Chapter 4: A California nitrogen mass balance for 2005

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What is this chapter about?

A mass balance of nitrogen inputs and outputs for California was calculated for the year 2005. This scientifically rigorous accounting method tracks the size of nitrogen flows which allows us to understand which sectors are the major users of nitrogen and which contribute most to the nitrogen in the air, water, and ecosystems of California. New reactive nitrogen enters California largely in the form of fertilizer, imported animal feed, and fossil fuel combustion. While some of that nitrogen contributes to productive agriculture, excess nitrogen from those sources contributes to groundwater contamination and air pollutants in the form of ammonia, nitric oxides, and nitrous oxide. In addition to statewide calculations, the magnitude of nitrogen flows was also examined for eight subsystems: cropland; livestock; urban land; people and pets; natural land; atmosphere; surface water; and groundwater. Understanding the major nitrogen contributors will help policy makers and nitrogen users, like farmers, prioritize efforts to improve nitrogen use.

Stakeholder questions

The California Nitrogen Assessment engaged with industry groups, policy makers, non-profit organizations, farmers, farm advisors, scientists, and government agencies. This outreach generated more than 100 nitrogen-related questions which were then synthesized into five overarching research areas to guide the assessment (Figure 1.4). Stakeholder generated questions addressed in this chapter include:

- **What are the relative contributions of different sectors to N cycling in California?**
- **What are the relative amounts of different forms of reactive nitrogen in air and water?**
- **Are measurements of gaseous losses and water contamination accurate?**

Main Messages

Synthetic fertilizer is the largest statewide import (519 Gg N yr^{-1}) of nitrogen (N) in California. The predominant fate of this fertilizer is cropland including cultivated agriculture (422 Gg N yr^{-1}) and environmental horticulture (44 Gg N yr^{-1}). However, moderate amounts of synthetic fertilizer are also used on urban land for turfgrass (53 Gg N yr^{-1}).

The excretion of manure is the second largest N flow (416 Gg N yr^{-1}) in California. The predominant (72%) source of this N is dairy production, with minor contributions from beef, poultry and horses. A large fraction (35%,) of this manure is volatilized as ammonia (NH_3) from livestock facilities (97 Gg N yr^{-1}) and after cropland application (45 Gg N yr^{-1}). However, there is limited evidence for rates of ammonia volatilization from manure. While liquid dairy manure must be applied very locally (within a few kilometers (km) of the source), the solid manure from dairies and other concentrated animal feeding operations can be composted to varying degrees and transported much longer distances (>100 km). However, because of the increased regulation of dairies in the Central Valley (see Chapter 8), it will soon be possible to determine what fraction of the dairy manure is used on the dairy farm compared to what is exported based on the nutrient management plans produced for each dairy.

Synthetically fixed N dominates the N flows to cropland. Synthetic fertilizer (466 Gg N yr^{-1}) is the largest flow of N to cropland, but a large fraction of N applied in manure and irrigation water to cropland is also originally fixed synthetically. On average, we estimated that 69% of the N added annually to cropland statewide is derived from synthetic fixation.

The biological N fixation that occurs on natural land (139 Gg N yr^{-1}) has become completely overshadowed by the reactive N related to human activity in California. While this flow was once the major source of new reactive (i.e., biologically available) N to California, it now accounts for less than 10% of new imports at the statewide level. The areal rate (8 kg N ha^{-1} yr^{-1}) representing the sum of all N inputs to natural lands, including N deposition, is an order of magnitude lower than either urban or cropland.

The synthetic fixation of chemicals for uses other than fertilizer is a moderate (71 Gg N yr^{-1}) N flow. These chemicals include everyday household products such as nylon, polyurethane, and acrylonitrile butadiene styrene plastic (ABS). These compounds have been tracked to some degree at the national level (e.g., Domene and Ayres 2001), but the data were largely compiled in expensive and proprietary reports. The true breadth and depth of their production, use, and disposal is poorly established.

Urban land is accumulating N. Lawn fertilizer, organic waste disposed in landfills, pet waste, fiber (i.e wood products), and non-fertilizer synthetic chemicals are all accumulating in the soils (75 Gg N yr^{-1}), landfills (68 Gg N yr^{-1}), and other built areas associated with urban land (122 Gg N yr^{-1}).

Nitrogen exports to the ocean (39 Gg N yr^{-1}) from California rivers accounts for less than 3% of statewide N imports. In part, this low rate of export is due to the fact that a major (45%) fraction of the land in California occurs in closed basins with no surface water drainage to the ocean. While concentrations of nitrate in some rivers can be quite high, the total volume of water reaching the ocean is quite low.

Direct sewage export of N to the ocean (82 Gg N yr^{-1}) is more than double the N in the discharge of all rivers in the state combined. Because of the predominantly coastal population, the majority of wastewater is piped several miles out to the ocean. A growing number of facilities (> 100) in California appear to be using some form of N removal treatment prior to discharge.

Nitrous oxide (N_2O) production is a moderate (38 Gg N yr^{-1}) export pathway for N. Human activities produce 70% of the emissions of this greenhouse gas while the remainder is released from natural land. Agriculture (cropland soils and manure management) was a large fraction (32%) of N_2O emissions in the state.

Ammonia is not tracked as closely as other gaseous N emissions because it is not currently regulated in the state. While acute exposures to NH_3 are rare, both human health and ecosystem health are potentially threatened by the increasing regional emissions and deposition of NH_3. However, rigorous methods for inventorying emissions related to human activities as well as natural soil emissions are currently lacking.

Atmospheric N deposition rates in parts of California are among the highest in the country, with the N deposited predominantly as dry deposition. The Community Multiscale Air Quality model predicts that 66% of the deposition is oxidized N and 82% of the total deposition is dry deposition not associated with precipitation events. In urban areas and the adjacent natural ecosystems of southern California, deposition rates can exceed 30 kg N ha^{-1} yr^{-1}, but deposition is, on average, 5 kg N ha^{-1} yr^{-1} statewide.

The atmospheric N emitted as NO_x or NH_3 in California is largely exported via the atmosphere downwind (i.e., east) from California. Approximately 65% of the NO_x and 73% of the NH_3 emitted in California is not redeposited within state boundaries making California a major source of atmospheric N pollution. Further, atmospheric exports of N are more than 20 times higher than riverine N exports.

Leaching from cropland (333 Gg N yr^{-1}) was the predominant (88%) input of N to groundwater. It appears that N is rapidly accumulating in groundwater with only half of the annual N inputs extracted in irrigation and drinking water wells or removed by denitrification in the aquifer. On the whole, groundwater is still relatively clean, with a median concentration ~ 2 mg N L^{-1} throughout the state. However, there are many wells in California that already have nitrate concentrations above the Maximum Contaminant Level. Because of the time lags associated with groundwater transport (decades to millennia), the current N contamination in wells is from past activities and current N flows to groundwater will have impacts far into the future.

The amount of evidence and level of agreement varies between N flows. The most important sources of uncertainty in the mass balance calculations are for major flows with either limited evidence or low agreement or both. Based on these criteria, biological N fixation on cropland and natural land, the fate of manure, denitrification in groundwater, and the storage terms are the most important sources of uncertainty.

In many ways, the N flows in California are similar to other parts of the world. In a comparison with other comprehensive mass balances - Netherlands, United States, Korea, China, Europe, and Phoenix - California stands out in its low surface water exports and high N storage, primarily in groundwater and urban land. Further, when compared to these other regions of varying size, California has a relatively low N use on both a per capita, but especially on a per hectare, basis.

4.0 Using a mass balance approach to quantify nitrogen flows in California

Human activities, including agriculture and urban development, have led to dramatic increases in biologically available or reactive nitrogen (N). As such, the anthropogenic alteration of the N cycle is emerging as one of the greatest challenges to the health and vitality of California's people, ecosystems, and agricultural economy. Input of N to terrestrial ecosystems has more than doubled in the past century due to nitrogen fixation associated with food production and energy consumption (Galloway 1998). This mobilization of anthropogenic N has been connected with increased N loading to aquatic ecosystems, emissions of nitrous oxide (a greenhouse gas), and associated ecosystem and human-health effects (Galloway et al. 2003). In some cases, the N flow itself is inherently a component of an ecosystem service (e.g., harvesting N in crops is an essential part of food provisioning), while in other cases N flows are more indirectly linked to impairing ecosystem services (e.g., excess nitrogen (i.e., eutrophication)) in surface water bodies leads to hypoxia and harmful algal blooms). This chapter will focus on the current state of N flows and the following chapter will address how the current N flows and trends in N flows are affecting ecosystem services and human well-being in California.

A mass balance is an efficient and scientifically rigorous method to track the flows of N in a system. The underlying premise of a mass balance is that all of the reactive N entering (i.e., inputs) the study area must be exactly balanced by N leaving (i.e., outputs) and N retained in the study area (i.e., change in storage):

$$\text{N Inputs} = \text{N Outputs} + \Delta\text{Storage}$$

A mass balance approach is not only very useful to compare the size of N flows but also to identify gaps in understanding the size and directions of these flows. Some flows are difficult to quantify – they are highly variable in time and/or space, or there are simply no methodologies to easily measure or predict the flows. Nevertheless, knowledge of the relative magnitude of the flows is needed to make informed management and policy decisions for targeting N reductions.

One fundamental decision in the process of calculating a mass balance is choosing the spatial boundaries and which flows to include or exclude. For example, some N mass balances only focus on anthropogenic inputs of N (e.g., Howarth et al. 1996) or agricultural areas (e.g., Antikainen et al. 2005). In most watershed N mass balances, all of the N inputs, but only the riverine N outputs are estimated (e.g., Boyer et al. 2002). A mass balance also differs from an emissions inventory which only tracks emissions to the atmosphere and only those from human activities. In terms of spatial extent, we defined the boundaries of the study area to be the state border of California, including the coastline. Thus, the study area includes both the plants and soils of the land surface as well as the atmosphere above and the groundwater below the land surface (Figure 4.1).

[Figure 4.1]

For the mass balance calculations, using the political boundaries of the state has many advantages. For many N flows like fossil fuel emissions and agricultural production, the data are compiled at the state level. Moreover, there are relatively minor atmospheric imports from upwind sources (i.e., the Pacific Ocean). Finally, with very minor exceptions (0.1% of the land area is in watersheds that drain to Oregon and 2% is in the Colorado River watershed which flows into Mexico), the rivers of the state that flow to the Pacific Ocean largely begin and end within the state boundaries.

Not all of the N flows can be easily calculated directly at the statewide level. Therefore, we calculated mass balances for eight interconnected subsystems – cropland, livestock, urban land, household (i.e., people and pets), natural land, atmosphere, surface water, and groundwater. The four land based subsystems - cropland, urban land, natural land, and surface water (rivers, lakes, and reservoirs) – were based on the land use map. The entire state was assigned to one of these four land cover categories (Figure 4.2). Cropland included all cultivated land for food, feed, and fiber (i.e. cotton) crops as well as irrigated pasture and land used for environmental horticulture (nursery, flowers, and turf). To avoid double counting and to highlight the transfer of agricultural products to and from agricultural land, we calculated N flows in the livestock subsystem and household subsystem separate from the land surface these populations actually inhabit. Finally, we calculated inputs and outputs for the groundwater subsystem and the atmosphere subsystem.

[Figure 4.2]

To distinguish the flows entering and leaving the state from the inputs and outputs representing N transferred among the subsystems, we use slightly different language: N inputs at the state level will be referred to as N imports and N outputs at the statewide level will be referred to as N exports (Box 4.1). We do not distinguish whether the imports represent the fixation of new reactive N in California (e.g., cropland N fixation) or the transfer of reactive N from outside the state boundary (e.g., feed imports). Similarly, we do not distinguish whether the exports represent the loss of reactive N via the formation of N_2 or the transfer of the various forms of reactive N. It is also worth noting that many of the subsystem inputs and outputs do not appear in the accounting of statewide imports and exports. For example, synthetic fertilizer represents an import of N to the state and an input to the cropland and urban land subsystems; however, while manure represents an input of N to the cropland subsystem and an output of N from the livestock subsystem, manure does not appear as a term in the statewide mass balance. In the case of agricultural products, we calculated a net statewide N import or export: while some commodities are shipped from California and others to California, we report the difference between production and consumption for the state and not the transport of individual commodities. There are certainly small flows of N that have been excluded from this analysis, such as NH4 volatilization from human sweat and N_2O emissions from wildfires. While we do not have a comprehensive list of excluded small flows, we believe we have included all of the N flows greater than 1 Gg or 1,000,000 kg N yr^{-1}.

[Box 4.1]

In addition to the spatial boundaries, it is important to consider temporal boundaries. Some flows, like crop harvest, vary inter-annually with climate and other factors, but are measured every year. Some N flows, like biological N fixation and gaseous soil emissions, tend to be average annual estimates without reference to a particular time period. Finally, other flows, like atmospheric N deposition, are estimated with data and computationally intensive methods and are only available for one year. Our aim was to create a budget for 2005. For agricultural production, the averages were calculated for 2002-2007 while for most other N flows, any data available between the years 2000-2008 were used. The N flows were calculated by compiling the necessary data from both peer-reviewed and non-peer reviewed literature, government databases, and in some cases expert opinion. When possible, we calculated multiple independent estimates of the N flows during this time period. A quantitative measure of uncertainty is reported in Section 4.1 as part of the estimates of the N flows.

The concurrent goals of this mass balance were (1) to quantify current statewide N flows and (2) to evaluate the scientific uncertainty in the magnitude of N flows. This chapter is divided into two sections. The first section (Section 4.1) provides a summary of the statewide N imports and exports and the N flows in the eight subsystems. Both the absolute and relative sizes of the N flows were grouped into categories to help highlight which flows are particularly important (Box 4.2). The second section (Section 4.2) provides a detailed description of the data sources and calculations used in the mass balance. The spatial and temporal variability of important stocks and flows of N will be addressed in detail in the Ecosystem Services and Human Well Being chapter (Chapter 5).

[Box 4.2]

Uncertainty in the mass balance is addressed in this chapter as well as the Data Tables. The discussion in this chapter largely focuses on comparing multiple independent estimates of the same N flow. In the data tables, we concentrate on the uncertaisnties associated with individual data sources and methodologies. Following the model of the Intergovernmental Panel on Climate Change, we use reserved words to quantify the level of scientific agreement and the amount of evidence (Box 1, Data Tables). The uncertainties associated with each N flow depicted in Figure 4.1 are presented both in Figure 4.3, in the various tables showing the state-level and subsystem mass balances, and in the Data tables.

[Figure 4.3]

4.1 Statewide and subsystem N mass balances

This section describes the magnitude of the N flows at the statewide level as well as the eight subsystems examined in the mass balance: cropland; livestock; urban land; household; natural land; atmosphere; surface water; and groundwater. For the statewide flows of agricultural products, we report net flows in the cases of food, feed, and fiber and not the transport of individual commodities. We calculate the net flow as the difference between production and consumption. Based on our results, feed and fiber represent statewide imports of N and food represents a statewide export of N. At the statewide level, the California atmosphere was considered internal to the system with advection resulting in N import to and export from the atmosphere.

4.1.1 Statewide N flows

There were six moderate to major statewide imports of N to California – synthetic N fixation, fossil fuel combustion, biological N fixation, atmospheric imports (i.e. advection of N) feed, and fiber in the form of wood products (Figure 4.1). Products created from synthetic N fixation by industrial processes, typically by the Haber-Bosch process, represent the largest statewide import (590 Gg N yr^{-1}) and a large (36%) fraction of the new statewide imports (Table 4.1a, Figure 4.4a). Of this synthetically fixed N, the predominant (88%) form was fertilizer. However, the mixture of other chemicals (e.g., nylon, polyurethane, acrylonitrile butadiene styrene plastic) created from synthetically fixed NH_3 also represented a moderate (71 Gg N yr^{-1}) N flow. Fossil fuel combustion was the second largest import (404 Gg N yr^{-1}) of N to California with NO_x the predominant (89%) form. This flow represents N emissions to the atmosphere and is not equivalent to atmospheric N deposition in California (Section 4.1.7). Biological N fixation was also a major statewide N import (335 Gg N yr^{-1}) with more occurring on the 400,000 ha of alfalfa compared to the 33 million ha of natural land. While there was medium evidence for this flow, there was low agreement. The import of livestock feed and fiber in the form of wood and wood products to meet the demand in California represented major (200 Gg N yr^{-1}) and moderate (40 Gg N yr^{-1}) statewide imports of N, respectively.

[Table 4.1a; Figure 4.4a]

To satisfy the mass balance assumption, statewide N exports and storage were defined to be equivalent to N imports at the statewide level. Atmospheric exports of N gases and particulate matter were estimated based on the assumption of no N storage in the atmosphere. All nitrous oxide (N_2O) and nitrogen gas (N_2) emitted was assumed to be exported from California while the export of NO_x and NH_3 was calculated as the difference of emissions and deposition to the land subsystems. The atmospheric N export (NO_x, NH_3, N_2O, and N_2) accounted for the predominant (86%) fraction of the N exports from California (Figure 4.4b, Table 4.1b). More NO_x (270 Gg N yr^{-1}) than NH_3 (206 Gg N) was exported. Nitrous oxide was a moderate (38 Gg N yr^{-1}) statewide export of N while N_2 represented a major statewide export (204 Gg N yr^{-1}). This total includes groundwater denitrification even though the N_2 produced may not reach the atmosphere for several decades until the groundwater is discharged at the surface. Including groundwater denitrification, the inert N_2 emissions account for 29% of the gaseous N export from the state. While most of the NO_x export was related to the N import related to fossil fuel combustion, the export of the other gaseous forms represents N that was transformed within the state. For example, a large fraction of the NH_3 derives from manure, which previously was feed, which in turn may have been imported to the state. California was a net exporter of food. That is, the total production of N in food was 79 Gg N yr^{-1} greater than the estimated consumption of N in food. The gross flow of food is likely significantly higher with many fresh fruits and vegetables as well as dairy products transported out of the state. Moderate statewide exports of N to the ocean occurred in both rivers (39 Gg N yr^{-1}) and direct sewage discharge (82 Gg N yr^{-1}).

