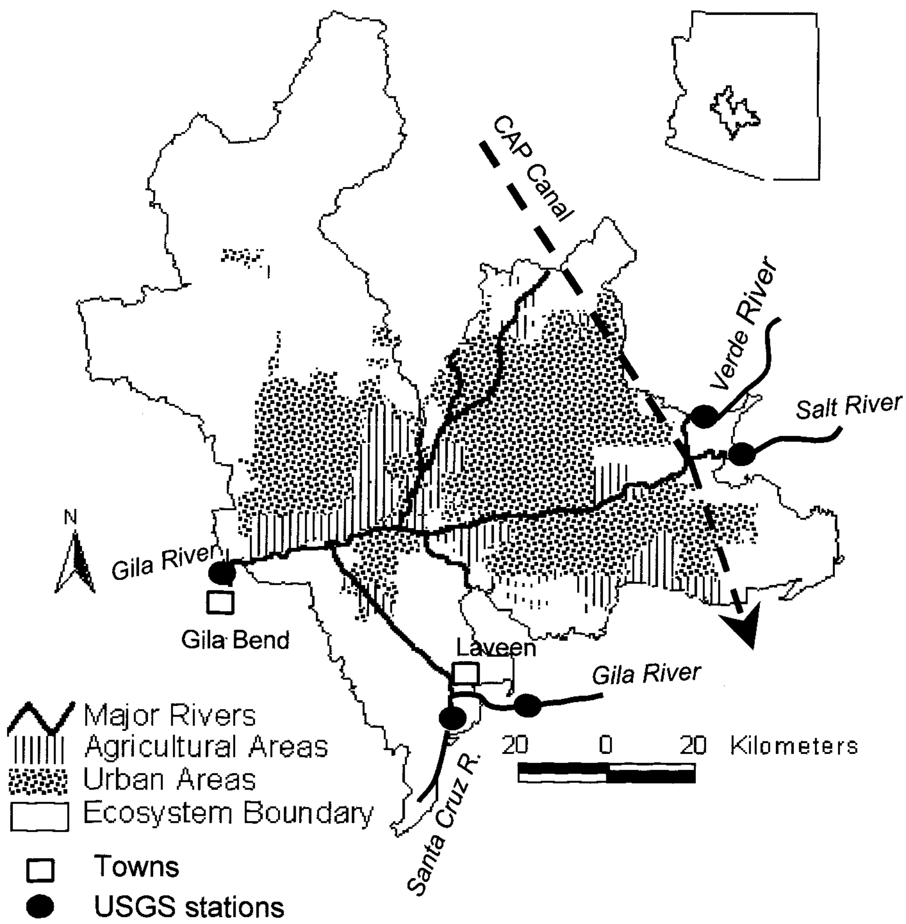

Figure 1. Map of the Central Arizona–Phoenix (CAP) ecosystem showing major rivers and land uses.

1.2×10^9 m^3 y^{-1} of water from upstream watersheds (the Salt, Verde, and Gila rivers) during spring runoff and then release it throughout the year. This water supply has been augmented in recent years by the Central Arizona Project Canal, which transports an additional 0.7×10^9 m^3 y^{-1} of water from the Colorado River into the CAP ecosystem. Upstream water inputs, if distributed evenly across the watershed, would approximately double natural precipitation.

Mass Balance Approach

In the mass balance presented here, N fluxes are broken down into natural inputs and human-mediated inputs. Natural inputs are those inputs not directly controlled by humans, including surface water inputs, fixation of nitrogen by desert plants, and atmospheric deposition. Human-mediated inputs include direct importation (for example, food), biological fixation by agricultural crops (mostly alfalfa), and the production of combustion-derived NO_x (abiotic fixation). Human-mediated inputs are further divided into deliberate and inadvertent inputs (Vitousek and others 1997b). Deliberate inputs include fertilizers and other chemicals, human food, pet food, and protein concentrates used in the dairy industry. The main inadvertent input is combustion-derived NO_x (Figure 2).

Within this overall framework, we have broken down the mass balance into the following major subsystems: near-surface atmosphere, desert, cropland, dairies, human food, domestic pets, wastewater, urban landscape, and subsurface. Much of the N in agro-urban ecosystems is transferred among subsystems within the ecosystem either deliberately or inadvertently. For example, much of the N in cow feed becomes manure, which is deliberately recycled to cropland. Similarly, a fraction of the NO_x produced by combustion in the near-surface atmosphere is deposited across the three major landscape types. Nitrate in groundwater pumped to the surface for irrigation is inadvertently recycled to crops and landscape plants.

Outputs include the atmospheric export of gases (N_2, NO_x, NH_3, N_2O), the exportation of food, and

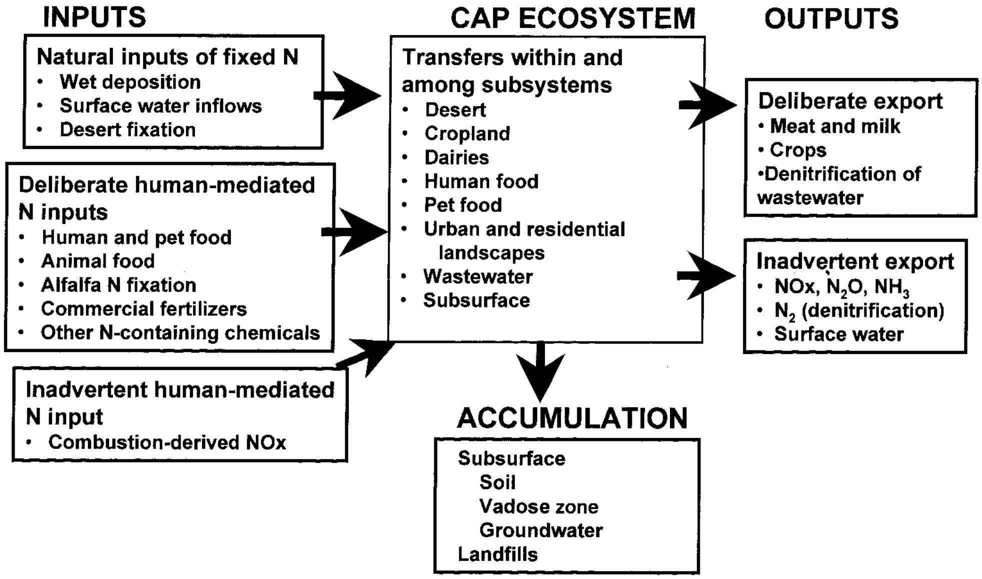

Figure 2. Components of the N budget for the CAP ecosystem.

riverine export. Accumulation of N in the ecosystem was computed in two ways: first, as the difference between ecosystem inputs and outputs, and second, as the sum of fluxes to the subsurface environment and landfills, minus the upward flux of pumped groundwater.

Some fluxes are, by necessity, net fluxes. For example, enough milk is produced within the ecosystem to supply humans, with some left over for exportation. We therefore assumed that all milk consumed by humans living in the system was actually produced within the system. In reality, some milk used by humans is probably imported, meaning that gross exports are probably slightly higher than we estimated. The net flux, however, will be the same in either case. Throughout this paper, protein content was divided by 6.25 to yield N content.

Results: Mass Balance Components

Surface Water Inputs and Outputs

United States Geological Survey (USGS) records were used to develop estimates of surface water inputs and exports. Surface water N loadings were computed for three major rivers that enter the CAP ecosystem: the Salt River above Roosevelt Lake, the Verde River above Horseshoe Reservoir, and the Gila River below Laveen. Loadings were also calculated for diversions from the Central Arizona Project Canal and for water leaving the ecosystem via the Gila River at Gila Bend. All loadings were computed for a common time frame, 1988–96, using the midpoint method (Dolan and others 1981). Each annual period was divided into time segments such that each segment included a chemical datum at the midpoint. Total flow for each time segment was computed by summing daily flows. Loading for each segment was calculated as the product of total flow times the midpoint concentration; these were summed to compute annual loadings. We used a long period of record because there were few concentration data points (typically less than 10) for any given year. High interannual variability—in particular the flood of 1993, a 100-year event—skewed the average N loading for the 1988–96 period. The median loading was therefore used as a more representative estimate of typical conditions than the mean.

The southern upstream boundary of the CAP watershed is the Gila River below its confluence with the Santa Cruz River near Laveen, Arizona. Because there is no gauging station on the Gila River below the confluence, we summed flows for the Gila and Santa Cruz rivers immediately above Laveen to represent the flow of the Gila River below Laveen. Because neither of these sites is a chemical monitoring station, we assumed that N concentration in the Gila River at this point was the same as the flow-weighted mean for the upper Salt and Verde rivers. Much of the flow of the lower Gila and Santa Cruz rivers is diverted to agricultural areas above Laveen, so runoff for the Gila River at Laveen is only 0.01 cm y^{-1}.

Finally, N loading from the Central Arizona Project Canal was computed by multiplying the average flow diverted to Maricopa County from 1996 to 1998 (diversions prior to 1996 were very

Table 1. Surface Water Inflows and Outflow for the CAP-LTER Ecosystem

Component	N loading ($Gg\ y^{-1}$)
Inputs	
Salt above Roosevelt	+0.47
Verde above Horseshoe Reservoir	+0.28
Central Arizona Project Canal (diversions to Maricopa County)[a]	+0.48
Gila River below Laveen	+0.01
Total surface water inputs	+1.24
Outputs from Gila River at Gila Bend	−2.63

Values marked by + are inputs to the ecosystem; values marked by − are outputs from the ecosystem.
[a]The Central Arizona Project Canal transports a portion of the flow of the Colorado River to central Arizona.

small) times the average N concentration as measured monthly during the 1st year of the Central Arizona–Phoenix Long-term Ecological Research Program (CAP-LTER).

Total N input from surface-water inflows to the CAP ecosystem was 1.2×10^6 Gg y^{-1} (Table 1). Exportation of water was approximately 10% of surface-water inputs. Groundwater recharge and pumping are roughly equal (ADWR 1998); this means that about 90% of water imported into the system was lost by evaporation. However, the total N concentration was about 20 times higher in the outflow than the inflow, reflecting N gained from agricultural drainage, urban runoff, and wastewater. N export from the ecosystem via the Gila River (2.6 Gg N y^{-1}) was therefore twice as high as the surface-water input.

Near-surface Atmospheric Subsystem

The atmosphere immediately overlying the terrestrial ecosystem (from the ground surface to a height of a few hundred meters) was considered as a subsystem within the ecosystem. Sources of fixed N (NO_x, mainly NO, NO_2, N_2O, and NH_3) to the atmospheric subsystem include combustion processes and emissions from landscapes, manure, and wastewater. Combustion is the main source of NO_x in the CAP-LTER ecosystem. Using a transportation model (Mobile 5) and emissions factors for eight vehicle types, Heisler and others (1997) estimated that combustion processes in the CAP-LTER ecosystem emitted 33.8 Gg NO_x-N y^{-1}, primarily from mobile sources (trucks, autos, and off-road machinery). A rough estimate of N_2O emissions from combustion processes was made by scaling down the national emissions estimate based on the ratio of population in the CAP-LTER ecosystem and the United States (EPA 1999). An emissions factor of 0.01 kg N_2O/kg wastewater N was used to estimate N_2O emissions from wastewater treatment plants (IPCC 2000); the N_2O flux was subtracted from the total denitrification flux to estimate the N_2 flux.

Fixed N enters the atmospheric subsystem via the denitrification and volatilization of ammonia from land surfaces. We estimated that the total volatilization loss from cropland is one-half of “excess” N. Ammonia volatilization is typically 10% of fertilizer addition (Schlesinger 1992). The sum of N_2O and NO is probably no more than 5% of N inputs (Veldkamp and Keller 1997; Mosier 1994; Eichner 1990; Matson and others 1998; Davidson and Kingerlee 1997), with each species contributing a roughly equal amount (Matson and others 1998).

For lack of better information, the same percentages were used to compute volatilization losses for urban landscapes. Because N inputs other than commercial fertilizer were important to cropland and urban landscapes, total N inputs were used as the basis for estimating volatilization losses. For the desert, we assumed that denitrification was the main N volatilization process, with 5% of N input being volatilized as N_2O and NO (2.5% each). Gross denitrification (sum of N_2, N_2O, and NO_x fluxes) was considered a loss of fixed N (nitrate) from individual subsystems.

Much of the NO_x and ammonia entering the atmospheric subsystem is recycled to land surfaces via atmospheric deposition, whereas N_2O is considered conservative. In arid areas, the majority of atmospheric deposition is in the form of dry deposition to surfaces (deposition of particles, adsorption of gases). The modeling of dry deposition was well beyond the scope of this study, so the ratios of dry deposition: emissions that were developed in a detailed modeling effort in the South Coast Air Basin (Russell and others 1993) were extrapolated to Phoenix. This extrapolation is a reasonable first approximation for the following reasons: (a) both areas include a low-density urban core surrounded by cropland and pasture, which is in turn surrounded by large areas of rangeland; (b) both areas are arid; and (c) mobile NO_x emissions dominate inputs to the atmosphere in both systems. Russell and others (1993) found that 52% of NO_x emissions and 53% of ammonia emissions were deposited within their modeled air shed. These fractions were applied to emissions of NO_x and NH_3 in the Phoenix ecosys-

Table 2. Atmospheric Submodel for Fixed N in the CAP-LTER Ecosystem Fluxes in Gg N yr^{-1}

	NO_x	N_2O	Ammonia
Inputs to atmospheric subsystem			
Combustion NO_x emissions	+33.8	+2.5	0.0
Volatilization from desert	0.5	0.5	0.0
Volatilization from cropland	0.9	0.9	3.6
Volatilization from urban landscapes	0.4	0.4	1.8
Denitrification from WWTPs	0.0	0.1	0.0
Volatilization of dairy manure	0.0	0.1	2.6
Total inputs to atmospheric subsystem	35.6	4.6	8.0
Outputs from atmospheric subsystem			
Dry NO_x deposition (0.52* emissions)	18.5	0.0	0.0
Dry NH_3 deposition (0.53* emissions)	0.0	0.0	4.3
Export from ecosystem	−17.1	−4.6	−3.8
Total outputs from atmospheric subsystem	35.6	4.6	8.0

Values marked by + are inputs to the ecosystem; values marked by − are outputs from the ecosystem. Change in storage within the atmospheric subsystem was assumed to be 0.

tem to estimate dry deposition, yielding an N dry-deposition rate of 18.5 kg ha^{-1} y^{-1}. Uncertainties related to this approach will be discussed later.

N emissions from landscapes and atmospheric dry deposition are inextricably linked. Emissions of gaseous N species from landscapes are proportional to N inputs, and a fraction of N emissions entering the atmospheric subsystem becomes dry deposition, which is recycled to landscapes via dry deposition. It was therefore necessary to develop the atmospheric N balance iteratively, starting with an initial estimate of atmospheric deposition and then refining this estimate until the new estimate of dry deposition and the previous estimate converged. Convergence was considered complete when the latest estimate of atmospheric deposition was within 1% of the previous estimate.

Net exchange of gases between the atmospheric subsystem and the external atmosphere was computed as the difference between dry deposition and emissions. Annual export of fixed N from the ecosystem via the atmospheric subsystem included 17.1 Gg NO_x-N, 4.6 Gg N_2O-N, and 3.8 Gg NH_3-N (Table 2). The 48.3 Gg N_2 produced annually by denitrification almost exactly balanced the consumption of 46.9 Gg N_2 by abiotic and biotic fixation.

Wet deposition of NO_3^- + NH_4^+, as measured at eight sites throughout the CAP-LTER ecosystem in 2000, averaged 2.4 kg N ha^{-1} y^{-1} (D. Hope unpublished). This value is only slightly higher than the average 1992–95 wet deposition rates of NO_3^- and NH_4^+ of 0.7 kg ha^{-1} y^{-1} and 1.2 kg ha^{-1} y^{-} measured at the two closest National Atmospheric Deposition Program stations (Oliver Knob, AZ99; and Organ Pipe Cactus National Monument, AZ06, respectively) (Clarke and others 1997) and 1.6 kg ha^{-1} y^{-1} measured at seven sites in southeast Arizona (Emmerich 1990). We assumed that N deposited via wet deposition was imported from beyond the ecosystem boundary during infrequent precipitation events.

Desert Subsystem

Desert landscapes in the ecosystem received 17.6 Gg N y^{-1} N from dry deposition (recycled N), 2.3 Gg N y^{-1} from wet deposition, and additional N from biological fixation (Table 3). Many woody legumes common in the Sonoran Desert are believed to fix N_2 (Rundel and others 1982; Shearer and others 1983; Crawford and Gosz 1982). In what is apparently the only extensive effort to quantify N_2 fixation in the Sonoran Desert, Rundel and others (1982) found that stands of *P. glandulsosa* fixed 25–30 kg N ha^{-1} y^{-1}. In their study, *Prosopis* covered 34% of ground surface, yielding an ecosystem-wide N fixation rate of 9–10 kg N ha^{-1} y^{-1}. In a recently completed synoptic study of 200 randomly sampled plots throughout the CAP ecosystem, the average cover of three species of woody legumes (*Prosopis, Olneya*, and *Cercidium*) in 11 plots classified as desert was 26%. *Prosopis* alone accounted for 11% of the cover in these plots, mostly because one plot was a pure stand (C. Gries personal communication). Woody legume cover was multiplied by the midpoint of the range reported by Rundel and others (1982) to produce an estimated N fixation in the

Table 3. N Budget for the Desert Subsystem

Component	N flux ($Gg\ y^{-1}$)
Inputs	
Dry deposition[a]	17.6
Wet deposition	+2.3
N fixation	+7.1
Total inputs to desert subsystem	26.9
Outputs	
Runoff	−0.1
Volatilization	−26.2
Total outputs from desert subsystem	−26.3
Accumulation in desert subsystem	0.6

Values marked by + are inputs to the ecosystem; values marked by − are outputs from the ecosystem. Other fluxes are transfers from one subsystem of the ecosystem to another.
[a]Total N dry deposition to desert = ecosystem NH_3 + NO_3 dry deposition (from Table 2) times fraction of CAP-LTER ecosystem in desert (0.75).