[Table 4.1b; Figure 4.4b]

A large (43%) fraction of the N imports were stored in some form in California (701 Gg N yr^{-1}). Accumulation of N in groundwater was estimated to be 258 Gg N yr^{-1}, with the input predominantly from cropland. Storage in the soils or vegetation of the three land subsystems was estimated to be 230 Gg N yr^{-1}. Within the urban subsystem, there was N storage associated with landfills (71 Gg N yr^{-1}), but a major (122 Gg N yr^{-1}) source of storage was related to the buildup of synthetic chemicals and wood products in structures and long-lived household items like nylon carpets, electronic equipment and lumber. Finally, storage in surface water bodies (i.e. lakes and reservoirs) was 20 Gg N yr^{-1}. We assumed no storage in the atmosphere subsystem.

There are some examples of measured increases in N storage in California, but there is more evidence related to carbon storage. Agricultural soils in California (Singer 2003) and turfgrass soils (Raciti et al. 2011) have been shown to accumulate both carbon (C) and N. Ornamental lawns in southern California were found to accumulate 1400 kg C ha^{-1} yr^{-1} for more than three decades after lawn establishment (Townsend-Small and Czimzik 2010). Assuming a soil C:N ratio of 10, this would represent 140 kg N ha^{-1} yr^{-1}, similar to the results of N accumulation reported by Raciti et al. (2011) for Maryland. In other contexts, storage of N can be inferred from measurements of carbon storage. For example, the increasing acreage of perennial crops in California (Kroodsma and Field 2006) results in net uptake of carbon by ecosystems in California (Potter 2010). The disposal of organic materials like wood products and food waste in landfills results in 10% of the total dry mass of solid waste sequestered in the form of carbon (C) (Staley and Barlaz 2009). Depending on the chemical environment in the landfill and the C:N ratio of the materials, varying amounts of N would be accumulating as well. With these multiple avenues for C sequestration, it is very likely that N storage would be increasing as well in these settings. Some of these storage pools (soils and vegetation) have an asymptotic capacity for N uptake which may be saturated within years or decades. However, the disposal of waste in landfills and the use of long-lived wood and synthetic materials can potentially keep increasing over time. The high capacity for retention of N in surface water bodies is well established especially in reservoirs (e.g., Harrison et al. 2009), but the fraction buried in sediments versus the fraction denitrified is not.

Nitrogen flows can also be tracked through the land-based subsystems: cropland, urban land, and natural land. Because of the N flows among subsystems, the total sum of N inputs across all subsystems was greater than the statewide N imports. For example, manure N was an input to the cropland subsystem, but not an import to the state as it was considered a transformation of existing N at the scale of California. Agriculture, including cropland and livestock, dominated the N inputs in California (Figure 4.5a). Cropland had greater N inputs than urban land and natural land combined. Similarly, livestock feed was more than double the amount of human and pet food. The two biggest inputs to the three land subsystems were synthetic N fertilizer (to cropland and urban land) and manure (to cropland). Less than half of the N inputs to cropland and one quarter of the N inputs to livestock were converted into food or feed (Figure 4.5b). More than a third of cropland N inputs were leached to groundwater and a similar fraction (40%) of livestock N inputs was emitted as ammonia. Other gaseous N emissions from cropland and the other land subsystems were only minor N flows. Human food was largely converted to sewage with the exception of the food waste that was disposed of in landfills. While natural land and cropland were estimated to store small fractions of their N inputs, the predominant fate of N inputs to urban land was storage in soils, landfills, or as long-lived synthetic materials or wood.

[Figure 4.5a; Figure 4.5b]

4.1.2 Cropland N flows

Cropland covers only 4.9 million of the 40.8 million hectares in California, but accounts a disproportionate amount of the N flows (Table 4.2, Figure 4.6). A total of 1027 Gg N yr^{-1} was added to cropland resulting in an average areal N input to cropland of 250 kg N ha^{-1} yr^{-1}.

[Table 4.2; Figure 4.6]

4.1.2.1 Cropland N imports and inputs

The use of synthetic fertilizer on cropland represented the largest flow of N in California (Figure 4.6, Table 4.2). The 2002-2007 average statewide synthetic N fertilizer sales were 762 Gg N yr^{-1}. However, it is unclear why there was nearly a 50% increase in sales from 2001-2002 or similarly a 50% increase from the 1980-2001 mean to 2002-2007 mean fertilizer sales (Box 4.3). There was no significant linear change ($p=0.28$) in fertilizer sales over the period 1980-2001. We believe that the mean from this period, 519 Gg N yr^{-1}, provides a more realistic estimate of statewide fertilizer sales than the 2002-2007 mean. The fraction of fertilizer sales applied to cropland was calculated as the difference between turfgrass use (53 Gg N yr^{-1}, see Section 4.1.4) and total fertilizer sales. Synthetic fertilizer use was therefore a major flow of N (466 Gg N yr^{-1}), representing a large (45%) fraction of total N flows to cropland soils. Manure application was also a major (263 Gg N yr^{-1}) N input to cropland (see Section 4.1.3). A large uncertainty is related to the partitioning of manure between gaseous NH_3 losses and application to cropland (Figure 4.3). In our accounting methodology we only considered synthetic N applied as fertilizer as a N import (i.e., new input of N) in the budget calculations at the statewide scale. However, many of the other sources of N to cropland (e.g., manure, irrigation, atmospheric deposition) also originally derive in part from synthetic fertilizer applied to cropland (Box. 4.4). We assumed that half of the biosolids produced in the state were applied to cropland soils.

[Box 4.3; Box 4.4]

Synthetic fertilizer applied to cropland can also be estimated based on the crop-specific fertilization rates and harvested acreages. For the period 2002-2007, cultivated crops were estimated to receive 539 Gg N yr^{-1}. This value would be expected to be higher than the synthetic fertilizer sales data for cropland if any manure was used as fertilizer. A total of 263 Gg N yr^{-1} of manure was estimated to be applied to cropland. If 73 Gg N yr^{-1} of manure was used instead of synthetic fertilizer then the two estimates would agree perfectly. While some manure likely does replace synthetic fertilizer to meet the nutritional needs of crops, a significant fraction could have been applied in excess of plant needs on dairy-forage crops as a form of waste disposal, or as an amendment to increase soil organic matter.

Synthetic fertilizer use in environmental horticulture was calculated separately because it relied on different sources of data. There were 7,100 ha of sod, 6,200 ha of floriculture, and 13,100 ha of open grown nursery stock which were estimated to receive 44 Gg N yr^{-1}.

Biological N fixation was also a major (196 Gg N yr^{-1}) flow to cropland and almost entirely associated with alfalfa (Table 4.3). We were not aware of any N fixation rates for alfalfa measured in California, where productivity, and thus N fixation, is much higher than the Midwestern states where data have been collected. While there was variability associated with the productivity – N fixation relationship, the biggest source of uncertainty in the estimate of N fixation is the amount of fixed N belowground.

[Table 4.3]

Two moderate N flows to cropland are atmospheric deposition and N applied in irrigation water. The total atmospheric deposition of N to cropland was estimated at 43 Gg N yr^{-1} based on the results of the Community Multiscale Air Quality (CMAQ) model (Table 4.2). The mean N deposition rate for cropland, 8.7 kg N ha^{-1} yr^{-1}, was higher than the state average of 5.0 kg N ha^{-1} yr^{-1}. Irrigation water provided a similar quantity of N (59 Gg N yr^{-1}) to cropland statewide as N deposition. Surface water was withdrawn at a rate of $2.6*10^{13}$ L yr^{-1} for irrigation use in California in 2000 (Hutson et al. 2004). In 2000, a total of 0.6 $*10^{13}$ L yr^{-1} was pumped from the Sacramento-San Joaquin Delta (the Delta) at Tracy for the Delta Mendota Canal and the California Aqueduct (Blue Ribbon Task Force Delta Vision 2008). Because the Delta pumps are located downstream of the location of river gauges (which we consider to be the boundary of the study area), this pumping resulted in the return of 8 Gg N yr^{-1} to the state. The remaining surface water withdrawals for irrigation, calculated as the difference between total surface water use and Delta pumping, provided another 18 Gg N yr^{-1} to cropland. Groundwater nitrate (NO_3^-) concentrations (2.6 mg N L^{-1}) were even higher than the N concentration in the water pumped from the Delta. However, only 1.3 $*10^{13}$ L yr^{-1} were pumped from groundwater in 2000 for irrigation, resulting in a total of 33 Gg N yr^{-1}.

4.1.2.2 Cropland N outputs and storage

Harvesting crops was a major flow of N and the largest N output from the cropland subsystem. The top twenty crops in terms of harvested N are shown in Table 4.4. For 2002-2007, total harvest of food crops was 185 Gg N yr^{-1} and feed crops was 357 Gg N yr^{-1}. Cotton lint was the only fiber crop grown on California cropland (timber was considered harvested from natural land), with only 1 Gg N yr^{-1} harvested. The production of nursery and floriculture crops was 14 Gg N yr^{-1}. While there is transport of this nursery material in and out of California, we estimate that CA produces 14% of the national total and would use 12% based on its population resulting in no net flow of nursery material.

[Table 4.4]

The total production showed minimal variability over this time period with less than a 10% difference between the lowest (2002) and highest (2003) quantity of N harvested. The two sources of crop acreages, the county Agricultural Commissioners and National Agricultural Statistics Service (NASS) annual surveys, were highly correlated (r > 0.95) for the common crops that are reported by both agencies. The largest source of uncertainty in the crop calculations is in the conversion of production to the N content of the biomass. The USDA crop nutrient tool is a compilation of data from several decades ago, but no more recent database exists. The potential for large errors are greatest for the forage crops where the whole plant is harvested and for the vegetables with high water content.

Gases were emitted from cropland soils as a result of both physical and biological processes. Ammonia volatilization is a physical process based on the temperature and pH dependent equilibration of gaseous NH_3 and dissolved ammonium (NH_4^+) in the soil. Based on an emission factor of 3.2% for the various synthetic fertilizers in California, as well as emissions from land applied manure, NH_3 outputs were a moderate flow (60 Gg N yr^{-1}). The other gas outputs are associated with the microbial processes of nitrification and denitrification. Based on the average of all sources of data (Table 4.5), nitric oxide (NO) and N_2O outputs were also minor flows (12 and 10 Gg N yr^{-1}, respectively; Table 4.2). Using the limited number of published literature estimates from California cropland soils, the median NO and N_2O fluxes were 1.9 kg NO-N ha^{-1} yr^{-1} and 2.9 kg N_2O-N ha^{-1} yr^{-1}, respectively (Supplementary 4.1[1]). These rates are considerably higher than the global median for NO (0.9 kg NO-N ha^{-1} yr^{-1}) and N_2O (1.4 kg N_2O-N ha^{-1} yr^{-1}) from the largest global compilation of gaseous emissions from cropland soils (Stehfest and Bouwman 2006). The total emissions of N_2O calculated from the California areal rates and cropland area was 14 Gg N yr^{-1}. This value is similar to the estimate of 9 Gg N yr^{-1} using the emissions factor approach. Emissions of nitrogen (N_2) gas from soils from denitrification were also a minor flow (17 Gg N yr^{-1}), estimated using a fixed N_2:N_2O ratio of 1.66. Because of the high variability in N_2:N_2O ratios and the high reported rates measured in California in the 1970s, we estimated a lower and upper bound for the N_2:N_2O as 1.25 and 2.31 as the mean ± 2 SE of the Schlesinger (2009) dataset. Taking into account the uncertainty, the range of N_2 emissions would be 13 to 23 Gg N yr^{-1}.

[Table 4.5]

[1] Supplementary materials will be available through the Agricultural Sustainability Institute's website at www.nitrogen.ucdavis.edu.

Dissolved outputs of N to surface water from cropland were estimated based on a predicted N yield (14 kg N ha^{-1} yr^{-1}). As only 2.9 million ha of California cropland was located in watersheds with surface water drainage, outputs of N to surface water (i.e., runoff) from cropland was a moderate N flow (41 Gg N yr^{-1}). Kratzer et al. (2011) reported similar N yields for the Central Valley sub-watersheds with the highest fraction of agricultural land, the Orestimba Creek watershed (17.9 kg N ha^{-1}) and the portion of the San Joaquin River near Patterson (16.3 kg N ha^{-1}).

Leaching below the rooting zone was a major flow (333 Gg N yr^{-1}) of N from cropland. This value is the average of two approaches which differ considerably in magnitude (Supplementary 4.2). Multiplying recharge volume by the median concentration of NO_3^- from published studies in California estimating leaching below the rooting zone, cropland leaching was estimated to be 395 Gg N yr^{-1}. In contrast, using the median of the fraction of applied fertilizer (synthetic + manure) that leaches from published studies in California predicted only 272 Gg N yr^{-1} leached. Thus, the level of agreement on the magnitude of N leaching is low. Conditions in the vadose zone in California are not conducive to denitrification (Green et al. 2008a). Therefore, this leached nitrate would be predicted to reach the groundwater table. Like many other fluxes, there was high spatial and temporal variability. However, while it is relatively simple to measure NO_3^- concentrations in leachate, it is more difficult to estimate N load as it also requires an estimate of the recharge volume. One recent estimate of leaching that actually calculated the areal rate of N loading in recharge was nearly 100 kg N ha^{-1} yr^{-1} in an almond orchard near the Merced River (Green et al. 2008b). Based on our statewide total N load and cropland area, we estimated that the average areal rate of cropland N loading would be 68 kg N ha^{-1} yr^{-1}. It is possible to use models (e.g., Watershed Analysis Risk Management Framework, Soil and Water Assessment Tool) to estimate nitrate leaching; however this approach is typically used for much smaller regions than an entire state, or even the entire Central Valley, and requires a large number of parameters to be estimated.

Based on the difference between inputs and outputs, soil storage was calculated as 65 Gg N yr^{-1}. There was limited evidence for storage of N in cropland soils in California. Based on the repeated sampling of agricultural soils throughout California, on average, N content in cropland soils increased from 0.9% to 0.29% in the upper 25 cm (Singer 2003). Assuming no change in bulk density over the 55 year period between samples, cropland soils would accumulate 1 kg N $ha^{-1}yr^{-1}$ for a total of 5 Gg N yr^{-1} statewide. This suggests that the estimate of storage by difference is too high. If we used the estimate of soil storage and calculate leaching by difference, the N flow would be 395 N yr^{-1}, equivalent to the higher of the two estimates for leaching based on recharge volume and concentration. Based on data from Post and Mann (1990), soils will accumulate carbon when carbon concentrations are less than 1% in the top 15 cm, assuming an average soil bulk density of 1 g cm^{-3}. Many of the agricultural areas in the state, with the notable exception of the Delta, were established in areas with relatively low organic matter soils. Therefore, increases in soil N would be expected as well. However, these increases in soil N are not linear over time; with the highest increases expected soon after land conversion and saturating after a certain time (e.g., Garten et al. 2011).

4.1.3 Livestock N flows

The N flows for the livestock subsystem assumed that all of the livestock in the state (with the exception of beef cows and all calves) were on feed.

4.1.3.1 Livestock feed

The majority of crop production (357 Gg N yr^{-1}) in California was harvested to feed livestock (Table 4.2). However, this production must be supplemented with another 200 Gg N yr^{-1} of feed imported from out of the state. Corn grain from the Midwest is a major source of livestock feed. The waybill samples from the Surface Transportation Board suggest that over 300 million bushels of corn arrive in California annually on trains originating in Nebraska and Iowa (US DOT 2010). This feed supply was converted into 141 Gg N yr^{-1} of food and 416 Gg N yr^{-1} of manure (Table 4.6). Dairy cows and replacement stock dominated the demand for livestock feed and manure production, but beef cattle, poultry, and horses contributed a significant fraction as well (Table 4.7).

[Table 4.6; Table 4.7]

4.1.3.2 Livestock manure

The majority of the N in livestock feed is excreted. Livestock manure is potentially a nutrient resource, but concentrated quantities can pose a waste disposal problem (Table 4.8). The fraction of manure that is volatilized as NH_3 depends on the type of livestock. Using the US Environmental Protection Agency (EPA) emission factors and our estimates of excretion, we calculated an emission of 97 Gg NH_3-N yr^{-1}. from livestock facilities. When combined with manure-associated emissions from cropland (45 Gg NH_3-N yr^{-1}), this N flow is almost identical to the reported tonnage of NH_3 in EPA (2004); however, this is far larger than the value of 69 Gg N yr^{-1} in the 2005 EPA National Emissions Inventory for California (EPA 2008). While there is a high amount of evidence for the amount of manure excreted by livestock, there is limited evidence for the fate of that manure. There are relatively few data measuring NH_3 emissions for the management practices and climate specific to California. Therefore, the emissions of NH_3 and the land application of manure are speculative (Figure 4.3). However, as the residence time of NH_3 in the atmosphere is relatively short, this reduced N may essentially be land applied from atmospheric deposition downwind of dairy facilities. The underestimate of modeled compared to measured N deposition in the ecosystems on the west slope of the Sierra Nevada could result from an underestimate of NH_3 emissions in the model.