CAP desert of 7.4 kg N $ha^{-1}\ y^{-1}$, yielding a total N fixation rate of 7.1 Gg N y^{-1} (Table 3).

N fixation in cryptogamic crusts is important in some deserts (West and Skujins 1977), but Rundel and others (1982) found little evidence of N fixation by free-living organisms in their study of N fixation in the Sonoran Desert. MacGreagor and Johnson (1971) reported rates of 0.003–0.004 g $ha^{-1}\ h^{-1}$ in algal crusts from the Sonoran Desert following a rainfall, but they did not develop an annual estimate of fixation for the desert crust. Jeffries and others (1992) estimated N accumulation in cryptogamic crusts to be less than 2 kg ha^{-1} y^{-1}. Thus, we assumed, as do Peterjohn and Schlesinger (1990), that N fixation in the desert crust is minimal.

Exports of N included surface runoff, deep seepage, and denitrification. Areal N export for the Verde River watershed above Horseshoe Reservoir, 0.15 kg N $ha^{-1}\ y^{-1}$, was used as a reasonable estimate for N in surface runoff from the desert portion of the CAP ecosystem, yielding a runoff flux of 0.1 Gg N y^{-1}. Deep seepage is probably close to zero (Peterjohn and Schlesinger 1990) because potential evaporation greatly exceeds precipitation. Peterjohn and Schlesinger (1990) concluded that N accumulated in desert soils at a rate of 0.6 kg N ha^{-1} y^{-1}. This figure may be an overestimate, because they assumed that initial storage 10,000 years ago was zero. The denitrification rate for the CAP-LTER desert subsystem, computed as inputs–runoff–accumulation, was 28 kg $ha^{-1}\ y^{-1}$ (26.2 Gg y^{-1}). This is far higher than the values that have been reported for the Chihuahuan Desert—(2.3 kg $ha^{-1}\ y^{-1}$ computed by difference (Peterjohn and Schlesinger 1990) and 7.2 kg $ha^{-1}\ y^{-1}$ by direct measurement (Peterjohn and Schlesinger 1991), reflecting higher productivity and higher N deposition in the CAP-LTER ecosystem.

Cropland Subsystem: N Inputs

Commercial fertilizer. The extent of areas in various land uses was determined by using land-use maps from the Maricopa Association of Governments (MAG) that had been truncated to the CAP ecosystem boundaries. A small part of the CAP ecosystem lies outside Maricopa County, but none of this land is agricultural. Crop production within the CAP ecosystem was computed using crop statistics for Maricopa County Arizona Agricultural Statistics Service (AASS) 1997, adjusted using the ratio of cropland in the CAP ecosystem to cropland in the entire county (0.65). Recommended fertilizer N input for each crop (except alfalfa) was computed by multiplying cropped area times the midpoint of the recommended range of fertilization rates for the given crop (Doerge and others 1991) (Table 4). The total recommended N fertilizer rate for agricultural crops in the CAP ecosystem was 14.0 Gg N y^{-1}, and the total for all of Maricopa County was 21.6 Gg y^{-1}. A check between total N input computed from recommended application rates for both cropland and urban landscapes and county fertilizer sales is presented in the Urban Landscape Subsystem section.

N fixation by alfalfa. The main N-fixing crop in the CAP ecosystem is alfalfa. The amount of N harvested in alfalfa was computed by adjusting county-level yields to the ecosystem boundaries, then multiplying this figure by an average N content of 2.8% (AASS 1997; Doerge and others 1991). This computation resulted in an alfalfa N harvest of 7.5 Gg N y^{-1} (Table 4). Most N fixed by alfalfa is removed during harvest (Barry and others 1993; Puckett and others 1999; Heichel and others 1984). In this region, alfalfa is generally grown on a 3-year rotation basis with up to eight harvests per year, so N loss by leaching is likely to be small. We therefore assumed that all N fixed by alfalfa was removed by harvesting. Nearly all of the alfalfa produced within the ecosystem is fed to dairy cows.

Other N inputs: Manure, groundwater, waste-water effluent, and atmospheric deposition. Manure from dairies is recycled to agricultural fields. There is substantial N input to crops and landscape plants from nitrate-contaminated groundwater and wastewater effluent used for irrigation and from wastewater biosolids (Table 5). These fluxes are

Table 4. Agricultural crops and fertilization rates in the CAP ecosystem

Crop	Area (km^2)	Recommended fertilization rate (kg N ha^{-1} y^{-1})	Total recommended fertilizer use (Gg N y^{-1})	Crop yield (Gg N y^{-1})
Upland cotton	310	195	6.09	4.25
Pima cotton	19	195	0.37	0.25
Field corn	20	240	0.48	0.58
Silage corn	27	240	0.63	0.6
Alfalfa	142	0	0	7.51
Other hay	7	200	0.15	0.11
Wheat (all types)	131	250	3.26	2.6
Barley	48	215	1.06	0.78
Row crops (lettuce, etc.)	73	180	1.30	0.80
Citrus	44	155	0.69	0.22
Total	821	—	14.0	17.71

discussed in the sections on Waste-water Subsystem and Subsurface. Atmospheric wet deposition (external input) and dry deposition (recycled from atmospheric subsystem) comprised about 6% of total N input to the crop subsystem (Table 5).

Cropland Outputs

Harvested crops. Data on harvested crops for 1996 were obtained from state agricultural records (AASS 1997). Data on the N content of harvested crops were obtained from several other sources (Legg and Meisinger 1982; Olson and Kurtz 1982; Doerge and others 1991). Total crop N yield was 17.7 Gg N y^{-1} (Table 4). About 81% of the total crop N (14.4 Gg N y^{-1}) was fed to animals within the ecosystem (mainly dairy cows) as protein concentrates (primarily cottonseed and corn) and forage (alfalfa and other hays), or exported as animal food (a small amount of alfalfa; Table 5). The rest of the crop N (3.3 Gg N y^{-1}) was human food (mostly wheat and barley) consumed within the ecosystem (Table 5).

Other losses from the crop system. N added to cropland but not removed by crop harvest or riverine export was lost by volatilization or transported to the subsurface. Riverine N output attributable to agriculture was computed by subtracting contributions from wastewater and urban runoff from total N output for the Gila River at Gila Bend (Table 5). Volatilization losses included direct volatilization of ammonia-based fertilizers, ammonia volatilization from manure applied to fields, and denitrification. Based on a range of values from other agricultural watersheds (Correll and others 1992; Puckett and others 1999; Hall and Risser 1993), we assumed that half of the excess N was volatilized while the other half was leached to the subsurface (Table 5). Apportionment of volatile N into ammonia, N_2, N_2O, and N_2 is discussed in the Atmospheric Subsystem section.

Dairy Industry Subsystem

The only significant source of animal protein production within the ecosystem is the dairy industry. In 1996, there were 180,000 cows, including 103,000 milking cows, in Maricopa County (AASS 1997). The difference between these populations represents calves and replacement heifers. The ratio of stockyard area in the CAP-LTER ecosystem to stockyard area in the entire county (0.83) was multiplied by the number of cows in the county to estimate the number of cows within the CAP ecosystem (150,000). The average weight of a replacement cow was assumed to be one-third that of a milking cow. The rate of cows leaving the herd was computed from a milking life of 3.5 years (D. Armstrong personal communication), yielding a turnover rate of 0.28 y^{-1}, or 24,500 cows/year.

Inputs to dairies. N input to the dairy industry was computed separately for milking cows and heifers. The average weight of a milking cow at the time of slaughter is 500 kg, and average milk production is 9283 kg y^{-1} (AASS 1997). These values were used in conjunction with recommended feed tables (Harris 1992 NRC 1988) to estimate crude protein intake. Protein supplied by concentrates (high-protein feeds, mainly grains) fed to dairy cows was based on statewide data on the use of concentrates, the number of milkcows (AASS 1997), and an estimated protein content of 20% for concentrates (Ensminger 1993). The amount of forage required by milkcows was computed by subtracting protein

Table 5. N Balance for the Crop Subsystem

Component	Flux ($Gg\ y^{-1}$)
External inputs to crop subsystem	
Commercial fertilizer (from Table 4)	+14.0
Alfalfa N fixation (from Table 4)	+7.5
Wet deposition	+0.30
Total external inputs to crop subsystem	+21.8
Transfers from other subsystems	
Dry deposition (from Table 2)[a]	2.3
Manure (from Table 6)	7.9
Pumped groundwater nitrate (from Table 11)	9.9
Wastewater effluent (from Table 9)	0.6
Wastewater biosolids (from Table 9)	1.4
Total transfers from other subsystems	22.2
Total N input to crop subsystem (external inputs + transfers)	44.0
Outputs from crop subsystem	
Total crop harvest	17.7
Animal food[b]	
Concentrates	6.9
Alfalfa (from Table 4)	4.7
Consumed by dairy cows	5.7
Exported from system	−1.8
Human food[c]	3.3
Total volatilization	12.3
Leaching to subsurface	12.3
Flux to Gila River outlet	−1.7
Total output from crop subsystem	44.0

Values marked by + are inputs to the ecosystem; values marked by − are outputs from the ecosystem. Other fluxes are transfers from one subsystem of the ecosystem to another.
[a] *Total N dry deposition to cropland = ecosystem NH_3 + NO_3 dry deposition (from Table 2) times fraction of CAP-LTER ecosystem in cropland (0.10).*
[b] *Concentrates include cottonseed, corn, and other hay (from Table 4) plus small amounts of hay from wheat and barley crops.*
[c] *Human food includes wheat, barley, row crops, and citrus (from Table 4).*

Table 6. N Balance for Dairy Subsystem

Component	N flux ($Gg\ y^{-1}$)
External inputs to dairy system (feed)	
Concentrates	+2.7
Transfers from other subsystems	
Alfalfa (from Table 5)	5.7
Concentrates (from Table 5)	6.9
Total inputs to dairy subsystem	15.2
Outputs	
Milk produced	4.2
Consumed within system	1.8
Exported from ecosystem	−2.4
Meat (100% consumed within system)	0.1
Cows for slaughter outside ecosystem	−0.1
Manure (100% recycled)	10.6
Volatilized during storage	−2.7
Transferred to crop system	7.9
Total outputs from dairy subsystem	15.0

Values marked by + are inputs to the ecosystem; values marked by − are outputs from the ecosystem. Other fluxes are transfers from one subsystem of the ecosystem to another.

supplied from concentrates from the total protein requirement.

The number of replacement heifers was estimated from the normal turnover rate for the milking herd and the length of time from birth to maturity (24 months) (D. Armstrong personal communication). The difference between this value (51,500) and the total number of nonmilking cows (64,200), as computed by the Arizona Agricultural Statistics Service (1977), probably reflects the deaths of calves, which we assumed did not consume significant N. The amount of N needed for a calf to grow to maturity was computed from the N content of a mature cow and a protein conversion efficiency of 9% (Ensminger 1993). The N content of a mature cow was computed from the average weight of a mature milkcow in Arizona, a computed ratio of 0.6 for the conversion of beef on the hoof to marketable beef based on national statistics (USDA 1995), and a protein content of 17% for beef carcass (USDA 1998). We assumed that heifers consumed only forage.

Total N consumption for the dairy industry was computed by summing the N consumption of the milking and replacement herds (Table 6). For the entire herd, concentrates provided 62% of the N and forages provided the remaining 38%. Importation of concentrates was computed as the difference between within-CAP production and the total concentrate requirement (Table 6). Alfalfa grown within the ecosystem (Table 5) provided 95% of the protein requirement for the dairy herd.

Outputs from dairies. Nitrogen leaves the dairy subsystem as milk, manure, and cows for slaughter. Nitrogen contained in milk was computed using statewide milk production statistics and a protein content of 3.29% (USDA 1998) (Table 5). Based on a consumption rate of 277 g milk d^{-1} (Borrud and others 1996) and allowing for 31% wastage (Kantor and others 1997), consumption of milk by humans within the system was one-third of total milk production. The rest was exported from the ecosystem (Table 6).

Cows left the dairy herd by slaughter within the CAP system or by the export of live cows for slaugh-

Table 7. Protein and Nitrogen Intake for Humans in the CAP Ecosystem

Age (yr)	Male Population	Male Protein (gd^{-1}) (% RDA)	Male Total N input ($Gg\ y^{-1}$)	Female Population	Female Protein (gd^{-1}) (% RDA)	Female Total N input ($Gg\ y^{-1}$)
0–5	126,900	49 (267)	0.36	131,000	49 (267)	0.38
6–11	116,100	70 (240)	0.48	119,900	62 (213)	0.44
12–19	142,000	98 (184)	0.81	146,700	65 (145)	0.56
>20	941,500	95 (152)	5.22	972,100	63 (127)	3.59
Total	1,326,500	—	6.87	1,369,700		4.96

Protein intake values from Borrud and others (1996).

ter elsewhere. Exportation of live cows was computed by subtracting within-county slaughter (11,000 cows/year) from total herd replacement. The N content of cows being exported or slaughtered was computed as described above. We assumed that beef slaughtered within the ecosystem was consumed within the ecosystem (Table 6).

Finally, manure N was computed using a manure production rate of 0.085 kg wet manure per kg cow and an N content of 0.005 kg N (kg wet manure)$^{-1}$ (Ensminger 1993). In computing manure production, replacement cows were assumed to weigh one-third as much as mature milkcows. Total manure production was 10.6 Gg N y^{-1}. We assumed that one-fourth of the manure production was lost by volatilization during storage (Ensminger 1993) (see Table 2).

Computed inputs to the dairy system were within 1% of outputs. Calculated protein conversion efficiency for the CAP dairy herd was 34%—very close to the 37% cited by Ensminger (1993). Nearly all of the protein consumed by cows that is not converted to milk becomes manure.

Human Food Subsystem

Human food requirements: Consumption. Actual protein intake by age groups (under 5, 6–11; 12–19; over 20) and sex was computed using data from the USDA's Food Survey Research Group (Borrud and others 1996; USDA 1999). US. census data for 1990 (US Census Bureau 1990) were used to compute the age and sex distribution of the population of Maricopa County (Table 7). Total population was updated using a 1996 population estimate (MAG 1996). Total direct human N consumption was 11.8 Gg N y^{-1} (sum of males and females in Table 7).

Food waste. According to Kantor and others (1997), average food waste in the United States, computed as the difference between food production and actual consumption, is 0.45 kg capita^{-1} d^{-1}. We estimated the protein content of various food types in the Kantor study (for example. "grains"; red meat) by finding the closest match to these categories in nutrition tables (USDA 1998). The weighted-average protein content for all wasted food was 4.7%, yielding a total food waste of 3.2 Gg N y^{-1}. Because most food protein was contained in easily matched categories (for example, red meat), the error in this estimate is probably small.

Inputs to human food subsystem. The total human food requirement—the sum of actual consumption plus food waste—was 15.0 Gg y^{-1} (Table 8). About one-third of human food was produced within the system, including all wheat, barley, citrus, and row crops grown within the system (Table 5), enough milk to satisfy human requirements (Table 6), and all of the meat slaughtered within the system (Table 6). The remaining protein requirement was imported (Table 8).

Outputs from human food subsystem. Ninety percent of the N consumed by humans is excreted as urine (M. Manore personal communication), so 10.6 Gg N y^{-1} entered the wastewater system as urine (Table 8). Most food that is not consumed (3.2 Gg N y^{-1}) is transported to landfills or sewers (via garbage disposals). Landfill wastes in Phoenix (Garbage Project 1988) include 0.16 kg person^{-1} d^{-1} residential food waste and 0.16 kg person^{-1} d^{-1} commercial food waste, for a total of 0.32 kg person^{-1} d^{-1}. Food disposed via garbage disposals (0.13 kg person^{-1} d^{-1}) was calculated as the difference between the national survey estimate for total waste food (0.45 kg person^{-1} d^{-1}) and the Phoenix-based estimate of food going to landfills (0.32 kg person^{-1} d^{-1}). Assuming that food sent to landfills and food entering sewers via garbage disposals

Table 8. N Balance for Human Food Subsystem

Component	N Flux ($Gg\ y^{-1}$)
Inputs of human food	
Imported	+9.9
Produced internally (from Tables 5 and 6)	5.1
Total input to human food subsystem[a]	15.0
Outputs from human food system	
To landfills	2.3
Excretion (to wastewater)	10.6
Waste food to wastewater (garbage disposal)	0.9
Total output from human food system	13.8
Accumulation of human biomass	0.2

Values marked by + are inputs to the ecosystem; values marked by − are outputs from the ecosystem. Other fluxes are transfers from one subsystem of the ecosystem to another.
[a]Total input to human food system includes actual consumption (11.8 Gg y^{-1}, from Table 7) and food waste (3.2 Gg y^{-1}).

have the same protein content (4.7%), 2.3 Gg N y^{-1} was sent to landfills and 0.9 Gg N y^{-1} entered the wastewater system (Table 8).