[Table 4.8]

We assumed that all non-volatilized manure was applied to cropland. Dairy manure is unique because it occurs in both solid and liquid form and its disposal is now regulated in the Central Valley. With the 2007 General Order from the Central Valley Regional Water Board, there should soon be information available on the amount of dairy manure applied on the dairy facility and the amount transferred off the dairy. The crops that receive manure in any form and the amount of manure applied are not well established and whether the manure is used more as an organic amendment or a source of nutrients is not clear.

4.1.4 Urban land N flows

Urban land covers 2.3 million ha or 6% of the state. Nitrogen flows of 284 Gg N yr^{-1} correspond to an areal input of 124 kg N ha^{-1}, with much of the N remaining in the soils, structures, and landfills in the urban system (Figure 4.7).

[Figure 4.7]

4.1.4.1 Urban land imports and inputs

Atmospheric N deposition was relatively high in urban areas (11 kg N ha^{-1} yr^{-1}) adding 25 Gg N yr^{-1} (Table 4.9). Synthetically fixed N was a major (124 Gg N yr^{-1}) flow of N and accounted for a large (44%) fraction of the N flow to urban land subsystem. Synthetic fertilizer use, predominantly for residential, commercial, and recreational turfgrass, was an import of 53 Gg N yr^{-1}. Other synthetic N-containing chemicals, such as resins, plastics (in particular acrylonitrile butadiene styrene (ABS)), polyurethane, and nylon, was an input of 71 Gg N yr^{-1} that largely remains in urban landscapes. Wood and wood products (i.e., fiber), though relatively low N content materials, still contribute 51 Gg N yr^{-1}. Finally, a variety of materials such as retail and consumer food waste (54 Gg N yr^{-1}), pet waste (16 Gg N yr^{-1}), and biosolids (11 Gg N yr^{-1}) were added to the urban subsystem (soils or landfills).

[Table 4.9]

4.1.4.2 Urban land N outputs and storage

The estimated outputs of N from urban land are relatively minor. Gaseous outputs in all forms, from the fraction of urban areas covered by turfgrass, amounted to only 7 Gg N yr^{-1}. Few data exist on gas fluxes from turfgrass in California. For N_2O, Townsend-Small et al. (2011) found that the turfgrass direct emission factor ranged from 0.6 to 2.3% of fertilizer inputs, similar to the emission factor for cropland. The literature-based N yield in surface water runoff (5.6 kg N ha^{-1} yr^{-1}) was higher than for natural land areas resulting in urban runoff being a minor (10 Gg N yr^{-1}) output similar in magnitude to gas outputs.

The vast majority of N entering urban land remains there in some form. Storage occurs in soils (75 Gg N yr^{-1}), landfills (68 Gg N yr^{-1}), and in the built environment (134 Gg N yr^{-1}) While there are some data related to N storage in landfills, there is limited evidence for most other forms of storage. Turfgrass soils are well known for their capacity to accumulate N in soils for decades (e.g., Raciti et al. 2011), but there are no data for California. Synthetically fixed N in forms other than fertilizer often is used for long-lived components of structures or is disposed of in landfills along with N from food and yard waste like grass clippings. For example, polyurethane resins and nylon carpets will remain in buildings for years to decades. A major use of ABS plastic is for the housing of electronic equipment and in cars. There is no quantitative information on the ultimate fate of these synthetic N-containing chemicals. While plastic disposal to landfills is tracked, there is no information on what fraction of that plastic is ABS. There is also a growing recycling capability for these compounds as technologies for separating materials have improved. Much of the synthetic N and organic N in urban land is eventually disposed of in landfills. Of the known sources to landfills, food waste is the predominant (64%) source of N, but yard waste (i.e., prunings, stumps, and leaves and grass; 14%) and wood products (e.g., lumber; 13%) comprise a medium fraction of the landfill nitrogen disposal (Table 4.10). In the same way that the inputs and outputs of the livestock subsystem were quantified apart from the cropland subsystem, the household (food and waste) subsystem was considered separately from the urban land subsystem. Therefore, food was only considered part of the urban subsystem if it was disposed of in a landfill.

[Table 4.10]

4.1.5 Household N flows

We assumed that the food supply for humans and their household pets (dogs and cats only) consisted of the same materials.

4.1.5.1 Human food

On average there was 6.4 kg N yr^{-1} in food available per person in the United States (US) according to the USDA Economic Research Service (USDA 2013d) on average from 2002-2007. Therefore, with a population of 35.6 million people, a total of 228 Gg N yr^{-1} of food was available for California's human population. Assuming a demographic based food consumption of 4.9 kg N yr^{-1} per capita (Baker et al. 2001), a statewide total of 174 Gg N was consumed leaving 54 Gg N, or 23%, as food waste. This is close to the 27% food waste reported by Kantor (1997). With a total production of 185 Gg N yr^{-1} of food crops and 141 Gg N yr^{-1} of animal products, we estimated that there was a net export of 79 Gg N from California.

4.1.5.2 Human waste

The analysis of the fate of food was based on three decision points. First, 25% of the available food was not consumed by people, but was disposed of in landfills while the other 174 Gg N yr^{-1} was excreted and became sewage. Secondly, ~10% of households in California use on-site waste treatment (i.e., septic) for waste disposal instead of centralized wastewater treatment. Based on the literature, we assumed that

9% of septic N would be removed as biosolids, but there is limited evidence for the fate of the other 91%. It is very likely that some N from septic systems is taken up by vegetation near the leach fields or quickly reaches surface water bodies; however, we assumed that all of this N would reach groundwater to maximize the potential impact of septic systems on groundwater N. Finally, the N entering wastewater treatment plants can be disposed of in liquid form (effluent), solid form (biosolids), or gaseous form (predominantly denitrification to N_2).

Because the population of California tends to live along the coast, the predominant (61%) fate of wastewater influent is discharge into the Pacific Ocean (82 Gg N yr^{-1}) (Table 4.11). This includes the discharge from the Sacramento regional wastewater treatment plant (WWTP) and the Stockton regional wastewater treatment facility. Even though they discharge into the Sacramento River and San Joaquin River, respectively, their effluent is discharged downstream of the US Geological Survey (USGS) gauges where N concentrations are measured. Only a small amount (12 Gg N yr^{-1}) of wastewater N was discharged into other surface water bodies of California from WWTPs. Discharge of treated wastewater to land (11 Gg N yr^{-1}) that largely leaches to groundwater was a small (9%) fraction of wastewater based on the sum of N from facilities without a NPDES permit but with a “NON 15” land discharge permit from the State Water Resources Control Board. The statewide production of biosolids is estimated to be 22 Gg N yr^{-1}, which we assumed was equally split between application to cropland and use as alternative daily cover at landfills. A fraction of the sewage is converted to gas during wastewater treatment, although facilities with advanced secondary or tertiary treatment convert approximately two-thirds of the total N into gaseous forms by denitrification. A small (2 Gg N yr^{-1}) amount of N_2O is produced during treatment, but the N removal by advanced wastewater treatment produces largely N_2. Based on the assumption that half of the N load is converted to gaseous forms in the facilities in advanced treatment, 16 Gg N yr^{-1} would be emitted from wastewater facilities. If 2 Gg N yr^{-1} were in the form of N_2O based on the greenhouse gas inventory, then 14 Gg N yr^{-1} would be emitted as N_2.

However, calculating all of the outputs independently results in a discrepancy of 15 Gg N yr^{-1} between sewage input (174 Gg N yr^{-1}) and output pathways (159 Gg N yr^{-1}). This discrepancy could be explained by several potential errors. First, the empirical relationship of effluent N and WWTP design flow is based on NH_3 discharge and not total N discharge. Many, but not all, of the WWTPs in the state are required to monitor NH_3 concentrations monthly, but the data in most cases are only publicly available in paper form at the regional Water Quality Control Board offices. Further, the other dissolved N forms (NO_3^-) and organic N are rarely monitored because the predominant form of discharged N is NH_3 unless the facility uses advanced treatment to remove N. Secondly, we may underestimate the N content of biosolids. The literature values vary widely, but the N content of biosolids in California are not monitored. A third possibility is that there are emissions of N_2 in facilities without advanced wastewater treatment. Finally, the missing N might never have reached the wastewater treatment plants. That is, 15 Gg N yr^{-1}, or ~ 10% of the N in human waste could be leaking out of sewer pipes into groundwater during the collection process. While the magnitude of N leaking from sewer pipes is difficult to measure directly, the presence of leaky sewer pipes in urban areas is well documented (e.g., Groffman et al. 2004). For the purposes of the mass balance we assumed that the missing N was in the form of N_2, resulting in a 29 Gg N yr^{-1} as N_2 instead of the 14 Gg N yr^{-1} calculated based on the amount of N denitrified (Table 4.11).

4.1.5.3 Household pets

With 7.0 million dogs and 8.8 million cats in the state, 19 Gg N yr^{-1} of food N was needed to feed household pets. Assuming household pets and humans eat from the same food supply, total food demand was 242 Gg N yr^{-1}. The predominant fate of pet waste was urban soils (12 Gg N yr^{-1}) with some cat waste (3 Gg N yr^{-1}) disposed in landfills and a minor (4 Gg N yr^{-1}) flow of N emitted as NH_3.

4.1.6 Natural land flows

Natural land covers 33 million ha, or more than 80% of the area of the state. Total N inputs of 271 Gg N yr^{-1} resulted in an average areal input of 8 kg N ha^{-1} yr^{-1} (Figure 4.8).

[Figure 4.8]

4.1.6.1 Natural land N inputs

The input from atmospheric N deposition was 132 Gg N yr^{-1} for natural land rates reported in Fenn et al. (2010) (Figure 4.8, Table 4.12). This value is based on the results from the CMAQ model but modified for several ecosystems that have higher measured than modeled N deposition rates. However, the spatial distribution of N deposition measurements is too sparse statewide to rigorously evaluate the model's results.

[Table 4.12]

Based on the biome-specific approach, biological N fixation in natural land ranged from 139 to 411 Gg N yr^{-1} for an average areal fixation rate of 4-13 kg N ha^{-1} yr^{-1}, depending on the value of relative cover of N fixing species. This total includes non-symbiotic fixation which is estimated to produce 10% of biologically fixed N. A second approach using the empirical relationship predicting N fixation from modeled evapotranspiration (ET) found statewide natural land N fixation ranged from 59-381 Gg N yr^{-1} for an average rate of 2-12 kg N ha^{-1} yr^{-1}. Finally, with the mass balance approach (i.e. outputs minus inputs assuming no storage), the statewide N fixation on natural land was estimated at 53 Gg N yr^{-1} or 1.6 kg N ha^{-1} yr^{-1}. The overall range of these values translates to 30-75% of the new reactive inputs of N to natural land and 4-23% of the inputs statewide (Table 4.1a, Table 4.12).

The estimates of natural land N fixation are speculative. One problem with using the compilation of data to estimate N fixation is that the data may not be representative of the landscape as a whole. That is, measurements are likely made in areas where N fixation is higher. For example, the N fixation value of 16 kg N ha^{-1} yr^{-1} for forests is likely to be an overestimate for California since there is relatively little area that has high cover of N-fixing species. In addition, many biomes in the state have relatively few N-fixing species with medium to high fixation rates present at all. Further, as atmospheric N deposition has increased by an order of magnitude from 0.5 to 5 kg N ha^{-1} yr^{-1} over the last century, there may have been a corresponding decrease in N fixation with increasing N availability. This could be due to changes in the amount of N fixed by N-fixing species or the decreased cover of N fixing species (Suding et al. 2005). On the other hand, there are increasing numbers of invasive N-fixing species which are likely expanding their areal extent. Therefore, we feel that the low-end estimate of 139 Gg N yr^{-1}, based on the biome-specific rates, would be the most appropriate value for statewide natural land N fixation.

Prior to the human disturbance of the N cycle related to industrialization, biological N fixation was the major source of reactive N to the biosphere. At pre-industrial rates of atmospheric N deposition (0.5 kg N ha^{-1} yr^{-1}), natural land fixation would have accounted for more than 75% of the N imports to the state. For natural land, N fixation remains the predominant (52%) source of N input. At the statewide level, however, biological N fixation in natural land has become a minor (9%) fraction of the total N inputs because of the increase in anthropogenic N.

4.1.6.2 Natural land N outputs and storage

The largest N output from natural land soils is in gaseous forms. The biome-specific rates of gaseous emissions and biome areas result in the output of 11 Gg NO-N yr^{-1}, 47 Gg NH_3-N yr^{-1}, 13 Gg N_2O-N yr^{-1}, and 13 Gg of N_2-N yr^{-1}. While the biome level rates of N_2O and NO are averages of multiple datasets often based on many published papers, it is difficult to discern how well they represent California ecosystems. For example, abiotic NO emissions are possible in desert regions, where the surface temperature can reach over 50 degrees C (McCalley and Sparks 2009).

Wildfire produces another 30 Gg N yr^{-1} of gaseous N emissions. The area burned annually is monitored carefully by the California Department of Forestry and Fire Protection. However, the amount and form of N released by fire is more difficult to discern because it varies depending on the amount of biomass and the burn characteristics. The 2005 EPA National Emissions Inventory reported 2 Gg N yr^{-1} emitted as NO_x and 2 Gg N yr^{-1} emitted as NH_3 related to natural land fires for California. Insignificant (< 1 Gg N yr^{-1}) amounts of N_2O were also emitted. Thus, by difference N_2 must be the dominant N form of wildfire emissions. Nitrogen volatilization from fires is considerably larger than the harvest of timber (11 Gg N yr^{-1}) from natural land for wood products.

Runoff to surface water accounts for 44 Gg N yr^{-1} output from natural land soils based on an export coefficient of 2.4 kg N ha^{-1} yr^{-1}. However, based on the California specific-data in Kratzer et al. (2011), we estimated the export coefficient to be only 1.3 kg N ha^{-1} yr^{-1}. A large part of this difference may be associated with the managed hydrology in California. Significant fractions of the Sacramento and San Joaquin watersheds, especially the natural land, are located upstream of dams. Surface water bodies, especially reservoirs, can retain large amounts of N (Harrison et al. 2009). In closed basins, dissolved constituents cannot be transported to the ocean via surface water, but can only be leached through the soil to groundwater. In desert regions of the southwest with a deep water table, the estimated flux of 0.6 kg N ha^{-1} yr^{-1} would result in 10 Gg N yr^{-1} leaching to groundwater. This annual rate is based on the NO_3^- stock of subsoil horizons that has accumulated over millennia. This subsurface inorganic N storage can be considerably larger than the surface soil organic N pool.

The mass balance calculations indicate that storage is a moderate N flow (91 Gg N yr^{-1}) in natural land. There are three possible explanations. First, our estimate of N inputs may be too high, especially the N fixation. Secondly, our estimate of N outputs may be too low, especially gaseous emissions. Finally, N may be accumulating in vegetation and soils in California. The estimated storage term, while large with respect to the annual mass balance, was small in terms of the soil N pool. Assuming that the top 10 cm of soil in natural land is 0.1% N with a bulk density of 1 g cm^{-3}, the addition of the calculated annual change in N storage averaged across all natural land represents an increase of 0.25% in the size of the soil N stock. That is, the top 10 cm would increase from 100 to 100.25 g N m^{-2}. This increase would be difficult to detect analytically, and even more so considering that the top 10 cm of soil only contains a fraction of the total soil N pool.

4.1.7 Atmosphere N flows

The atmosphere is 78% N_2 gas: this is an essentially unlimited supply of N as it represents more than 1 million times the annual flows of N to and from the atmosphere globally. At the scale of California, we assumed the atmospheric stock of N_2 is not changing, but we did estimate the export of fixed N as N_2 related to denitrification. For the atmosphere subsystem N mass balance, we estimated (1) how much reactive N was added to the portion of the atmosphere above the state, (2) deposition from the atmosphere to the land surface, and (3) export from the state (with all N_2O and N_2 emissions considered N exports because of their long atmospheric residence times). We discuss the uncertainties in the estimates of atmospheric inputs in the sections where the gas emissions represent outputs. Overall, California is a large source of reactive N to the atmosphere with the majority of the N exported beyond the political boundaries of the state via the atmosphere (Table 4.13).

[Table 4.13]

4.1.7.1 Atmosphere N imports and inputs

Fossil fuel combustion is the major (40%) source of N to the atmosphere and NO_x is the predominant (89%) form of fossil fuel N generated. A total of 359 Gg NO_x-N yr^{-1}, 36 Gg NH_3- N yr^{-1}, and 9 Gg of N_2O- N yr^{-1} were emitted during fossil fuel combustion (Table 4.13).

Soils and manure were also large sources of N to the atmosphere and are discussed in more detail in previous sections. Soils were the second largest contributor of N to the atmosphere with 24 Gg NO - N yr^{-1}, 110 Gg NH_3- N yr^{-1}, 24 Gg of N_2O- N yr^{-1}, and 31 Gg N_2- N yr^{-1}. These emissions encompass all land cover types, as well as emissions from the land application of manure. Direct emissions from manure management on livestock facilities and after land application was a moderate (97 Gg N yr^{-1}) flow and a major (36%) source of NH_3 to the atmosphere. Dairy manure was the predominant (80%) source of the NH_3 emissions from manure management. Manure management on livestock facilitieswas also a small (2 Gg N yr^{-1}) source of N_2O.