Accumulation of human biomass N. The human population of the CAP ecosystem is increasing at a net rate of 4% per year, largely due to immigration. The protein content of humans, by age and sex strata (Groff and Gropper 2000), was multiplied by the ecosystem population in each age and sex stratum to yield the net accumulation rate for human biomass (Table 8).

Domestic Pet Subsystem

The number of dogs and cats in the CAP ecosystem was based on national population estimates. According to the Pet Incidence Report (PFI 2000), in 1996 there were 67.9 million cats and 55.8 million dogs in the United States. A more refined study by Patronek (1995) showed that the dog population of the United States is around 52 million. Using the latter figure for dogs, and assuming that pet ownership in Phoenix parallels the national figure, there were 507,000 dogs and 662,000 cats in the CAP ecosystem. Nutritional content information and feeding instructions for several popular pet foods yielded an average recommendation of 1.6 g protein $1b^{-1}$ d^{-1} for dogs and 2.5 g lb^{-1} day^{-1} for cats.

Registration statistics for the American Kennel Club (AKC) were compiled for the top 20 breeds. The average weight of each breed was compiled from the AKC breed descriptions (AKC 2000). The weighted-average weight for the top 20 breeds was 20 kg. Although most dogs are not registered breeds, it is likely that the average weight of mixed breeds is similar, reflecting pet preferences throughout the US. The average weight of a cat is probably around 3.6 kg (M. Raasch personal communication).

Thus, the total N consumption of pet food within the CAP ecosystem was calculated as 2.7 Gg N y^{-1}. Dogs consume 76% of pet food. Consumption is approximately balanced by the excretion of urine. We assumed that all N excreted by dogs and 50% of N excreted by cats enters urban landscapes, for a total of 2.4 Gg N y^{-1}. The rest (urine in cat box litter, 0.3 Gg N y^{-1}) presumably enters landfills.

Wastewater Subsystem

Sources of wastewater N. Sewers transported 15.8×10^6 Gg N y^{-1} to wastewater treatment plants (Lauver and Baker 2000). Approximately 205,000 humans in the CAP ecosystem disposed of waste to septic tanks. Assuming that wastewater discharged to septic tanks has the same characteristics as wastewater discharged to sewers, the N loading to septic tanks was 1.5 Gg N y^{-1}, bringing total wastewater N (municipal + septic tank discharges) production to 17.3 Gg y^{-1} (Table 9). Sources of wastewater N include human excretion, food from garbage disposals, and other N-containing wastes, computed by difference (Table 9). We assumed that "other N-containing wastes" would include the N in detergents, shampoos, and other imported chemicals. The nature of this component of wastewater has apparently not been well characterized. This N is presumably imported into the ecosystem.

Fate of wastewater N: Wastewater treatment plants. N output from wastewater treatment plants was computed as the product of mean annual flow and total N concentration for the effluents of the 18 largest wastewater treatment plants in the region (Lauver and Baker 2000). Wastewater effluent in Phoenix undergoes one of four fates: It is reused for irrigation, deliberately recharged to aquifers, used for cooling water in a nuclear power plant, or discharged to the Salt River. Wastewater used for cooling at the Palo Verde nuclear power plant is evaporated to dryness in brine ponds, where salts (including nitrate) are stored permanently. Most of the biosolids (sludge) produced in the treatment process are spread on cotton fields; a very small amount is sent to landfills (Lauver and Baker 2000) (Table 9). Denitrification loss was computed as the

Table 9. N Balance for Wastewater Subsystem

Component	N flux (Gg y^{-1})
Inputs to wastewater subsystem	
Human excretion (from Table 8)	10.6
Garbage grinder waste (from Table 8)	0.9
Imported chemicals	+5.8
Total inputs to wastewater system	17.3
Outputs from wastewater subsystem	
Denitrification	−11.4
Biosolids (sludge)	
Sent to landfills (includes septic tank solids)	0.2
Sent to agricultural fields	1.4
Effluent from wastewater treatment plants	
Irrigation	
Crops	0.6
Urban landscape	0.8
Effluent recharge	0.1
Cooling water at Palo Verde nuclear plant	0.8
Exported from ecosystem	−0.6
Septic tank leacheate (to subsurface)	1.3
Total outputs from wastewater subsystem	17.2

Values marked by + are inputs to the ecosystem; values marked by − are outputs from the ecosystem. Other fluxes are transfers from one subsystem of the ecosystem to another.
Most values taken from Lauver and Baker (2000).

Table 10. N Balance for Urban Landscape Subsystem

Component	N flux (Gg y^{-1})
External inputs to urban landscapes	
Commercial fertilizer	+10.2
Wet deposition	+0.4
Transfers from other subsystems	
Wastewater used for irrigation (from Table 9)	0.8
Groundwater used for irrigation (from Table 11)	1.1
Dry deposition[a]	2.9
Pet waste	2.4
Total inputs to urban landscape subsystem	17.7
Outputs	
Lawn waste (to landfills)	5.0
Urban runoff	−0.3
Volatilization	−6.2
Flux to subsurface	6.2
Total outputs from urban landscape subsystem	17.7

Values marked by + are inputs to the ecosystem; values marked by − are outputs from the ecosystem. Other fluxes are transfers from one subsystem of the ecosystem to another.
[a]Total N dry deposition to urban landscapes = ecosystem NH_3 + NO_3 dry deposition (from Table 2) times fraction of CAP-LTER ecosystem in urban landscape (0.13).

difference between total N input and nonvolatile N outputs (effluent + biosolids).

Septic tanks. Lauver and Baker (2000) estimated that 9% of the N entering septic tanks is removed by the settling of solid, so 1.3 Gg N y^{-1} is sent to leach fields, where it migrates to the subsurface.

Urban Landscape Subsystem

N inputs. Nearly all fertilized urban and residential landscapes in Maricopa Country are within the CAP ecosystem, which accounts for 99% of the county's population. Areas in various nonagricultural land uses that are likely to be fertilized (for example, residential areas and parks) were divided into pervious and impervious surfaces. For some land-use types (for example, golf courses and parks), we assumed that 100% of the area was pervious. For others, we used the estimates of impervious areas for various land-use types proposed by Lopes and others (1995). A preliminary analysis of the vegetation in residential areas showed that 50% of the pervious surfaces in these areas were fertilized (C. Martin, personal communication). Based on the recommended N fertilization rate for turf grass (223 kg N ha^{-1} y^{-1}) (Doerge and others 1991), N fertilization of urban and residential landscapes was 10.2 Gg N y^{-1} (Table 10). As a check, we compared the figures for recommended fertilizer N use with country fertilizer sales records. The total amount of fertilizer N sold in Maricopa County in 1996 was 30.8 Gg (AASS 1997). This figure compares very favorably with our estimate of countywide fertilizer N use based on the recommended N application rates for cropland and urban landscapes (31.8 Gg y^{-1}).

Other N inputs to urban and residential landscapes—atmospheric deposition, pet excretion, wastewater effluent used for irrigation, and groundwater used for irrigation—have been described previously. The approach for estimating N in groundwater used for irrigation is presented in the Subsurface System section.

N outputs from urban landscapes: Urban storm runoff. Lopes and others (1995) studied the chemical composition of storm runoff in 13 subwatersheds throughout the Phoenix region during 1991–93. Average runoff was only 2.8 cm y^{-1}, reflecting the low rainfall and extensive flood control measures intended to reduce runoff. Total N export from urban watersheds for the entire study area (all 13 subwatersheds), as predicted from regression equations calibrated in the study, was 0.3 Gg N y^{-1} (0.44 kg ha^{-1} y^{-1}). We assumed that N exported from the urban area reaches the Gila River and is exported from the CAP ecosystem.

Lawn waste. The average rate of lawn waste production in Phoenix, which includes residential wastes plus wastes hauled to landfills or transfer stations by individuals (professional lawn care firms, municipalities, and so on), was 0.48 kg $person^{-1}$ d^{-1} (Coopers and Lybrand 1991). A separate study (Garbage Project 1988) reported that Phoenicians in residential areas discarded lawn waste at a rate of 0.35 kg $person^{-1}$ d^{-1}. Thirty-seven percent of the residential lawn waste consisted of leaves and branches; the rest was grass. Neither study reported on the water content of the landscape waste, so we assumed that the average water content was 50%. We estimated an N content of 1% for leaves and twigs and 3% for grass (C. Martin personal communication). The calculated flux of N in landscape waste going to landfills was 5.0 Gg N y^{-1} (Table 10), 20% of the total N input to urban landscapes.

Volatilization and subsurface flux. As with cropland, we assumed that excess N was partitioned equally between volatilization losses and subsurface flux (Table 10).

Plant aggradation. Aggradation of N in the form of plant biomass is likely to be occurring in response to irrigation and fertilization of urban landscapes, but no data on the magnitude of this increase are currently available. However, because landscape plants in this area reach maturity quickly (in less than 10 years), aggradation of plant N is probably limited to newly developed areas.

Subsurface Subsystem

Inputs to the subsurface. Inputs to the subsurface include N leached from cropland and urban landscapes, infiltration from septic tanks, recharged wastewater, and wastewater reused for irrigation (Table 11).

Outputs from the subsurface. The upward flux of nitrate from the aquifers to the surface was calculated by multiplying the pumping rate times the nitrate concentration for 1145 wells that pumped 92.3% of all groundwater in the region. The other 7.7% of wells lacked location information. The 426 wells with nitrate concentration data and well-defined screened depths were stratified by depth intervals (0–100, 100–200, over 200 m). Nitrate concentrations were then estimated using Thiessen polygons for all wells that had location data but lacked nitrate data. As a check, nitrate concentrations for wells that lacked nitrate data were also estimated using the inverse distance weighting (IDW) method. The upward N flux for each well was then computed as the product of the measured pumping rate and the estimated or measured nitrate concentration. Total pumping (Thiessen polygon method) was 1.1×10^9 m^3 y^{-1}; total upward N flux was 11.2 Gg N y^{-1}. The IDW method yielded a flux 1.5% lower than this. Assuming that the average nitrate concentration in the remaining 7.7% of wells (those lacking location data) was the same as that of wells with location information, the total upward N flux was 12.3 Gg y^{-1} (Table 11).

Table 11. N Balance for Subsurface

Component	N flux (Gg N y^{-1})
Inputs	
Leaching from agriculture (from Table 5)	12.3
Leaching from urban landscapes (from Table 10)	6.2
Leaching from septic tanks (from Table 9)	1.3
Effluent recharge (from Table 9)	0.1
Accumulation in desert soils (from Table 3)	0.6
Total inputs to subsurface subsystem	20.5
Recycling (groundwater pumping)	
Cropland irrigation	9.9
Urban landscape irrigation	1.1
Denitrification in sewers	−1.1
Total recycling from groundwater	12.2
Accumulation in subsurface (inputs–pumping)	8.3

Values marked by − are outputs from the ecosystem. Other fluxes are transfers from one subsystem of the ecosystem to another.

Eighty-one percent of the pumped groundwater was used for agriculture; municipalities used the remaining 18% (ADWR 1998). Assuming that the water withdrawn for agriculture and municipal use has the same average nitrate concentration, groundwater used for irrigation provided 9.9 Gg N y^{-1} to cropland and 2.2 Gg N y^{-1} to municipal water supplies. Because well water nitrate levels are often greater than the maximum contaminant limit for drinking water, well water supplied to municipalities is often blended with low-nitrate surface water and is rarely used directly.

Total municipal water use in the Phoenix area is 903 L $person^{-1}$ d^{-1} (ADWR 1998). Of this, an average of 446 L $person^{-1}$ d^{-1} becomes wastewater

(49% of the total); the rest is used for irrigation. Thus, 1.1 Gg N y^{-1} becomes an input to urban landscapes (Table 11), and the remaining 1.1 Gg N y^{-1} is used within households. Nitrate in household wastewater is almost certainly denitrified in the highly reducing environment of sewers before it reaches wastewater treatment plants and would not be measured as wastewater N. This flux is therefore considered a loss from the subsurface subsystem (Table 11).

N accumulation in the subsurface environment. Net N accumulation in the subsurface environment (soil, vadose zone, and aquifers), calculated as the difference between the sum of downward fluxes and the upward flux of pumped groundwater, was 8.3 Gg y^{-1} (Table 11).

N accumulation in landfills. Nearly all of the municipal waste generated in the CAP ecosystem is sent to landfills within the system. There is no importation of garbage for disposal within the system and no incineration of garbage. Lawn waste added 5.0 Gg N y^{-1}, food waste added 2.3 Gg N y^{-1} to landfills, sewage biosolids added 0.2 Gg N y^{-1}, and pet waste added 0.3 Gg N y^{-1}. Brine stored in drying ponds at the Palo Verde power plant added 0.8 Gg N y^{-1}, for a total of 8.6 Gg N y^{-1} (Table 12).

Table 12. Summary of Inputs, Outputs, and Accumulation in the CAP Ecosystem

Inputs	N flux (Gg y^{-1})
Surface water (from Table 1)	1.2
Wet deposition	3.0
Human food (from Table 8)	9.9
N-containing chemicals (from Table 9)	5.8
Food for dairy cows (from Table 6)[a]	0.8
Pet food	2.7
Commercial fertilizer (from Tables 5 and 10)	24.3
Biological fixation	
Alfalfa (from Table 6)	7.5
Desert plants (from Table 3)	7.1
Fixation by combustion (from Table 2)	36.3
Total inputs of fixed N	98.4
Outputs	
Surface water (from Table 1)	2.6
Cows for slaughter (from Table 6)	0.1
Milk (from Table 6)	2.4
Atmospheric NO_x (from Table 2)	17.1
Atmospheric NH_3 (from Table 2)	3.8
N_2O from denitrification (from Table 2)	4.6
N_2 from denitrification	46.9
Total outputs	77.5
Accumulation (inputs–outputs)	20.9
Accumulation by summing terms	
Net subsurface storage (from Table 11)	8.3
Landfills	
Lawn waste (from Table 10)	5.0
Food waste (from Table 8)	2.3
Pet waste	0.3
Brine stored at Palo Verde (from Table 9)	0.8
Biosolids from wastewater treatment (from Table 9)	0.2
Subtotal for landfills	8.6
Aggradation of humans (from Table 8)	0.2
Total accumulation by summing terms	17.1

[a] *Net input: 18 Gg N y^{-1} exported as alfalfa; 2.7 Gy N y^{-1} imported as concentrates.*

Discussion

Summary of N Mass Balance

Total input of N to the CAP ecosystem was 98.0 Gg N y^{-1} (Table 12); whereas total N output was 78.0 Gg N y^{-1}. Computed by difference, accumulation was 21 Gg N y^{-1}, or 21% of input; computed by summing accumulation flux terms, accumulation was 17.0 Gg N y^{-1}, or 17.0% of input (Table 12 and Figure 3). The similarity between these two accumulation rates, which were computed by two semi-independent methods, allows considerable confidence that N accumulation is actually occurring and that we have identified the major mechanisms involved, with some limitations.

Inputs

Deliberate human inputs (human and animal food, N-containing chemicals, alfalfa fixation, and commercial fertilizer) comprised 52% of total inputs. Inadvertent input of NO_x from combustion processes was 36%. Humans therefore mediated 88% of N inputs to the system. Surface water inflow, desert N fixation, and wet deposition together comprised only 12% of N input.

Outputs

Exports of fixed N totaled 78 Gg N y^{-1}. One fourth of fixed N export was NO_x (mainly from combustion); products of denitrification accounted for two-thirds of N export, and ammonia comprised 5%. Volatile products therefore accounted for over 90% of the N losses from the ecosystem. Riverine export was only 3% of total export. The only deliberate export was a small amount of milk and meat (3% of total export).

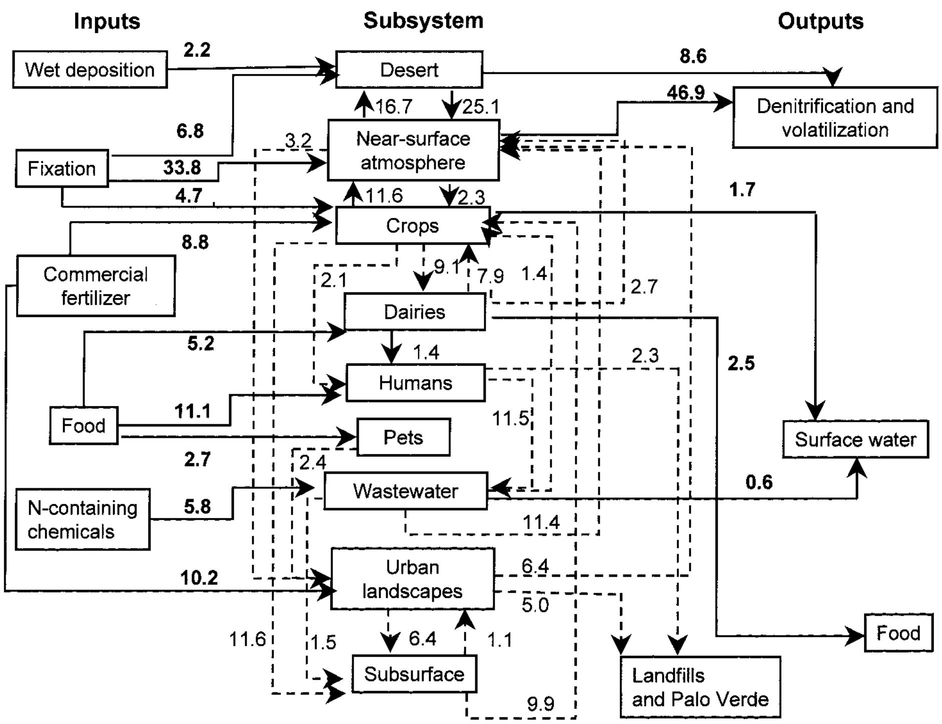

Figure 3. Summary of the N balance for the CAP ecosystem. From left to right: inputs, internal transfers, and outputs. All values are given in Gg N y^{-1}. Values for inputs and outputs are shown in boldface. Internal transfers are shown as dashed lines; and ecosystem inputs and outputs are shown as solid lines. For simplification, fluxes less than 1 Gg are not shown.