Wildfires, wastewater treatment, and surface water were all moderate N flows of similar magnitude to the atmosphere (30 to 36 Gg N yr^{-1}). For these three sources, unlike soils or fossil fuel combustion, N_2 is the dominant form of emissions.

A fraction of the reactive N in the atmosphere originates from areas upwind of California. Based on the atmospheric deposition rates generated by the CMAQ model in areas off the coast of California, the current background deposition rate is 1 kg N ha^{-1} yr^{-1}, split evenly between oxidized and reduced N. This rate does not represent the preindustrial N deposition rate because it includes anthropogenic N from other regions of the world, particularly Asia. This deposition rate applied for the whole state would result in 40 Gg N yr^{-1} deposited in California even in the absence of any N emissions to the atmosphere in California. This background N deposition is considered an N import to California's atmosphere because it originates beyond the political boundaries of the state. We cannot estimate how much reactive N enters California's atmosphere from outside California and passes through the state without being deposited.

4.1.7.2 Atmosphere N exports and outputs

We assumed that there was no N storage possible in the atmosphere. Therefore, NO_x and NH_3 emissions had to be redeposited in California or exported downwind from the state. In addition, all of the N_2O and N_2 emitted were assumed to be exported. For both oxidized (33%) and reduced (25%) forms of N, less than half of the emissions were redeposited in the state. Oxidized N emissions (NO_x) were 4 times higher than reduced N emissions (NH_3) while oxidized deposition was only double that of reduced deposition, highlighting that a greater fraction of oxidized emissions are exported. The emitted N compounds can be exported in more stable forms after transformation to compounds like ammonium nitrate particles, nitric acid, or various organic N compounds.

4.1.8 Surface water N flows

Surface water drainage differs in California for several reasons. First, more than 40% of the state has no surface water drainage to the ocean. The watersheds in the Mojave Desert, Great Basin, Carrizo Plain, and Tulare Basin, were assumed to have no external drainage. Secondly, almost every major river in the state is dammed and water is transferred among river basins. Finally, the timing and amount of nutrient inputs to surface water may differ from other parts of the United States because of the Mediterranean climate (Sobota et al. 2009, Ahearn et al. 2004).

4.1.8.1 Surface water N inputs

We estimated that the N input to rivers from runoff from the three land cover types was 95 Gg N yr^{-1} with an additional loading of 12 Gg N yr^{-1} from wastewater treatment plants (Table 4.14, Table 4.15). Non-point sources in natural land (44 Gg N yr^{-1}), cropland (41 Gg N yr^{-1}), and urban land (10 Gg N yr^{-1}) dominated the N inputs based on the export coefficients for these three land cover types. A small amount of deposition (2 Gg N) fell directly on water bodies in the state.

[Table 4.14; Table 4.15]

4.1.8.2 Surface water exports, outputs and storage

Of the N entering rivers, less than half (39 Gg N yr^{-1}) reached the ocean (Table 4.15). Nitrogen dissolved in irrigation water withdrawals accounted for 18 Gg N yr^{-1} of the output from the surface water subsystem. We estimated denitrification to N_2 from rivers, lakes, and reservoirs to be 30 Gg N yr^{-1} and production of N_2O to be 2 Gg N yr^{-1}. By difference, we calculate storage in surface water bodies as 20 Gg N yr^{-1} (Table 4.14). The independent measures of N in surface water storage were similar. First, using the sedimentation rate and N concentration of sediments, we estimated 65 Gg N yr^{-1} buried in sediments. Based on Harrison et al. (2009), N retention was 8 Gg N yr^{-1} in lakes and 57 Gg N yr^{-1} in reservoirs. The denitrification estimate of 30 Gg N yr^{-1} means that 37 Gg N yr-1 would be accumulating in sediments. The dominance of reservoirs in N retention is consistent with the results of Harrison et al. (2009) that found that reservoirs retained N at rates ten times higher than lakes.

[Table 4.14; Table 4.15]

4.1.9 Groundwater N flows

Groundwater N flows are rarely quantified directly, but we estimated their magnitude at the statewide level as a function of recharge or withdrawal volume and N concentration.

4.1.9.1 Groundwater inputs

Leaching to groundwater was a major (380 Gg N yr^{-1}) flow of N (Table 4.16). Almost 90% of the N flow to the groundwater leached from cropland soils (333 Gg N yr^{-1}). Small fluxes of N were related to leaching from manure in dairy facilities (10 Gg N yr^{-1}), natural land in areas with no surface drainage (10 Gg N yr^{-1}), and discharge of treated wastewater (27 Gg N yr^{-1}). The latter was a combination of septic systems (16 Gg N yr^{-1}) and treatment plants that dispose of treated wastewater on land (11 Gg N yr^{-1}). The estimate for septic systems is likely an overestimate of inputs to groundwater as we assumed that all of the N, with the exception of the biosolids, would reach the groundwater, but even if 50% of the septic N had some other fate, the impact on total groundwater N inputs would be minimal.

4.1.9.2. Groundwater outputs and storage

Groundwater pumping for irrigation removed 33 Gg N yr^{-1}, with water containing, on average, 2.6 mg NO_3^--N L^{-1}. Denitrification produced 91 Gg N yr^{-1} as N_2 in 2005, but this flow is tentatively agreed by most (Box 4.5). The three estimates ranged from 26 Gg N yr^{-1} using a fixed rate of denitrification, to 85 Gg N yr^{-1} using historical estimates of N loading and a fixed half-life of N, to 162 Gg N yr^{-1} using a fixed ratio of denitrification to N inputs based on current inputs. Taking into account the irrigation withdrawals and denitrification of historical nitrate in groundwater, almost 70% of the annual groundwater inputs for 2005 would contribute to an increase in groundwater N storage of 258 Gg N (Table 4.16). This assumes no net exchange of N with surface waters because the bidirectional flow is close to zero and the N concentrations in groundwater and surface water are similar. We assumed that groundwater denitrification produces solely N_2 and not N_2O. However, this N_2 would not actually be returned to the atmosphere until the groundwater discharges to surface waters which could take decades to millenia.

[Box 4.5]

4.2 Mass balance calculations and data sources

The ***imports*** of new reactive N for the statewide mass balance were fossil fuel combustion, biological N fixation, synthetic N fixation, agricultural feed, and fiber. The ***exports*** were gas/particle exports in the atmosphere, food exports, discharge of rivers to the ocean, and discharge of sewage to the ocean. ***Storage terms*** include soils and vegetation, reservoirs, landfills, and groundwater. We assumed no storage in the atmosphere. In addition to the calculations at the statewide level, mass balances were calculated for various ***subsystems*** within California: natural land, cropland, urban land, livestock, households, surface waters, groundwater, and the atmosphere. In most cases the flows in the subsystems could be estimated with one or more independent approaches, but some flows could only be estimated by differences (e.g., groundwater in cropland).

For the calculations of flows in the three land-based subsystems, California was classified into four main land cover classes: natural land, cropland, urban land, and water. An updated version of the California Augmented Multisource Landcover (CAML) map was produced by the Information Center for the Environment at the University of California – Davis (ICE 2006). The base map layer of CAML was the 2002 Multi-Source Land Cover dataset produced by the California Department of Forestry and Fire Protection (FRAP). This layer was the source for the type of ecosystem vegetation in all of the natural land and also delineated surface waters. For biome level estimates, the FRAP vegetation types were lumped into biomes based on the California WHR13 classes: barren, desert (desert shrub and desert woodland), forest (hardwood and conifer), herbaceous, shrub, woodland (hardwood and conifer), water, and wetland. The agricultural land was further subdivided to individual crops based on the class and subclass of the polygons in the most current digitized county maps produced by the California Department of Water Resources (DWR). For counties without digitized DWR maps, agricultural land was identified based on the categories in the FRAP base layer, supplemented with crop information from pesticide use reports produced by the California Department of Pesticide Regulation. Urban areas were identified by combining the urban boundaries indicated in the California Department of Conservation Farmland Mapping Program and urban land-use types in the 2001 USDA National Land Cover Dataset. The water pixels in CAML were divided into lakes, reservoirs, and rivers in two ways: first, areas identified as riverine and estuarine wildlife habitats were categorized as rivers, while lacustrine wildlife habitats were categorized as lakes. In pixels identified only as water, the spatial location of the pixel was compared to the USGS National Hydrography Dataset (USDI 2013). If the pixel matched a lake or reservoir, the pixel was designated a lake or reservoir; otherwise the water pixel was considered a river. The final map was produced at a 50 m resolution.

4.2.1 Fossil fuel combustion

Fossil fuel combustion produces NO_x, NH_3, and N_2O as incidental byproducts and are tracked and regulated for different reasons. Nitrogen oxides are considered a criteria pollutant and all of the anthropogenic sources of NO_x included in the statewide inventory conducted by the California Air Resources Board (ARB) and the US EPA were considered emissions. The emissions from the 2002 EPA inventory (EPA 2007) were used for the calculations because that dataset was the basis for the N deposition model described below. Ammonia is an unregulated pollutant, but it has become part of the criteria pollutant monitoring program because of its role in forming secondary fine particulate matter ($PM_{2.5}$) in the atmosphere as either ammonium nitrate or ammonium sulfate. As with NO_x, the 2002 EPA dataset was used to estimate NH_3 emissions; however, only categories related to fossil fuel combustion (fuel combustion, highway vehicles, and off-highway vehicles) were included. Finally, N_2O emissions are not yet regulated, but are estimated as part of greenhouse gas inventories by both ARB and the EPA. All "included" fossil fuel combustion sources from the ARB inventory, regardless of sector, were used to calculate fossil fuel related N_2O emissions and an average for 2002-2007 was calculated.

While not necessarily exclusively from fossil fuel combustion, there is import of reactive N to the atmosphere above California from outside the boundaries of the study area. Some of this N will be transmitted completely through the state and this fraction will be ignored. However, we estimated the import of this reactive N by assuming that the offshore N deposition rate would occur across the entire state of California in the absence of any emissions from California. Based on the atmospheric deposition rates generated by the CMAQ model in areas off the coast of California as modeled by Tonnesen et al.

(2007), the current offshore deposition rate is 1 kg N ha^{-1} yr^{-1}, split evenly between oxidized and reduced N.

4.2.2 Atmospheric deposition

Atmospheric deposition was based on the results of Fenn et al. (2010). Their Geographic Information System (GIS) map layer uses output from the CMAQ model based on 2002 emissions data. The CMAQ model results for most of the state were available from Tonnesen et al. (2007) at a resolution of 4 km, but for northern and southeastern California only the 36 km CMAQ output from the EPA was used to create a statewide map. In certain biomes, based on the availability of field measurements, the model output was replaced by measured deposition data. Total N deposition was partitioned statewide on the various land-use types (natural land, cropland, urban land) based on the land-cover map. However, as the composite statewide map in Fenn et al. (2010) only provided total N, the ratios of oxidized to reduced and wet to dry N deposition were calculated based on the area modeled by Tonnesen et al. (2007).

We assumed that storage was not possible in the atmosphere. Therefore, the export of NO_x and NH_3 was calculated as the difference between all inputs and N deposition. By the time the export from California occurs, secondary reactions will have occurred in the atmosphere such that NO_y (NO_x plus its oxidization products like HNO_3 or organic nitrates) and NH_x (NH_3 plus the NH_4^+) better describe the forms of N. We assumed that all of the emitted N_2 and N_2O was exported from the study area.

4.2.3 Biological N fixation

Biological N fixation is also discussed in Chapter 3. A variety of field measurements of biological N fixation have been used including ^{15}N isotope methods, acetylene reduction, N accretion, and N difference, which vary in their assumptions and limitations.

4.2.3.1 Natural land N fixation

Based on the USDA Plants database (USDA 2013c), a total of 56 native and 34 non-native non-crop species are known to be symbiotic N fixers on natural land in California. However, field measurements of rates and the relative abundances for most of these species are poorly known. Therefore, we used three approaches to estimate biological N fixation in natural land based on Cleveland et al. (1999). First, the biome areas calculated from the land-use map were multiplied by the biome-specific N fixation rates compiled in this global synthesis of published rates. A range in values was estimated using the biome-specific low, medium, and high percent cover abundance of the N fixing species. Second, Cleveland et al. (1999) developed an empirical linear relationship between biome-specific modeled values of actual ET and N fixation rates. The mean modeled statewide ET (provided by Q. Mu, University of Montana) from 2001 (33.6 cm yr^{-1}) was used because it was the only year when precipitation, modeled ET, and cropland irrigation rates were available for the entire state. Third, we used a mass balance approach. That is, we estimated all of the other N flows in and out of natural land, assumed steady-state conditions (i.e., no N storage) and calculated N fixation by difference.

4.2.3.2 Cropland N fixation

Cropland N fixation rates were based on published species specific rates and harvested acreages. The most comprehensive analysis of legume N fixation rates is a meta-analysis for Australia described in Unkovich et al. (2010). These authors found highly variable rates, but a strong positive relationship between fixed N in aboveground tissues and productivity. This may help explain, in part, the high variability in the published rates. The only crop included in this analysis that is grown on a significant acreage in California was alfalfa where the empirical relationship was aboveground fixed N (kg ha^{-1}) = 18.2*Production (Mg ha^{-1}) + 0.13. The rates for the other leguminous crops grown in California (dry beans, dry and fresh lima beans, snap beans, and clover), but not included in the analysis, were based on Smil (1999). We also include the fixation rates for rice paddies reported by Smil (1999) associated with the cyanobacteria symbiotically associated with the aquatic ferns in the genus *Azolla*. Crop acreages for all legumes except clover were calculated as the 2002-2007 average of the annual harvested acreages reported in the statewide database of California Agricultural Commissioners' reports (USDA 2013b). Clover used to be planted widely in irrigated pastures, but now is estimated to compose only 10% of the cover in these systems (M. George UCDavis). The acreage of irrigated pasture was calculated as the average of the 2002 and 2007 Agricultural Census acreage for irrigated pasture (Table 10; USDA 2004, 2009).

4.2.4 Synthetic N fixation

Synthetic N fixation is largely the result of the Haber-Bosch process although a small amount of ammonium sulfate is still produced as a byproduct from coke oven gas during steelmaking (Kramer 2004). This industrial process converts atmospheric N_2 to NH_3 at high temperature and pressure with natural gas being the source of hydrogen and energy. National estimates of fixed N are annually compiled by the US Geological Survey including national production, imports and exports. Fixed NH_3 is the feedstock for essentially all synthetic N fertilizers as well as a variety of industrial N-containing chemicals and explosives (Kramer 2004). Less than 2% of the national explosives use occurs in California because of the limited amount of mining (USDI 2000). Ammonium nitrate/fuel oil mixtures are the dominant form of explosives, but we assumed that the N emissions from their use was N_2 gas. Therefore explosives were not considered as part of the budget.

4.2.4.1 Non-fertilizer synthetic chemicals

Non-fertilizer use of some individual compounds can be tracked, but as a whole it is typically calculated as the difference between total NH_3 fixation and fertilizer use. Other common non-fertilizer uses include synthetic chemicals, such as melamine, nylon, plastics (e.g., acrylonitrile butadiene styrene), and polyurethane (Table 4.17). Several estimates of synthetic N consumption are available, but the Kramer (2004) source was used because it breaks down the non-fertilizer N consumption most completely (Table 4.18). The national total for non-fertilizer consumption of N was 1,722 Gg N yr^{-1} (Kramer 2004). Excluding the synthetic N for explosives, 567 Gg N yr^{-1} of non-fertilizer N was consumed nationally in 2002 (Kramer 2004). We scaled the national estimate to California based on the mean 2002-2007 population of California (35.6 million) and the United States (295 million) from the US Census Bureau (USDC 2013). We used the US Census as opposed to the California Department of Finance population estimate in order to make the most consistent estimate of California's proportion of the US population. Most of these synthetic forms of N are assumed to be long-lasting chemicals, which become part of infrastructure and household items and eventually are disposed of in landfills (Table 4.17). One chemical class that is poorly tracked is N-containing compounds found in many common household products, such as surfactants and detergents that end up as part of the wastewater stream.

[Table 4.17, Table 4.18]

4.2.4.2 Synthetic fertilizer

Fertilizer sales, not necessarily fertilizer use, have been reported annually since the 1950s in the tonnage reports of the California Department of Food and Agriculture. These data are identical to the California data compiled by The Fertilizer Institute as part of their national survey. To prevent duplication, reporting of sales is supposed to occur when a licensed fertilizer dealer sells fertilizer to an unlicensed purchaser. The data are collected as tonnage of fertilizing materials and are converted to tons of nutrients based on the reported fertilizer grade. Fertilizer use was assumed to be on average equivalent to fertilizer sales at the state level. Because of uncertainty in these data starting in 2002, we used the average synthetic fertilizer sales for 1997-2001.

Synthetic fertilizer use was first partitioned between agricultural and urban (i.e., turfgrass) use based on data provided by the Scotts Miracle-Gro Company. Annually, an estimated 2.7 million tonnes of fertilizer is applied nationally to turfgrass divided equally between homeowner use, commercial application to home lawns, and golf courses/athletic fields. This fertilizer tonnage was converted to N tonnage based on the typical N grade of lawn fertilizer (29%) based on the popular Scotts Turf Builder product. The national estimate was scaled down to California using remote-sensing based estimates of turfgrass acreage. California contains 11,159 km^2 of turfgrass, or 6.8% of the total national turfgrass acreage (Milesi et al. 2005). The Scotts company also was willing to share their sales figures for the state and reported sales of 4 Mg N sold in 2005 for the do-it-yourself homeowners market. Their research suggests that they supply approximately half of the do-it-yourself homeowners market.

Synthetic fertilizer use for cropland was calculated separately for ornamental horticulture and other crops. The amount used for environmental horticulture was based on the acreage of open grown commodities in the USDA Census of Agriculture, an annual irrigation rate of 2 m water yr^{-1}, and an N concentration of 100 ppm N assuming no recycling of N in irrigation water (R. Evans, personal communication). Sod farms were assumed to use 400 kg N ha^{-1} (R. Green, personal communication).

Synthetic fertilizer use on other crops was calculated by subtracting urban and environmental horticulture use from the total sales. Fertilizer use can also be validated based on crop-specific recommendations. Current (since 1999) fertilization rates by crop were extracted from UC Davis cost studies and the USDA Chemical Use Surveys and the two data sources were averaged (see Chapter 3 for further details on data). The fertilization rates were combined with the crop-specific acreages reported in the statewide Agricultural Commissioners dataset to calculate a total fertilizer recommendation that could be met with synthetic fertilizer or manure. Any difference between the calculated fertilizer use and the synthetic fertilizer sales for these crops indicates fertilization needs met by manure.

4.2.5 Agricultural production and consumption: food, feed, and fiber

The production and consumption of food, feed, and fiber involve the majority of N flows in California. The N tonnage of all agricultural products, with the exception of wood products and ornamental horticulture, was calculated from production data compiled by the county Agricultural Commissioners (USDA 2013b). The 253 crop commodities in the database were consolidated into 121 classes based on similar characteristics. The 2002-2007 average N tonnage was calculated by matching each crop class to the most similar crop in the USDA Crop Nutrient Tool (USDA 2013c). This database, which is the most comprehensive source of its kind, is a compilation of the nutritional content of crops from a variety of published sources, but most of the sources are at least several decades old. The only commodity not present in the database was olives whose nutritional information was based on the 2009 USDA National Nutrient Database for Standard Reference (USDA 2013e). Commodity boards in the state were contacted to determine if they had more recent and California-specific data, but only the Almond Board of California provided information. The following crop classes were considered feed crops: alfalfa hay, almond hulls, grain and silage corn, cottonseed, non-alfalfa haylage, small grain hay, grain and silage sorghum, tame hay, and wild hay.

Consumption of agricultural products was based on the population of humans, household pets, and livestock in the state. The average population of California during the period 2002-2007 was 35.6 million people. The consumption of food was calculated in two ways. First, on average from 2002-2007, the national per capita food availability was 6.5 kg N yr^{-1} (USDA 2013d). Second, per capita N consumption varies globally, but in the United States, 5.0 kg N yr^{-1} is typical (Boyer et al. 2002). The waste of food by retailers, food service, and consumers has been estimated at 27%. Combining food waste with food consumption leads to a per capita demand of 6.4 kg N yr^{-1}, almost identical to the USDA Economic Research Service (USDA 2013d) estimate of food availability. Thus, a per capita value of 6.4 kg N yr^{-1} was used to calculate human food supply. Household pet populations were determined from the American Veterinary Medical Association (AVMA) survey of pet ownership (AVMA 2007). Total household pet food consumption was based on an average body mass of dogs and cats (Baker et al. 2001) and daily N intake requirements (NRC 2006).

Nursery and floriculture N harvest was based on annual biomass production of 750 kg N ha^{-1} (R. Evans, personal communication) and the average of the reported acreage from the 2002 and 2007 USDA Census of Agriculture for all open grown horticultural commodities. We assumed that there was no net export of horticultural commodities. Based on the value of sales reported in the 2009 Census of Horticultural Specialties (USDA 2010), California produced 20% of the total national horticultural specialty crops. However, of the nursery and annual bedding/garden plants (which likely contribute the most to harvested N), California only produced 14%, similar to the state's proportion of the national population (12%).

The N tonnage of lint cotton, the only fiber commodity harvested on cropland, was calculated identically to the food crops. Annual cotton consumption for the population of California from 2002-2007 was on average 1 Mg cotton (USDA 2013d). The wood harvest in California in 2004 was 56 million m^3 (Morgan 2004). This was converted to N production based on the specific gravity (0.5 g cm^{-3}) of Douglas fir (*Pseudotsuga menziesii*), and a typical wood N content (excluding bark) of 0.15% (Cowling and Merrill 1966, USDA 1999). The consumption of wood for California was based on the national per capita estimate of 67 ft^3 per year of wood products scaled to the 2002-2007 average population of 35.6 million. This volume was converted to N tonnage with the same factors as the volume of wood harvested.

Livestock feed was determined based on animal populations and dietary needs. For non-cattle livestock that are raised for meat (broilers, turkeys, pigs), the population was the average of the 2002 and 2007 USDA Agricultural Census quantity of animals sold. The feed requirements for these types of livestock were estimated on a grow-out basis (Van Horn 1998). For dairy cattle, steers, and layers the population estimates were the 2002-2007 average of the USDA National Agricultural Statistics Service (NASS) annual year-end inventory. All beef cows, beef replacement heifers, and all calves were assumed to be grazed on rangelands. We assumed that all dairy cattle were on feed, as more than 95% of the dairy cows were located in the counties of the Central Valley or in the Chino Basin (USDA 2013a) where confinement is the typical practice. The feed requirements for dairy cows were from Chang et al. (2006) with the assumption that for one-sixth of the year, the cows were dry. The feed requirement for dairy replacement heifers was based on a 440 kg Holstein heifer (ASAE 2005). Although horses are included in the USDA Agricultural Census, this survey underestimates their population because it excludes animals that are not working animals. Instead, the horse population was based on the AVMA (2007) survey of pet populations and N intake requirements were from NRC (2007). Unlike dogs and cats, the horse population was estimated regionally: the California horse population was estimated assuming that the number of horses per household was the same across the entire Pacific region (Washington, Oregon, and California). In addition, there is anecdotal evidence that horse owners in California feed alfalfa to horses in the state because it is perceived to be higher quality feed (C. Stull, personal communication). A diet of 100% alfalfa feed with the suggested dry matter intake would provide 50% more N to horses than is needed.

Livestock-based food production (milk, eggs, meat) was based on 2002-2007 average production estimates from USDA annual surveys with the exception of broilers which were the average production from the 2002 and 2007 USDA Agricultural Census (USDA 2004, 2009). The N content of various products was from NRC (2003), except that turkey N content was assumed to be the same as broilers (Table 4.19).

[Table 4.19]

4.2.6 Manure production and disposal

Manure production was calculated based on the populations used for feed requirements and animal-specific excretion rates. For dairy cows, excretion was 169 kg N head^{-1} yr^{-1} for lactating cows and 81 kg N head^{-1} yr^{-1} for dry cows (Chang et al. 2006). It was assumed that all cows were dry for 1/6th of the year and lactating for 5/6th of the year resulting in an average manure production of 208 kg N head^{-1} yr^{-1}. Dairy replacement heifers excreted 43 kg N head^{-1} yr^{-1} (ASAE 2005). Excretion rates for beef steers, pigs and poultry were based on Van Horn (1998). Horse excretion was assumed to be equivalent to feed intake (i.e., what was consumed was excreted). As with the calculations for feed intake, we assumed that all beef cows, replacement heifers, and calves were permanently on range with insignificant N inputs and outputs.

Manure N from confined animals was either leached to groundwater from the animal facilities, emitted to the atmosphere, or applied on cropland. The leaching of manure N was based on the amount of dairy manure N produced and the fraction leached from facilities reported by van der Schans et al. (2009). One source of data for livestock NH_3 emissions was the 2005 EPA NH_3 emission inventory for California (EPA 2008). A second method to estimate NH_3 emissions was multiplying the manure production estimates described above by animal-specific NH_3 emission factors from EPA (2004). Nitrous oxide produced prior to land application of manure was based on the average for 2002-2007 manure management subsector of the ARB greenhouse gas inventory (CARB 2013). There are few quantitative estimates of N_2 emissions from the housing and production portion of dairies, but they are suggested to be small (Rotz 2004).

The predominant source of manure produced in California is confined dairies. The N content of solid and liquid excreta from dairy cattle is well established. However, the manure that is applied to cropland in solid and liquid form represents a mixture of N from urine and feces diminished in magnitude by volatilization and leaching. There are no data currently that would allow for partitioning the manure applied on and off dairies into solid and liquid form. However, if the nutrient management plans required by the Central Valley Regional Water Quality Control Board become publically available, they will be an invaluable resource for understanding N flows in the dairy-forage system. The manure from pigs, poultry, feedlot beef cattle, horses, and sold dairy manure was also assumed to be applied to cropland.

4.2.7 Household waste production and disposal

Per capita N availability nationally for 2002-2006 was reported as 110 g protein day^{-1} or 6.4 kg N yr^{-1} (USDA 2013d). Statewide per capita N consumption (4.9 kg N yr^{-1}) was estimated based on actual protein consumption reported for various demographic groups and the populations of these groups in the US Census for 2003-2007 following Baker et al. (2001). The consumed N was assumed to end up as sewage N. The difference between available food (228 Gg N) and food consumption (174 Gg N) was assumed to be waste. This 54 Gg N, or 23%, in waste is close to the 27% food waste reported at the retail and consumer level (Kantor 1997). Food waste has several potential fates: down the sink to wastewater, composted and applied to urban land or cropland, and disposal in landfills. While the number of communities collecting household green waste is growing, we assumed that food waste went to landfills.

The tonnage of N discharged as wastewater without advanced treatment in areas with centralized sewage was calculated directly from measurements of wastewater N effluent. A list of facilities classified as wastewater dischargers was obtained from the State Water Resources Control

Board's (SWRCB) publically available database, the California Integrated Water Quality System (CIWQS) (SWRCB 2013b). This list was supplemented based on manually examining the list of dischargers without a category or those in the 'other' category. In addition, effluent discharge, and in many cases effluent N concentrations, was obtained. An empirical relationship was developed between design flow, which is included as part of the SWRCB facility database, and the discharge of NH_3 for all of the facilities in the state that serve more than 100,000 people. Like the SWRCB, we refer to the sum of NH_3 and NH_4^+ in effluent as NH_3. In addition, NH_3 concentration and flow data were available electronically for facilities within the San Francisco Bay Regional Water Quality Board. Because the flow and N tonnage varied by more than 5 orders of magnitude, a log-log relationship was used with a polynomial fit (Figure 4.9). While NH_3 is the only N constituent commonly measured in effluent, in a few cases, organic N and/or NO_3^- were also monitored in facilities with no N treatment and they were <10% of the total N load. A minor amount of the N loading to wastewater treatment is from sink disposals and household chemicals (e.g., Baker et al. 2007), but these are typically insignificant sources of N.

[Figure 4.9]

The level of treatment in the known facilities was determined based on three data sources. First, the orders issued by the Regional Water Quality Control Boards (RWQCBs) were examined for the facilities with large (> 10 mgd) flows. Second, data on treatment level were compiled as part of a brine survey by the US Bureau of Reclamation (USBR) for coastal areas of southern California (USDI 2009). Third, the SWRCB wastewater user survey contains information on the treatment level of sewage agencies (SWRCB 2008). This database was matched based on the agency name in the CIWQS database. In some cases these databases disagreed, often because some facilities have a small water reclamation capability with advanced treatment, but the majority of the flow receives no advanced N removal treatment. In cases where the databases disagreed, the orders were assumed to be correct, followed by the USBR report, followed by the SWRCB wastewater use survey. Facilities with no information were assumed to have no advanced treatment. The average N load removed from these facilities with advanced treatment was ~50% based on dividing the median inorganic N (NH_3+ NO_3^-) concentration of the facilities with treatment by the median NH_3 concentration of facilities without treatment. Dissolved organic N is rarely measured by itself and was assumed to be a minor portion of the flow and unaffected by treatment. The decrease in inorganic N associated with advanced N removal was assumed to be converted to N_2 gas through denitrification.

The fate of discharged wastewater N was based on the permit type and facility location. Facilities with a National Pollutant Discharge Elimination System (NPDES) permit were assumed to discharge to surface water and are regulated by the US EPA and subject to the federal Clean Water Act. Facilities with a NON15 Waste Discharge Requirement Program, regulated by the SWRCB, were assumed to discharge to land. If a facility had both permit types, the discharge was assumed to go to surface water. For facilities with NPDES permits, the surface water body receiving the effluent is listed as part of the permit. In many cases, the receiving water body was the Pacific Ocean. In addition to facilities discharging directly to the ocean, facilities that discharged to San Francisco Bay, San Pablo Bay, Carquinez Strait, or Suisun Bay (as well as Sacramento and Stockton which discharge downstream of the river gauging stations on the Sacramento and San Joaquin Rivers) were also included in calculations of wastewater discharge to the ocean. In some cases land applied effluent is applied to fields growing crops, while in others applied to the surface of recharge basins. However, we assumed that all wastewater N discharged to land would flow completely to groundwater with no gaseous outputs or plant uptake after application. To calculate the N load in rivers associated with sewage discharge, a point vector layer of the georeferenced facility addresses was created and joined with the polygon layer of major (> 1000 km^2) watersheds in the state based on the USGS Hydrologic Units in ArcGIS.

In addition to dissolved forms of N in effluent, wastewater treatment also results in the production of waste biosolids and gaseous forms of N. The two most common uses for the treated solids, or biosolids, are application as an organic amendment to soils, often in degraded areas, or use as an alternative daily cover in landfills. We assumed that all of the biosolids were used on urban land equally split between land application and landfills. The tonnage and fate of biosolids in the state were estimated by the California Association of Sanitation Agencies (CASA). The biosolids N content was assumed to be 3% (Tchobanoglous et al. 2002).

A small fraction of the wastewater N is emitted as N_2O during treatment, which is tracked as part of the statewide greenhouse gas inventory by both the California ARB and the US EPA. In addition, N_2 can be produced most commonly in facilities that promote nitrification followed by denitrification during advanced wastewater treatment. Emission as N_2 would be expected during advanced secondary or tertiary treatment (see above for calculations), but we assumed that no N_2 was emitted in the absence of advanced N removal treatment.

Approximately 10.4% of households in California were not on centralized sewage systems in the 1990 US Census (USDC 1992) and the percentage with on-site waste treatment (i.e., septic systems) was essentially unchanged in 1999 (TCW Economics 2008). Based on Lauver and Baker (2000) we assumed that the N removal efficiency was 9%, which is already accounted for in the flow of biosolids from wastewater treatment plants. We assumed that the other 91% of the N from septic systems leached to groundwater.

Households produce other forms of N-containing waste besides sewage. Food waste was described earlier in this section, but a fraction of household and yard waste is disposed of in landfills. Surveys of the materials transported to landfills are conducted periodically by the California Department of Resources Recycling and Recovery (Cal Recycle). Landfill N disposal was calculated based on the tonnage of organic materials and their N content (Table 4.10).

Household pet waste was calculated based on the average body mass of dogs (20 kg) and cats (3.6 kg) from Baker et al. (2001) and feed intake requirements based on body mass (NRC 2006) with the assumption that all feed intake was excreted. Populations of dogs and cats for 2006 were from AVMA (2006). We follow the approach of Baker et al. (2001) by assuming that 100% of dog waste is added to urban soils as well as 50% of cat waste. Ammonia emissions from dog (24%) and cat (12%) waste were from Sutton et al. (2000).

4.2.8 Gaseous emissions

Gas emissions were tracked by individual gas (NO_x, N_2O, N_2, NH_3) for all sources. Fossil fuel combustion (section 4.2.1), upwind sources (section 4.2.2), manure (section 4.2.6), wastewater (section 4.2.7), and surface waters (section 4.2.9) all emit one or all of these gases, but are described elsewhere. This section provides the methods for gaseous emissions from soils and forest wildfires.

Total N volatilization during natural land fires was estimated as the product of average annual acreage burned (H Safford, personal communication) and an average areal N emission rate of 100 kg N ha^{-1} during fires (Johnson et al. 1998). The emission of NO_x and NH_3 from fires was based on the 2005 EPA National Emission Inventory (EPA 2008) while N_2O emissions were determined to be an insignificant flow based on the ARB greenhouse gas inventory. The balance of the volatilized N was assumed to be N_2.

Ammonia emissions for natural land soils were estimated from the biome-specific rates modeled by Potter et al. (2003) for California and extrapolated to the entire state based on the land cover map. Statewide emissions of NO and N_2O from soils on natural land were scaled up with the land cover map using the average of published sources reporting typical biome-specific rates (Table 4.5).

For cropland, unlike the natural land biomes, we also compiled published estimates of gaseous emissions in California. The only source of field NO emissions in California was the average daily flux of all crops reported in Matson et al. (1997). For N_2O, the median rate was calculated across all crops and management practices for N_2O emissions for California published in the last decade (Supplementary

4.1). A second unique approach for estimating N_2O emissions from cropland combined the estimate based on an emission factor for fertilizer combined with background emissions unrelated to fertilizer use. We assumed a direct emissions factor of 1% for both synthetic fertilizer and manure applied to cultivated cropland based on the ARB methodology in the greenhouse gas inventory. However, we also include a background soil emission rate of 1 kg N ha^{-1} yr^{-1} (Stehfest and Bouwman 2006) in order to estimate total N_2O emissions and not just anthropogenic emissions. This background rate is higher than most natural ecosystems, but there are no current estimates of N_2O emissions in California cropland soils that don't receive fertilizer. For both cropland and natural land, N_2 emissions were based on the mean N_2:N_2O ratios reported for natural land (1.03) and cropland (1.66) (Schlesinger 2009). Cropland NH_3 emissions for synthetic fertilizer were based on the direct emissions factor reported in Krauter et al. (2006). On average, across the range of fertilizer types and crops with varying agronomic practices that were studied, 3.2 % of applied synthetic fertilizer was volatilized as NH_3, but emissions ranged from 0.1 to 6.5% of applied fertilizer. Based on the crop mix in California, Krauter et al. (2006) suggested that the actual emission factor was only 2.4%. While the emission factor for urea can be significantly higher, most other fertilizers are reported to have an emission factor of less than 5% (Battye et al. 2003). Using the values in Battye et al. (2003) and the reported sales of fertilizer in California during the study period, the emissions factor ranges from 4 to 5%. Ammonia emissions associated with manure application on cropland were based on the reported values for each class of livestock in EPA (2004), ranging from 3% for beef cattle to 15% for poultry.