A key uncertainty in the N balance is the dry deposition of NO_x and ammonia. Dry bucket measurements of atmospheric dry deposition at eight sites located throughout the CAP-LTER ecosystem (D. Hope unpublished) provide a lower bound on a dry-deposition estimate (6.7 kg ha^{-1} y^{-1}) N. At the upper end, dry N deposition in the Los Angeles (LA) basin has been estimated at 22 kg ha^{-1} y^{-1} (Takemoto and others 1995) to 47 kg ha^{-1} y^{-1} (extrapolated by Russell and others 1993 from a one-day model under conditions that would favor dry deposition). Dry N deposition in the surrounding forest has been estimated to be 25–45 kg ha^{-1} y^{-1} (Bytnerowicz and Fenn 1996).

Dry deposition in the CAP-LTER system is certainly higher than measured by dry buckets (Baker 1991) and lower than dry deposition in the LA area, so our estimate of 18 kg ha^{-1} y^{-1} is reasonable. A closely related problem is that dry deposition is not evenly distributed, as we were forced to assume; instead, it is higher in the urban and agricultural core and lower in the surrounding desert. Because denitrification in the desert was computed by difference, our estimate of desert denitrification is probably biased high. For cropland and urban landscapes, erroneously low N deposition would cause a minor underestimate of leaching and denitrification. A key research goal within the CAP-LTER biogeochemical research program is to improve dry-deposition estimates.

Accumulation

N accumulation was computed two ways: by difference (input–output) and by summing downward fluxes (Table 12). Computed by difference, net N accumulation was 21.0% of input; computed by summing individual fluxes, net N accumulation was 17% of inputs. Both methods show very similar rates of net N accumulation, but both are subject to errors. A large uncertainty in computing accumulation as the difference between ecosystem-level inputs and outputs is the atmospheric deposition term. The computation of accumulation by summing downward fluxes and landfill accumulation is subject to additional uncertainties, most notably our assumption that half of the excess N applied to crops and landscape vegetation leaches to the subsurface.

Ideally, N accumulation in the subsurface environment would be measured directly to provide an independent check on accumulation terms determined by either the input–output method or the summing of downward fluxes. Pools of N in the subsurface environment include groundwater, leacheable nitrate in the vadose zone, and soil organic N. Groundwater nitrate levels have increased throughout much of the ecosystem. Since 1970,

Table 13. Approximate N Balance for Ecosystem Components

	Desert		Agriculture		Urban	
	kg ha^{-1} y^{-1}	% input	kg ha^{-1} y^{-1}	% input	kg ha^{-1} y^{-1}	% input
Input	28.5	—	358	—	425	
Output	26.4 +	98	200 (62)[a]	55	318	75
Accumulation	0.6 +	2	158	44	107	25

[a]*Food output*

nitrate concentrations have increased by more than 5 mg NO_3-N L^{-1} in 39% of all of the monitored wells within the CAP ecosystem as well as 64% of the monitored wells in areas that were used continuously for agriculture. Over the same period, less than 5% of wells in the ecosystem experienced a decline in nitrate by more than 5 mg L^{-1} (Y. Xu, L. A. Baker, P. Johnson unpublished). The upward trend in nitrate generally followed the rapid increase in the use of commercial fertilizers in the 1960s, with a lag period of approximately 10 years, roughly the travel time for the downward movement of irrigation water from the surface to aquifers (Y. Xu, L. A. Baker, P. Johnson unpublished). Direct determination of the magnitude of N accumulation in groundwater is difficult due to the presence of a complex (multilayered) aquifer system and rapidly fluctuating groundwater levels. In some areas, groundwater elevation has changed by more than 100 m over the period of a few decades. Thus, any direct computation of the change in N storage in aquifers over the period of a few decades would have a high degree of uncertainty.

Two studies have attempted to calculate the total stores of leacheable nitrate in the vadose zone of cropland in the CAP ecosystem, one yielding a value of 1420 kg ha^{-1} (Rice and others 1989) and the other a value of 1600 kg ha^{-1} (McPhearson 1999). Assuming that most of this accumulation has occurred over the past 30–40 years (following the huge increase in the use of commercial fertilizers), these values would correspond to an annual accumulation rate of 36–53 kg ha y^{-1} within agricultural areas. For the entire CAP ecosystem, the accumulation rate would be 4–6 Gg N y^{-1}, or one-fourth to one-half of computed total N accumulation.

Finally, the largest pool of N in most ecosystems is soil organic N (Jaffe 1992). Although the N content of vadose-zone soils in the CAP ecosystem is typically low (less than 0.1%), the depth of the vadose zone is often 30–200 m, so N storage could be thousands of kg ha^{-1}, at least in agricultural areas (McPhearson 1999). Long-term studies of agricultural soils have shown that soil N can change by ±30% over the period of a few decades in response to different management practices, corresponding to fluxes of tens of kg ha^{-1} y^{-1} (Parton and Rasmussen 1994; Paustian and others 1992; Steinheimer and others 1998). The introduction of irrigation also can lead to a flush of nitrate to the groundwater, presumably due to the mineralization of organic N (Albus and Knighton 1998). Given the large pool of soil organic N, even a small change in soil N storage may be significant in the context of ecosystem N cycling. It is therefore critical for further research to develop a better understanding of how the soil organic N pool changes in response to management changes.

Variation in N Cycling among Ecosystem Components

To evaluate N storage among the three main components of the ecosystem—urban areas, agriculture, and desert—we aggregated the appropriate subsystems (or portions of subsystems) together. The agriculture component included the cropland and dairy subsystems, plus associated subsurface accumulation. The urban component included the near-surface atmosphere (where combustion-derived NO_x is produced), human food, wastewater, pet food subsystems, and the associated subsurface subsystem (including landfills, which mainly receive wastes from the urban areas even though they may not actually be located in the urban core).

N cycling among these components varies greatly (Table 13). N input to the desert component, approximately 28 kg ha^{-1} y^{-1}, includes N fixation and atmospheric deposition. The main output from the desert component is probably denitrification.

N input to the entire agricultural component was 360 kg ha^{-1} y^{-1}. For fertilized cropland (not including fallow fields, alfalfa, and dairies), N inputs exceed 500 kg ha^{-1} y^{-1}. Because N input is so high, fertilization efficiency is low: only 30% of the N input to fertilized cropland is removed as crops. The entire agricultural system is only 18% efficient in converting N inputs to products for human consumption (milk, meat, and grains). The rest is leached to the subsurface (44% of input) or exported from the agricultural system via air or water (38% of input).

For the urban component, total N input (NO_x fixation, food, fertilizer, and other N-containing chemicals) was 425 kg ha^{-1} y^{-1}. About half of the input was combustion-derived NO_x. Outputs comprised 74% of inputs, with NO_x export (NO_x emissions minus dry deposition) accounting for 60% of outputs. The rest of the outputs consisted of denitrification from wastewater and landscapes and the export of treated wastewater and urban runoff. About 25% of N input to the urban area accumulates, about half by downward leaching and half by deliberate storage in landfills.

In summary, large, mostly inadvertent outputs and substantial rates of accumulation accompany large N inputs to the agricultural and urban components of the ecosystem.

Influence of Modified Hydrology on N Cycling

Water management practices in the CAP ecosystem tend to promote N volatilization and accumulation rather than riverine export in three ways. First, irrigation water is applied in a way that will minimize runoff. Agricultural fields are often laser-leveled to maximize irrigation efficiency, and irrigation scheduling is designed to maximize crop uptake, resulting in irrigation efficiencies that are often greater than 80%. Most excess irrigation water moves to groundwater rather than surface water. Second, very little wastewater is discharged from the system. Only 25% of the effluent is exported via surface water outlet. About half of the wastewater effluent is reused for irrigation or recharged to depleted aquifers. Another fourth is evaporated to dryness. Third, most runoff from newly urbanized areas (nearly all of Phoenix) is held in retention basins. This reduces downstream flooding (and N export) but increases infiltration and N accumulation. The need to conserve both agricultural water and wastewater effluent and prevent excessive urban runoff therefore results in little export of water or N from the ecosystem via rivers.