For urban land, gaseous emissions were assumed to occur only from turfgrass soils related to fertilization. Gaseous emissions were based on data compiled in Petrovic (1990) on the direct emissions of fertilizer N. The median fraction of fertilizer that volatilized as NH_3 or was denitrified in turfgrass areas was calculated for all the reported data. Total emissions were calculated based on the total synthetic N fertilizer use in urban areas.

4.2.9 Surface water loadings and withdrawals

Only 55% of California's land area drains to the ocean. This area does not include the Tulare Basin, which is now essentially a closed basin because of water management. The only point source of N to surface waters was the discharge of wastewater effluent as described in Section 4.2.7. We did not include any discharge of food processors to surface water. These facilities are regulated Regional Water Quality Control Boards either in either the stormwater program or in the wastewater program. To get a sense of the potential for discharge to surface water from food processors, we calculated total N discharge for the 162 facilities in the Central Valley included by HydroGeoPhysics Inc. as part of the Hilmar Supplemental Environmental Project (HydroGeoPhysics 2007). While many facilities do not have monitoring data, the sum of the loading from those that do was ~ 2 Gg N yr^{-1}. Because of the lack of complete data for these discharges, we do not include them in the calculations. We estimate atmospheric N deposition on surface water bodies by summing the modeled CMAQ deposition (described in Section 4.2.2) for all of the surface water pixels in the land use map.

Total loading to surface water from non-point sources was calculated based on the export coefficients for cropland (EC_C= 11.9 kg N ha^{-1} yr^{-1}), natural land (EC_N = 2.4 kg N ha^{-1} yr^{-1}), and urban land (EC_U = 9.3 kg N ha^{-1} yr^{-1}) in Wickham et al. (2008). To check if these values were reasonable for California, we calculated export coefficients for 25 of the subwatersheds of the San Joaquin and Sacramento Rivers in the Central Valley measured by Kratzer et al. (2011) and the area of cropland, urban land, and natural land from our land use map. We excluded two drainages as outliers (Colusa Basin Drain and Sacramento Slough). We used the Solver function in Excel to calculate the best fit EC_C, EC_U, EC_N for the Central Valley. We solved for the export coefficients by minimizing the sum of the squared difference between the measured and predicted yields with the predicted yield calculated as

EC_C* % Cropland + EC_U* % Urban Land + EC_N * % Natural Land. Similar to Wickham et al. (2008) we estimated EC_C= 14.2 kg N ha^{-1} yr^{-1}, EC_N = 1.6 kg N ha^{-1} yr^{-1}, and EC_U = 7.0 kg N ha^{-1} yr^{-1}.

The N loading to the ocean was estimated in two distinct ways. First, for the major watersheds (> 1000 km^2) where measured N discharge has been reported, we used the measured values from Sobota et al. (2009), Schaefer et al. (2009), and Kratzer et al. (2011). In watersheds where measurements have not been made, we used adjusted estimates from the export coefficients. The export coefficients provide a means to predict N loading to surface water, but not necessarily the N discharge to the ocean because of gaseous emissions and sedimentation in reservoirs. We calculated the log-log relationship between the measured values and predicted values for the 8 watersheds with measured data. We used the regression of this relationship log [(Measured N) = 0.5685 * log (Predicted N) + 1.2991 (R^2=0.71)] for these ungauged watersheds to adjust the predicted N discharge from the export coefficients to predict the actual discharge of N. We report the values predicted by the export coefficients, the adjusted values predicted by the export coefficients and the measured values for the watersheds in the state (Table 4.15). Nitrogen loads for the urbanized areas in the San Francisco Bay watershed and along the southern coast from Santa Barbara to the Mexican border were estimated in Davis et al. (2004) and Ackerman and Schiff (2003), respectively. However, in both cases the estimates are for stormwater inputs of inorganic N only, so they likely underestimate the total N load.

Water withdrawals for irrigation were considered an output from the surface water subsystem. The volume of water for irrigation was based on Hutson et al. (2004), which reported 26*10^{12} L yr^{-1} withdrawn for California in 2000. A fraction of this water (7.8*10^{12} L yr^{-1}) was pumped from the Delta on average from 2000-2004. The water pumped from the Delta was not included in the surface water mass balance as it was actually considered an N import to the state because of the location of USGS river gauges. That is, for the purposes of our N budget, the Delta pumps are located outside of the study area, so that the dissolved N in this water is considered an N import to the state. The water quality at the

Harvey O. Banks Pumping Plant (Station number KA000331), where water is pumped from the Delta, was historically monitored monthly (DWR 2013). The total N concentration for 2002-2007 was on average ~1 mg N L^{-1}, and was split almost evenly between nitrate and dissolved organic N. The N concentration was assumed to be the same for the $18.2*10^{12}$ L yr^{-1} withdrawn from other surface water bodies in California. A smaller volume of surface water was withdrawn for domestic use ($4.6*10^{12}$ L yr^{-1}): we ignored this flow as the majority of this water is used for indoor residential and industrial use which would likely be accounted for in wastewater effluent to surface water or the ocean (Gleick et al. 2003).

Gaseous outputs from surface water were only significant in the form of N_2 and N_2O, predominantly from denitrification. For rivers, gas emissions were estimated based on the areal rates of 2.8 kg N_2O-N ha^{-1} (Beaulieu et al. 2011) and 51 kg N_2-N ha^{-1} yr^{-1} (Mulholland et al. 2009). The gaseous emissions from lakes and reservoirs were also based on these sources given the similarity in denitrification rates in rivers and lakes reported in Seitzinger et al. (2006). The acreage of rivers, lakes and reservoirs was based on comparing the USGS National Hydrography Dataset to the CAML land use map. Pixels in the land use map not identified as lakes or reservoirs in the USGS dataset were categorized as rivers.

The burial of N in lake and reservoir sediments was considered surface water storage and was estimated by difference for the purposes of the mass balance. However there are two potential independent approaches to calculating N retained for comparison. The first provides an estimate for just reservoirs, and the second, for both lakes and reservoirs. First, the total volume of sediment in all California reservoirs was estimated by Minear and Kondolf (2009). Based on the reservoir age, an annual sedimentation rate was calculated. The annual rate of N sedimentation was calculated by assuming a bulk density of 1 g cm^{-3} (Verstraeten et al. 2001), a carbon content of these sediments of 1.9% (Stallard 1998) and a C:N ratio of 10 (Vanni et al. 2011). Second, Harrison et al. (2009) estimated that a global average of 306 kg N ha^{-1} yr^{-1} was retained in reservoirs. These authors also estimated that lakes retain

~30 kg N ha^{-1} yr^{-1}. The total annual N retention was calculated from the area of reservoirs (180,000 ha) and lakes (350,000 ha) in the state by partitioning the National Hydrography dataset. The difference between retention and denitrification as calculated above provides and estimate of burial in sediments.

4.2.10 Groundwater loading and withdrawals

Groundwater inputs included leaching from septic tanks and wastewater treatment discharge (Section 4.2.7), cropland soils, and natural land soils. For cropland, leaching to groundwater was calculated in two ways. First, the average NO_3^- concentrations in water leached below the rooting zone in crop soils was calculated from a compilation of California literature (See Chapter 7 for details on data). The N concentration (38 mg N/L) was multiplied by the total volume of recharge in agricultural regions, where the majority of groundwater recharge occurs. All of the recharge was assumed to occur in the Central Valley ($9.6*10^{12}$ L; Faunt et al. 2009), Salinas Valley ($2.3*10^{11}$ L; Montgomery Watson 1997) and Imperial Valley ($3.0*10^{11}$ L; Montgomery Watson 1995) groundwater basins. Second, the median fraction of applied fertilizer that leached was calculated from a compilation of California literature (see Chapter 7 for further details on data). This fraction (38%) was multiplied by the sum of statewide fertilizer use in cropland (synthetic fertilizer + manure). In natural land, groundwater inputs were assumed only to occur in areas lacking drainage to the ocean. Leaching inputs in the driest portions of the state which occur in closed basins have been estimated based on the N stock in the subsurface that has accumulated over millennia. The annual N flow was calculate as the product of a leaching rate of 0.6 kg N ha^{-1} yr^{-1} (Walvoord et al. 2003) and an area of 18 million ha. Leaching from turfgrass was estimated as the median of the fraction of applied fertilizer that leached summarized by Petrovic et al. (1990).

Groundwater outputs were only from water pumped from the ground. Nitrogen removal from groundwater was calculated as the product of groundwater volume withdrawn and average groundwater N concentration. The volume of groundwater withdrawal was reported in both Hutson et al. (2004) and DWR (2003). However, we used the former for the calculations because it partitioned use into municipal vs. irrigation and also provided estimates of surface water withdrawals. Nitrogen concentrations were calculated as the average of all wells available in the USGS Groundwater Ambient Monitoring and Assessment and EPA STORET databases for the years 2002-2007 available on the Geotracker website (SWRCB 2013a).

We calculated groundwater denitrification in three ways. (1) We estimated N inputs to groundwater since 1940 and used literature values for the half life of N to estimate denitrification losses. Green et al. (2008b) report a half life of 31 years at one site near Merced. These authors found limited evidence for denitrification in aquifers below cropland soils in California, with 50% N removal in groundwater after 31 years. This represents a rate of 2.3% yr^{-1}. A second estimate of the half life can be made from the $^{3}H/He$ and N_2 excess reported in Landon et al. (2011). The data from this study, which covered a much larger area of the Central Valley, would result in a half life of 80 years or a loss rate of only 0.9% yr^{-1} (C. Green, personal communication). Because of the more regional nature of this study, we chose the value calculated from Landon et al. (2011). We assumed that groundwater recharge of N has increased linearly since 1940 with only the 10 Gg N of natural inputs occurring prior to 1940. We chose this starting date based on the trend in fertilizer use (sales of synthetic fertilizer plus dairy manure since 1980). Manure production was assumed to start in 1980 because dairies had largely transitioned to confined feeding by then. Manure production was calculated based on milk production reported by USDA (2013a) with an assumed efficiency of 25%. Manure applied as fertilizer was calculated assuming 38% of manure production was volatilized. The x-intercept of the fertilizer-time relationship was 1940. Finally, groundwater N extraction was assumed to be zero in 1940 and increased linearly to 2005. Starting in 1940 10 Gg N was leached, 0 Gg N was extracted, 0.23 Gg N was denitrified, and 9.67 Gg N was stored. This process was assumed to continue with 0.9% of the annual input plus the groundwater storage denitrified annually. (2) We used the product of a concentration-based denitrification rate and the total volume of groundwater. Liao et al. (2012) reported denitrification in Merced County to be 0.2 mg N L^{-1} yr^{-1}. Based on the data in Landon et al. (2011), a more regional value of groundwater denitrification was estimated to be 0.04 mg N L^{-1} yr^{-1}. The volume of recharge water contaminated with N was assumed to be constant between 1940 and 2005 and was estimated the same way as for determining the load of N leaching from soils. (3) We used the average proportion of groundwater N inputs that were denitrified as reported for Europe (46%; Leip et al. 2011) and globally (40%; Seitzinger et al. 2006). The groundwater denitrification was the average of the three independent estimates.

We assumed that the net N exchange between groundwater and surface water was essentially zero. For the Central Valley aquifer, if anything, the flow of water ($0.2*10^{12}$ L yr^{-1}) moves from surface water to groundwater (Faunt et al. 2009). At a N concentration of 1 mg N L^{-1} as measured in the Delta representing the water in the Sacramento and San Joaquin rivers, this represents an insignificant flow of N. Nitrogen storage was calculated as the difference between inputs and withdrawals.

4.2.11 Storage

Storage in cropland and natural land subsystems was calculated by difference. That is, storage was equal to the difference of N flows in and out. This storage could occur in either soils or perennial vegetation. Storage in urban systems has three components. First, landfills are considered storage and the methods of calculating N flows to landfill are described in Section 4.2.7. Second, land (soils + vegetation) storage was calculated as the difference between inputs of fertilizer, atmospheric deposition, and dog waste and the outputs in the form of soil gaseous emissions and surface runoff. Finally, other storage was calculated as the difference between synthetic chemical and wood N inputs and landfill N storage.

The storage terms calculated for the surface water and groundwater subsystems are described in Sections 4.2.9 and 4.2.10, respectively.

4.3 Synthesis

Calculating nitrogen mass balances has been occurring for decades. The first global N budget was published by Delwiche in 1970 with the first watershed N budget published by Bormann et al. (1977) for Hubbard Brook. The general approach has largely remained the same ever since, but more types of fluxes (especially in urban areas) have been incorporated. The published N mass balances vary in their spatial extent (from watersheds < 100 km^2 to the entire planet) and the types of boundaries (political vs. watershed, just agriculture vs. the whole landscape).

One common approach developed in the 1990s is termed Net Anthropogenic Nitrogen Inputs or NANI (Jordan and Weller 1996; Howarth et al. 1996). The NANI approach estimates imports of new reactive N from atmospheric deposition (total or just oxidized which is more likely to be from fossil fuel combustion instead of recycled N), net food and feed imports, crop biological N fixation, and synthetic N fertilizer. Typically the goal is to calculate the fraction of N imports that are accounted for in surface water exports. One advantage of this approach is that the imports are standardized so it is easy to compare across watersheds. A recent synthesis by Howarth et al. (2012) suggests that on average one quarter of the N imports were exported from watersheds globally. However, the watersheds included are largely temperate with moderate precipitation. The fraction of surface water exports has been suggested to be much lower in arid areas, but relatively few arid watersheds have been examined (Caraco and Cole 2001). Further, this approach neglects several potentially important flows: fiber (particularly wood products) and synthetic chemicals like plastics. Including these would not affect the magnitude of surface water exports, but they would decrease the fraction of surface water exports.

In addition to the NANI method, several other approaches have been utilized (Table 4.20). These range from studies that focus solely on agricultural regions, intermediate studies that include more imports and exports than NANI, and comprehensive studies that include all significant N flows. The spatial extent of these studies can be watersheds or political boundaries ranging from regions (e.g., the

San Joaquin Valley) to states (e.g., Wisconsin) to countries (e.g., the United States) to continents and Earth (Galloway et al. 2004). The comprehensive mass balances have largely been attempted in the last decades. Because these comprehensive studies include measurements of all N flows, they can also be standardized by area, population, or as fractions of the total flow.

[Table 4.20]

We standardized five of the published comprehensive mass balances: Netherlands and Europe (Leip et al. 2011), the Guangzhou region of China (Gu et al. 2009), the Phoenix region (Baker et al. 2001), and South Korea (Kim et al. 2008) and compared them to the California N mass balance. These five area differ in the size, climate, and land cover, but the comparison among them can provide useful insight into N dynamics. In some cases this required adjustments to the boundaries of the study, but the flows included were the same to compare across the different areas. For example, in Europe the coastal regions were included in the study area whereas the boundary in California was the coastline. In a few cases, flows were not available. For example in both China and South Korea, there was no estimate of N_2O distinct from total denitrification and in South Korea there was no estimate of synthetic N chemicals. In some cases, storage or N accumulation, was not explicitly calculated, but we estimated it by difference between imports and exports. Based on the data available in these papers, the population, and the area of the study region, we calculated N imports and exports per unit area and per capita. We also calculated N flows as a percentage of the total.

When compared to other regions of various sizes, California has a relatively low N use on both a per capita, but especially on a per hectare basis (Figure 4.10, 4.11). The United States has by far the largest per capita imports of N (118 kg N person^{-1} year^{-1}). Similarly, the Netherlands has by far the largest imports of N on an areal basis (334 kg N ha^{-1} yr^{-1}).

[Figure 4.10; Figure 4.11]

Synthetic fertilizer is the largest N import in all studies, with the exception of the Netherlands where there was slightly more N feed imported. With the exception of the United States as a whole, all studies reported feed import, often as a large fraction of the total N imports (Figure 4.12). Similarly, only the United States as a whole, has a medium (22%) fraction of imports from crop N fixation with most studies reporting less than 10%. Food import is less common and typically only a small fraction of new imports. The N import from fossil fuel combustion ranges from 10% in the Netherlands to 38% in Phoenix.

[Figure 4.12]

Denitrification or N_2 production was the largest export of N except in California and South Korea. In both these studies export of NO_x + NH_3 was larger. In South Korea, surface water exports were the largest export flow. Surface water export ranged from 2.2% in California to 29% in South Korea. Low surface water export (2.7%) was also observed in Phoenix corroborating the phenomenon of low fractional export in arid areas. While most studies reported less than 20% of export in surface water, these values cannot be directly compared to the NANI approach because the imports are more inclusive. Nitrogen accumulation was reported or inferred from all the studies. The highest fraction (37%) occurred in California with other studies ranging from 14% in the United States to 30% in Europe.

In many ways the N flows in California are similar to other parts of the world. The two ways that it stands out are the low surface water exports and the high N storage, primarily in groundwater and urban land.

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Box 4.1. Language used to categorize different N flows

Import	Flows of nitrogen entering the state
Export	Flows of nitrogen leaving the state
Input	Flows of nitrogen entering a subsystem from another subsystem within the state
Output	Flows of nitrogen leaving a subsystem to another subsystem within the state
Storage	Nitrogen that remains (i.e., stored) within a subsystem

Box 4.2. Language for describing absolute and relative N flows

We adopted a specific vocabulary for categorizing the absolute and relative magnitude of N flows in the mass balance chapter. A gigagram (Gg) is equivalent to 1 million kilograms.

Absolute flow ($Gg\ N\ yr^{-1}$)	**Flow category**	**Relative flow (%)**	**Fraction category**
< 1	Insignificant	1 to 10	Small
1 to 25	Minor	10 to 25	Medium
25 to 100	Moderate	25 to 50	Large
> 100	Major	> 50	Predominant

Box 4.3. The problem of fertilizer accounting

Nitrogen (N) fertilizer use is virtually certain to be the largest single flow of N in the state. In general, fertilizer sales data are assumed to be the best proxy for fertilizer use. In California, fertilizer sales are tracked by the California Department of Food and Agriculture (CDFA). The values are calculated twice per year and compiled and published in semi-annual Tonnage Reports (CDFA 2013). The data is reported by licensed fertilizer dealers to track sales of fertilizer to unlicensed buyers. This system is designed to prevent double counting. Currently the licensed dealers fill out a “Tonnage report for commercial fertilizers” form for every county where they have sales indicating the tonnage of all the types of fertilizer. There are seventeen listed grades of N fertilizer (e.g., anhydrous ammonia (NH_3), ammonium nitrate (NH_4NO_3), urea ($CO(NH_2)_2$)) along with an “other” category without a grade listed. A similar list is used for phosphorus and potassium fertilizers as well as other agricultural minerals. The tonnage of each fertilizing material sold in each county by each licensed dealer for farm use is thus recorded. Farm use is defined as “Commercial Use, Farm, Golf Courses, Professional Landscaping, Not Home and Garden.” Non-farm use sales of “Registered Specialty Fertilizer/ Packaged Ag Minerals for Home and Garden Use” is recorded by the ton as well, but only subdivided into tons of dry bulk, dry packaged, liquid bulk, and liquid packaged with no grade associated with the sales. The tonnage reports are compiled by a third party that enters the data manually to convert it into a digital format. The raw data is then processed by Joe Slater, a professor at the University of Missouri – Columbia, into the final tonnage reports.

It is unclear where the breakdown in the reporting system lies. A few possibilities exist to explain the large jump in 2002. First, it is possible that there was a change in methodology at this time. We have been unable to get confirmation from CDFA regarding any changes in the reporting form or data processing. Secondly, it is possible that the conversion of tons of fertilizing material into tons of nutrients is a large source of error. As this process requires the grade of fertilizer (i.e., the nutrient content) be known. For example, the grade of anhydrous ammonia is 82-0-0 indicating 82% N, 0% P, and 0% K; however, the form does not require a breakdown of the nutrient content for “other” materials. For example in 2002, “other” farm-use fertilizing materials were reported at 395,115 tons. If the N grade were 10, the tonnage would be 39,115 tons whereas with an N grade of 30, this would represent more than 100,000 tons. At this point, it is not clear both what grade was assumed by CDFA for this calculation, but also what grade the materials actually were. Further, while the 2002 “other” tonnage was almost double the 2001 value, by 2003 the amount was back to within 10% of the 2001 value, suggesting that the grade of “other” fertilizing materials is not the major source of error. Third, it is possible that double reporting could be happening. It is unclear why the sales of anhydrous ammonia increased from a few thousand tons before 2002 to over 100,000 tons starting in 2002. The Calamco ammonia depot in Stockton, where ships bring in synthesized ammonia from around the world, is located in San Joaquin County. This facility sells anhydrous ammonia, aqua ammonia (solution of ammonia in water $(NH_4^+)(OH^-)$), and AN-20 (20% ammonium nitrate solution). This facility also supplies J.R. Simplot with ammonia for their N fertilizer production plant. Thus, it is possible that the anhydrous ammonia is being reported sold as well as the other products created from the anhydrous ammonia. Finally, the reporting system for non-farm fertilizer is problematic for estimating total N tonnage and partitioning fertilizer into farm use and non-farm use. This is not likely related to the high sales since 2002 as virtually no fertilizer is reported as non-farm use. One problem with the non-farm reporting is that there is no grade reported for any materials. One growing source of revenue is potting mixes amended with nutrients. While the tonnage of these materials is required to be reported as they are considered fertilizers, they tend to have a N grade of less than 2. Thus, it is unclear once again how the conversion from tonnage of materials to tonnage of nutrients is calculated.

Box 4.4. The Haber-Bosch process and cropland nitrogen

Synthetic fertilizer, which is almost exclusively produced by the Haber-Bosch process, is the largest source of N to cropland. However, Haber-Bosch derived N is not limited to the annual application of synthetic fertilizer. The N in applied manure also originates in part from feed that was grown with synthetic fertilizer and in part from biological N fixation by alfalfa. Of the 537 Gg N yr^{-1} needed to feed livestock, 170 Gg N yr^{-1} of the feed was in the form of alfalfa, Thus, alfalfa contributed 30% of the N supply in livestock feed, and presumably an equivalent fraction of manure N. The remaining manure (184 Gg N yr^{-1}) presumably originates as Haber-Bosch N. A large fraction of the biosolids applied to cropland also comes from Haber-Bosch N. The N applied in irrigation water could originate from any land use, but synthetic fertilizer application to cropland is likely the dominant source. Atmospheric deposition is a mixture of fossil fuel combustion with some contribution of reduced N from livestock manure NH_3 volatilization. If we assume that irrigation water was derived from synthetic N while atmospheric deposition was fossil fuel combustion, a total of 69% of N entering the cropland subsystem (Figure 4.4) was from synthetic N fixation. At the statewide level, there is also the import of grain crops, largely corn, to California from the Midwest that is largely Haber-Bosch N as well.

Box 4.5. Denitrification in groundwater

Denitrification is the process that converts nitrate (NO_3^-) to inert nitrogen (N_2) gas through a series of chemical reactions. It is typically a biological process in which micro-organisms, such as bacteria, respire NO_3^- instead of oxygen to meet their metabolic needs. Denitrification can occur when three conditions are met: nitrate is present, oxygen concentrations are low, and a source of electrons (e.g., energy) is available. Denitrifying organisms are ubiquitous in soils and sediments, as well as surface water and groundwater environments; these organisms can also be harnessed to remove nitrate from high nitrogen (N) waters such as in wastewater treatment plants and agricultural runoff. Denitrification is a key transformation in the N cycle as it is the dominant process that converts reactive N back to atmospheric N_2. As such, it reduces risks of excess N on human health and the environment (Moran et al. 2011).

In most environments, there are methods, albeit expensive and requiring specialized equipment, for measuring denitrification rates *in situ*. Part of the difficulty is that the product of denitrification, N_2, comprises almost 80% of the atmosphere. Therefore, it is impossible to detect the small flux of N_2 from surficial environments where atmospheric air is present. Because of these methodological issues, denitrification is often quantified by difference in mass balance studies because of the difficulties in measuring it directly. In groundwater, denitrification is typically detected by chemical signatures and dissolved excess N_2 gas left behind by the process. Analysis of the isotopes of nitrogen and oxygen in groundwater NO_3 can indicate whether denitrification is occurring but may also reflect a signature of the original source (e.g., manure vs. fertilizer) of the NO_3^-. Quantifying groundwater denitrification rates typically involves measuring excess N_2. Because groundwater is isolated from the atmosphere, the N_2 produced by denitrification remains dissolved. This “excess N_2” can be measured and the amount of NO_3 originally dissolved in the water can be determined.

Denitrification occurs in groundwater when nitrate-rich water recharged from the surface reaches portions of the aquifer with low dioxygen (O_2). In addition, either organic carbon leached from the surface or reduced minerals like sulfides need to be present in the sediments or rocks of the aquifer as a source of energy. In some aquifers, conditions are such that denitrification can convert a significant amount of the nitrate to N_2 while in others high O_2 or a limited supply of energy precludes the complete conversion of NO_3. Data on denitrification in groundwater are particularly difficult to obtain and much more research is needed on the subject (see for example Böhlke and Denver 1995; Fogg et al. 1998; Browne and Guldan 2005). It is tentatively agreed by most, that denitrification rates are relatively low in the major groundwater basins in the Central Valley, especially the shallow aquifers. The few studies that have been conducted have found that the aquifers in California do not typically have the combination of conditions that would be conducive for the removal of all NO_3 by denitrification (Moran et al. 2011; Landon et al. 2011; Green et al. 2008, 2010). King et al. (2012) suggest that it is practical and sensible to conclude that most NO_3^- in California aquifers used for irrigation and municipal supplies is unlikely to be denitrified. The most prominent exception, perhaps, are denitrifying conditions found in the vicinity of the major streams and near valley troughs that have accumulated lake and marshy sediments with significant organic matter (Landon et al. 2011; Moran et al. 2011). Additional studies using excess nitrogen/argon (N_2/Ar) ratios, natural N isotopes, and mass balance calculations could further our understanding of the spatial and temporal variability in denitrification in California's groundwater.

Figure 4.1. Significant nitrogen flows in California, 2005. The state of California is represented by the green box. Flows of N into the state (imports) are represented with green arrows. Flows of N from the state (exports) are represented with green arrows. Nitrogen flows among the eight subsystems in the state are shown in blue arrows. These flows represent internal transformations of N that do not show up in the accounting for the statewide mass balance. For example, manure represents an output of the livestock subsystem and an input to cropland, but does not appear in the statewide mass balance. The flows to and from the subsystems are called inputs and outputs respectively. The inputs for a subsystem can be either imports at the statewide level or can be the output from a different subsystem. Likewise, the outputs for a subsystem can either be exports at the statewide level or become the input for a different subsystem. Storage occurs in a subsystem when there are excess inputs compared to outputs. For agricultural production (food, feed, fiber), only the net flow of N is depicted. That is, while some food that is consumed in California is imported from elsewhere, the net flow of food is an output from California. Similarly, the net flow of feed and fiber (wood) is an input to California.

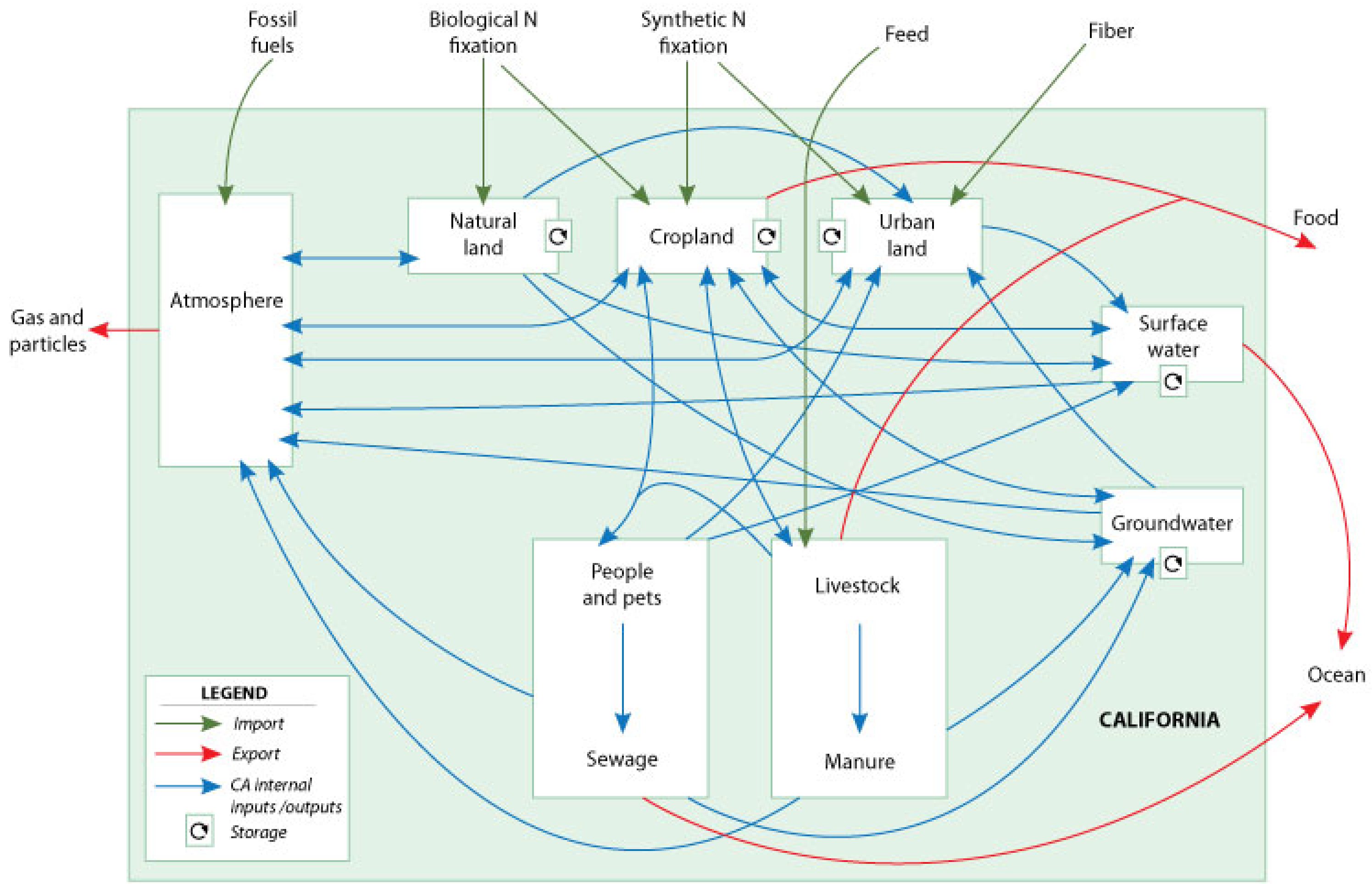

Fossil fuels
Biological N fixation
Synthetic N fixation
Feed
Fiber
Natural land
Cropland
Urban land
Atmosphere
Gas and particles
Food
Surface water
Groundwater
People and pets
Sewage
Livestock
Manure
Ocean
CALIFORNIA
LEGEND
Import
Export
CA internal inputs /outputs
Storage

Figure 4.2. Land cover map of California, 2005. The multiple categories for natural land and cropland were lumped for display purposes.

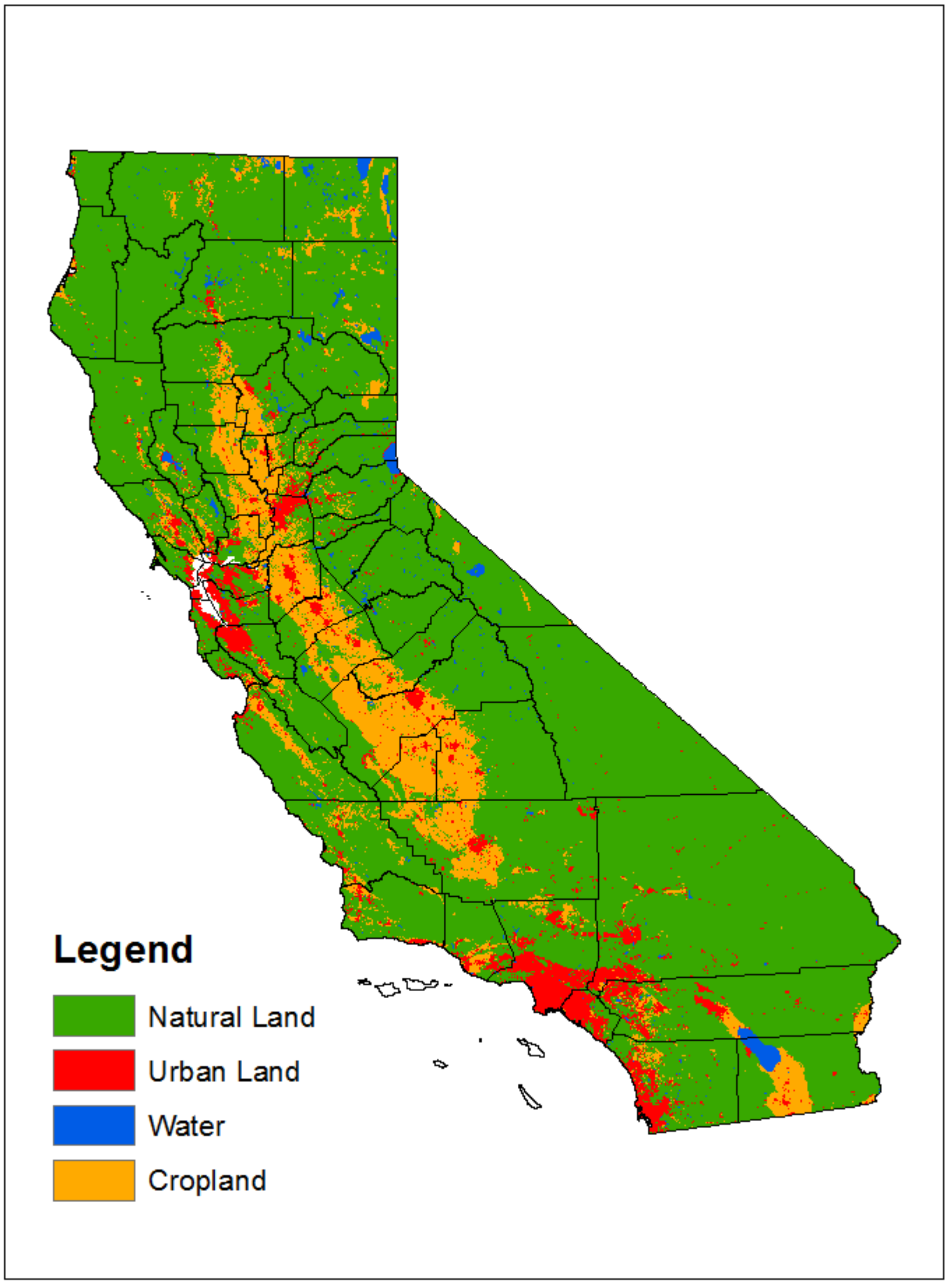


Figure 4.3 Measuring uncertainty in the California nitrogen mass balance. This figure reflects the amount of evidence and level of agreement for the various flows of nitrogen covered in the mass balance. Flows represent inputs and outputs as well as transfers of nitrogen within California. For a more complete catalog of evidence and agreement among data sources, see tables 4.1, 4.2, 4.6, 4.8, 4.9, 4.11, 4.12, 4.14, 4.16, and the supplemental data tables.