The relative amount of N exported via surface water compared to total N inputs is much lower for the CAP ecosystem than for most temperate watersheds. For nine regional watersheds draining into the northern Atlantic Ocean, Howarth and others

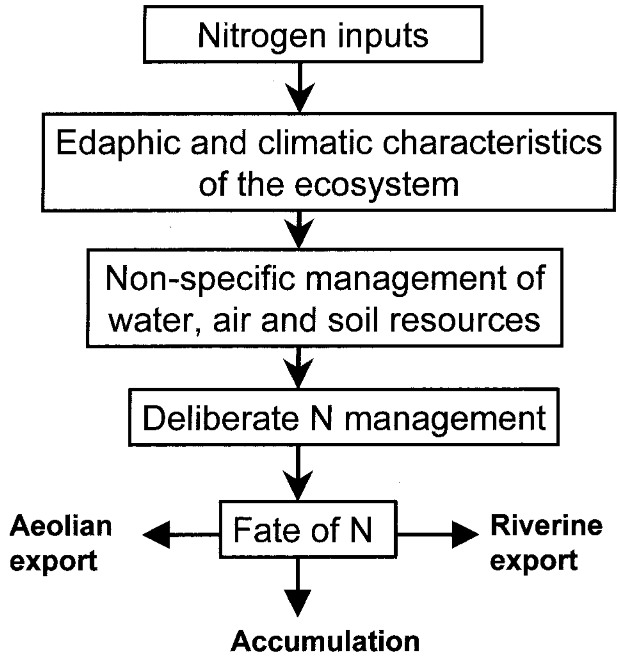

Figure 4. Conceptual schematic diagram of processes influencing the fate of N entering human-dominated ecosystems.

(1996) found that about 25% of total N input became riverine export. These authors found a linear relationship between areal N input and riverine flux (both in kg N km^{-2} y^{-1}) in the form $y = 0.2x + 102.5$. For the CAP system, actual riverine N flux was 212 kg N km^{-2} y^{-1}, only 13% of the predicted value for riverine export (1600 kg N km^{-2} y^{-1}) and only 3% of total N input.

Implications for N Management within the CAP Ecosystem

The fate of N in human-dominated ecosystems depends on the magnitude and form of N inputs, edaphic and climatic features of the ecosystem, nonspecific management practices, and finally, deliberate management practices intended to control the movement of N (Figure 4).

N inputs. On a per-capita basis, the largest N inputs to the system are (in kg $capita^{-1}$ y^{-1}) combustion-derived NO_x (13.3), human food (3.9), natural sources (4.5), commercial fertilizers applied to landscapes (4.0), commercial fertilizers applied to crops (5.5), N-containing chemicals other than fertilizer (2.2), cow feed (0.3), alfalfa fixation (3.0), and pet food (1.0). This ranking suggests that a reduction in total N input might be most readily accomplished by reducing NO_x emissions. For example, a 25% reduction in NO_x emissions in the atmospheric subsystem would decrease dry deposition to terrestrial landscapes by an average of 9%. An absolute reduction in the amount or form (meat vs vegetable) of imported human food, even if it could be accomplished would have little effect on N pollution within the ecosystem, because most human waste N enters the wastewater subsystem. N is removed efficiently by denitrification in wastewater treatment plants, thereby reducing export or transfers to the groundwater subsystem. Although the importation of N in commercial crop fertilizers and human food is similar, the potential for pollution caused by fertilizers is greater, because substantial quantities of N are lost during transfers (fertilizer → crop; crop → dairy cow; milk → human). Reduction of fertilizer inputs could be accomplished by managing transfers within the ecosystem more efficiently, resulting in less need for externally supplied commercial fertilizer.

Edaphic and climatic factors and nonspecific management. The arid climate, flat topography, and porous soils of this region tend to promote accumulation and volatilization rather than riverine N export. Water management practices for cropland, urban landscapes, and wastewater accentuate the tendency for N to be accumulated or volatilized rather than exported by rivers. Deliberate hydrologic modifications made by humans to adapt to the arid climate play a profound role in the fate of N in agro-urban ecosystems.

We postulate that human modifications of the hydrologic cycle play an important role in N cycling in all human-dominated ecosystems. In contrast to the arid setting of the CAP-LTER ecosystem, cities located in wetter climates have more runoff, so water management typically emphasizes rapid drainage (channelized streams, extensive storm sewer systems, and so on). There would also be a greater tendency in wetter climates for NO_x emissions to be removed from the atmosphere by washout and then deposited rather than exported via the atmosphere. These conditions may result in a greater fraction of input N subsequently exiting the ecosystem via riverine export.

Deliberate management of N transfers within the ecosystem. The most important deliberate N management practice in the CAP-LTER ecosystem is the advanced treatment (nitrification/denitrification) of wastewater, which removes 11.4 Gg N y^{-1} from the ecosystem (Table 8), or about 12% of total N input. Denitrification in wastewater treatment plants removes a sizable amount of N that would otherwise be exported via the Gila River or transferred to the subsurface. Otherwise, there is currently little deliberate management specifically directed toward controlling transfers of N with the intention of reducing pollution.

One substantial opportunity for reducing N accumulation can be found in the crop production system. Groundwater used for crop irrigation recycles 9.9 Gg N y^{-1} to the surface, resulting in far more application of N to crops than is necessary to achieve high crop yields. Much of this excess N is recycled back to the underlying aquifer, maintaining positive accumulation in the subsurface. One efficient method to reduce this recycling would be to develop a monitoring and feedback program so that farmers would know how much nitrate they are applying when they irrigate (kg N/m^3 water). Supplied with accurate information (for example, real-time monitoring of nitrate in irrigation water), farmers would tend to reduce applications of commercial fertilizers to reduce costs. Reducing excessive N fertilization of cotton (the primary cash crop) might also improve the harvest (Gerik and others 1998).

The N mass balance clearly identifies the N transfers among the various ecosystem subsystems. This is important because deliberate pollution management practices sometimes have the inadvertent effect of transferring pollutants from one medium to another. A holistic model, based on the approach presented here, could be used to identify potentially undesirable transfers and avoid the institution of policies that would inadvertently move pollutants from one medium to another.

Conclusions

A nitrogen mass balance for the CAP ecosystem shows that humans mediate 88% of N inputs. Humans deliberately imported about half of the total N input, mostly as food and fertilizer. Combustion processes comprised another third of total N input. Accumulation of N computed as input–output shows that 21% of input N accumulates within the ecosystem. Summation of subsurface fluxes indicates that 17% of input N accumulates. Leachable nitrate appears to be accumulating in the vadose zone and the underlying aquifer, but the rate of this accumulation could not be determined directly. N leaves the system mainly via the atmosphere; less than 3% of N output leaves via surface water.

N inputs to the urban and agricultural components of the ecosystem are an order of magnitude higher than inputs to the natural desert. Water management practices intended to conserve water tend to promote accumulation and volatilization rather than riverine export. Deliberate removal of N from wastewater eliminates about 10% of input N, but there is little other deliberate management to control N pollution. Reducing the recycling of N from pumped groundwater could significantly reduce the accumulation of N within the system.

An important outcome of this study has been the identification of several key uncertainties regarding the N budget that require further research. These include (a) dry-deposition processes in both urban and arid systems with patchy vegetation, high NO_x emissions, and complex patterns of air flow; (b) soil N dynamics; and (c) factors that control denitrification in urban landscapes and cropland.

We postulate that the most effective N management strategies are those that are specifically tailored to individual ecosystems. The creation of such tailored N management strategies requires the development of ecosystem-level N balances and an understanding of the interplay of N inputs, edaphic and climatic factors, nonspecific management practices, and deliberate N management practices that control the fate of N.

ACKNOWLEGMENTS

This project was supported in part by the Central Arizona–Phoenix Long-term Ecological Research Program (NSF no. DEB9714833). We are grateful to Nancy Grimm and Weixing Zhu for reviewing an earlier draft of this paper. We also thank Peter McCartney for assistance with database management and the following individuals for sharing data and technical insights regarding various components of the nitrogen budget and our ecosystem: Mike Armstrong, Department of Animal Science, University of Arizona; Dave Anning, Dorrie Gellenbeck, and Shirley Francisco, US Geological Survey; Corrina Gries and Chris Martin, Department of Plant Science, Arizona State University; Bob Freitas, Agricultural Extension Service, University of Arizona; Jim Holway, Arizona Department of Water Resources; Peter Hyde, Arizona Department of Environmental Quality; Wilson Hughes, University of Arizona Garbage Project; Melinda Manore, Nutrition Department, Arizona State University; Mike Ottman, Department of Plant Sciences, University of Arizona; Melody Raasch, Iams Company; Bill Schlesinger, Duke University; and Karol Wolf, Salt River Project.

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