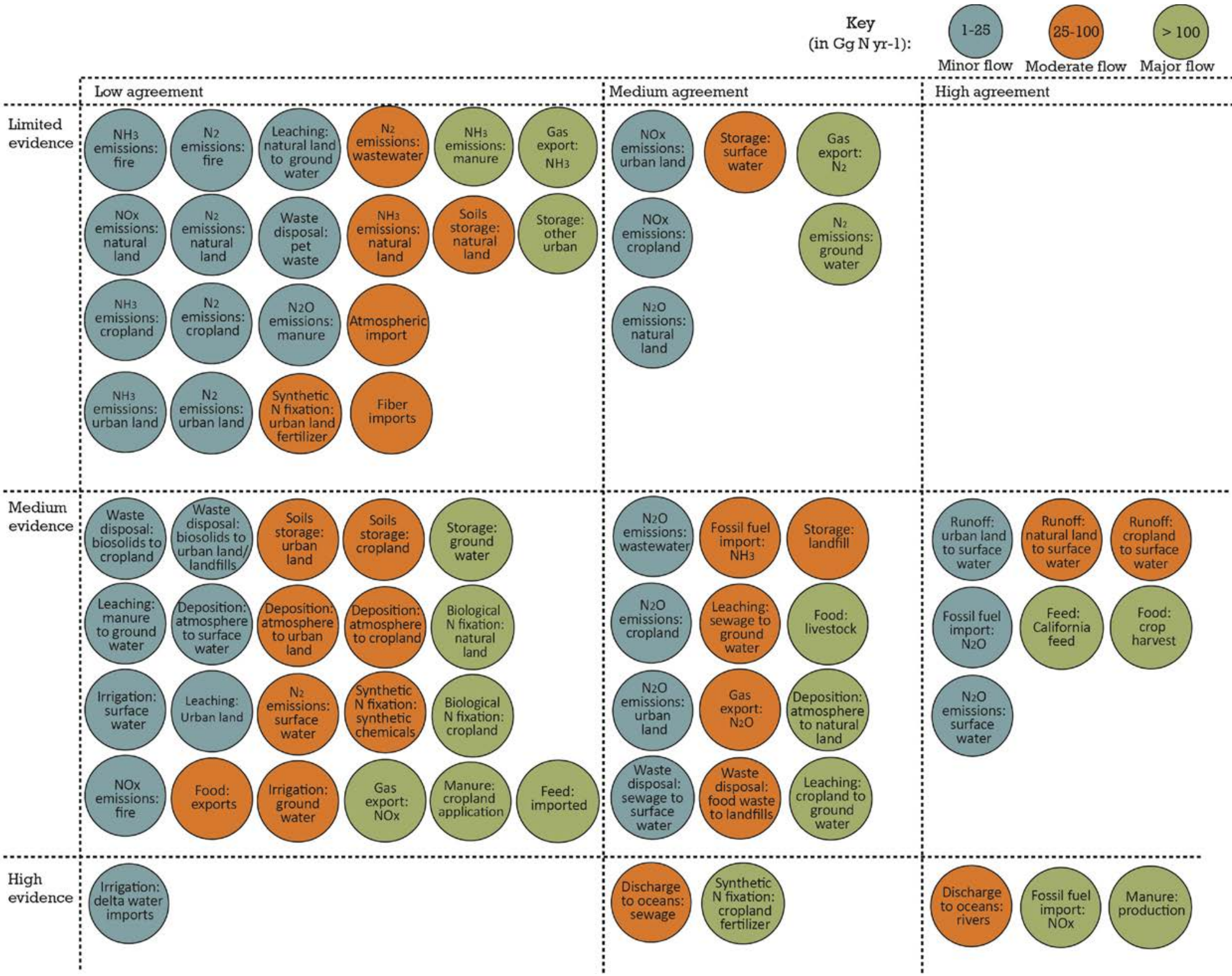

Key
(in Gg N yr-1):
1-25
Minor flow
25-100
Moderate flow
> 100
Major flow
Low agreement
Medium agreement
High agreement
Limited evidence
Medium evidence
High evidence
NH3 emissions: fire
N2 emissions: fire
Leaching: natural land to ground water
N2 emissions: wastewater
NH3 emissions: manure
Gas export: NH3
NOx emissions: natural land
N2 emissions: natural land
Waste disposal: pet waste
NH3 emissions: natural land
Soils storage: natural land
Storage: other urban
NH3 emissions: cropland
N2 emissions: cropland
N2O emissions: manure
Atmospheric import
NH3 emissions: urban land
N2 emissions: urban land
Synthetic N fixation: urban land fertilizer
Fiber imports
NOx emissions: urban land
Storage: surface water
Gas export: N2
NOx emissions: cropland
N2 emissions: ground water
N2O emissions: natural land
Waste disposal: biosolids to cropland
Waste disposal: biosolids to urban land/ landfills
Soils storage: urban land
Soils storage: cropland
Storage: ground water
Leaching: manure to ground water
Deposition: atmosphere to surface water
Deposition: atmosphere to urban land
Deposition: atmosphere to cropland
Biological N fixation: natural land
Irrigation: surface water
Leaching: Urban land
N2 emissions: surface water
Synthetic N fixation: synthetic chemicals
Biological N fixation: cropland
NOx emissions: fire
Food: exports
Irrigation: ground water
Gas export: NOx
Manure: cropland application
Feed: imported
N2O emissions: wastewater
Fossil fuel import: NH3
Storage: landfill
N2O emissions: cropland
Leaching: sewage to ground water
Food: livestock
N2O emissions: urban land
Gas export: N2O
Deposition: atmosphere to natural land
Waste disposal: sewage to surface water
Waste disposal: food waste to landfills
Leaching: cropland to ground water
Runoff: urban land to surface water
Runoff: natural land to surface water
Runoff: cropland to surface water
Fossil fuel import: N2O
Feed: California feed
Food: crop harvest
N2O emissions: surface water
Irrigation: delta water imports
Discharge to oceans: sewage
Synthetic N fixation: cropland fertilizer
Discharge to oceans: rivers
Fossil fuel import: NOx
Manure: production

Figure 4.4a. Statewide nitrogen imports to California in 2005 (1617 Gg N yr^{-1}). Synthetic fixation is the largest single import of N to California contributing 37% of the total. Fossil fuel combustion adds N in the form of NO_x (23%), NH_3 (2%), and N_2O (1%) to the atmosphere. Biological N fixation is an N input in both cropland (12%) and natural land (9%). The net import of agricultural products is a source of N in the form of feed (11%) and fiber (2%). Minor sources of N import are (1) water pumped by the Central Valley Project and State Water Project in Tracy because it occurs in the Delta downstream of the river gauges and (2) import of reactive N gases in the atmosphere from across the Pacific Ocean.

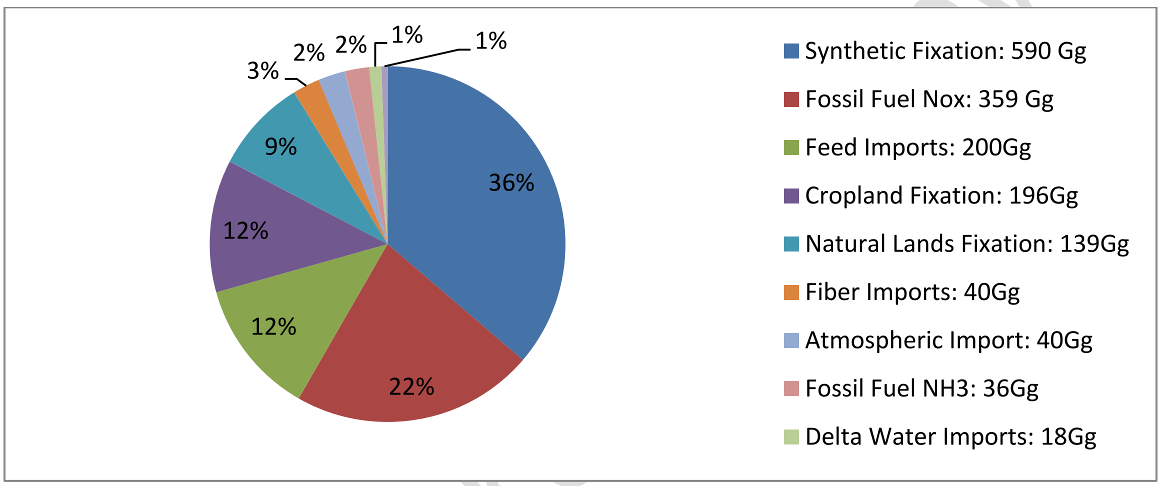


Figure 4.4b. Statewide nitrogen exports, and storage in California in 2005 (1617 Gg N yr^{-1}). The fate of N imports to California is almost divided between exports (56%) and storage (44%). Atmospheric export is the dominant fate with NO_x (17%), NH_3 (13%), N_2O (2%), and N_2 (13%) accounting for almost half of the N imports. Nitrogen is exported to the ocean in much smaller amounts from rivers (2%) and as sewage (5%). The net food balance contributes 5% of the N export. Groundwater (16%) is the single largest fate as storage with the various other forms of storage in soils and urban environments combining to account for 28% of the total N import.

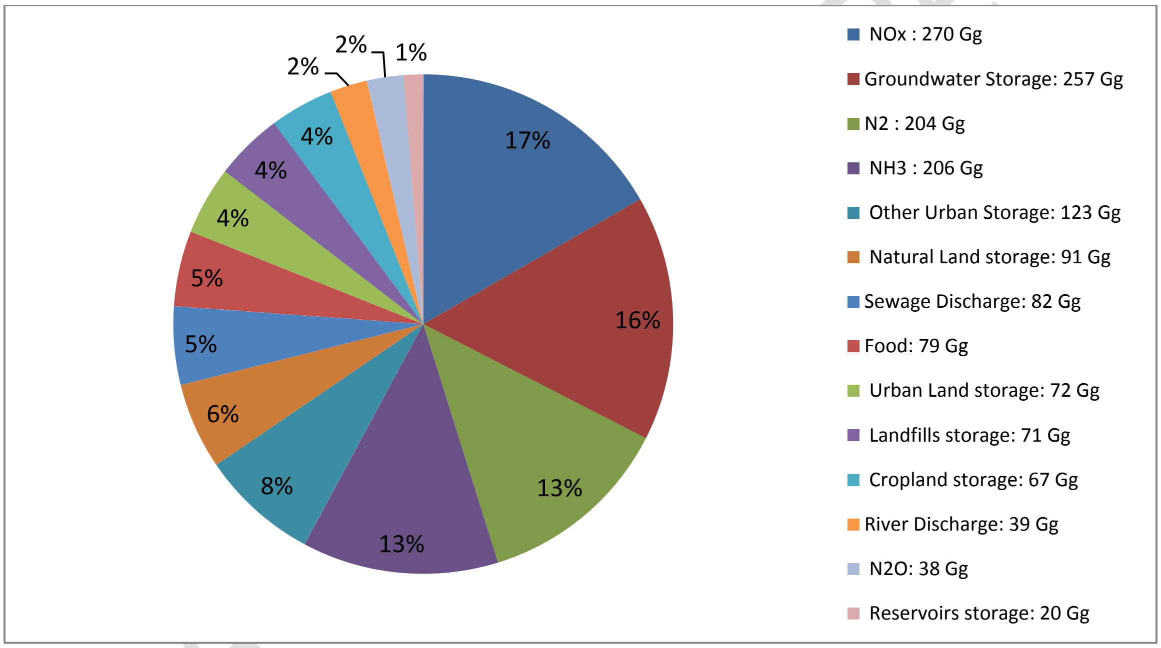
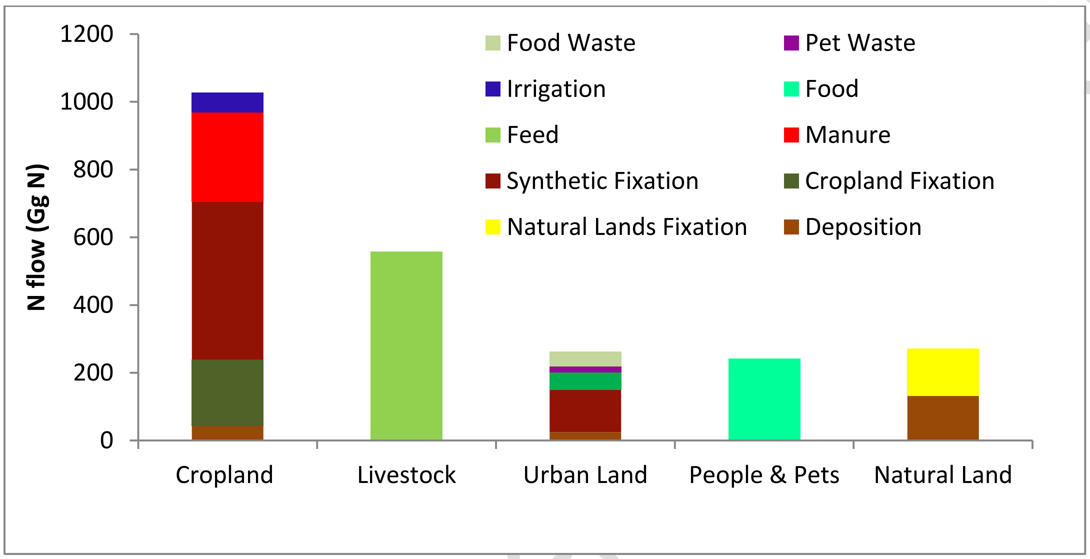


Figure 4.5. Summary of nitrogen imports/inputs (a) and exports/outputs/storage (b) for the three California land subsystems in 2005. The flows to and from the livestock subsystem (i.e. feed) and the people/pets subsystem (i.e., food) are shown for comparative purposes, but these subsystems are calculated independently from the land subsystems.

(a).



(b).

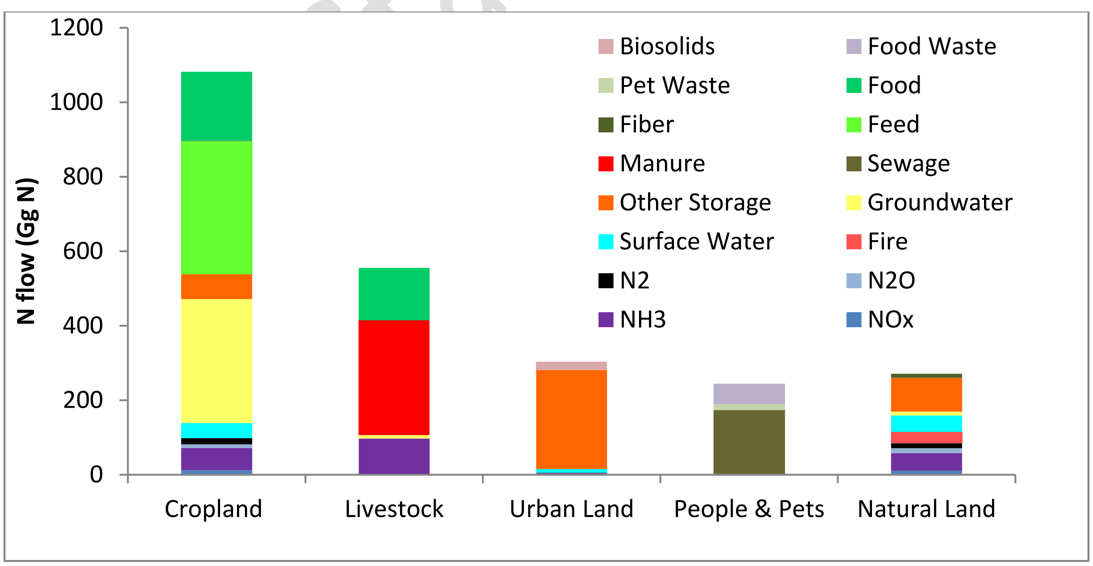


Figure 4.6. Flows of nitrogen in California cropland in 2005. The circled values indicate the absolute magnitude of the flow in Gg N yr^{-1} with arrow thickness specifying the relative magnitude of the flow. Storage terms are indicated with arrows on the circled values.

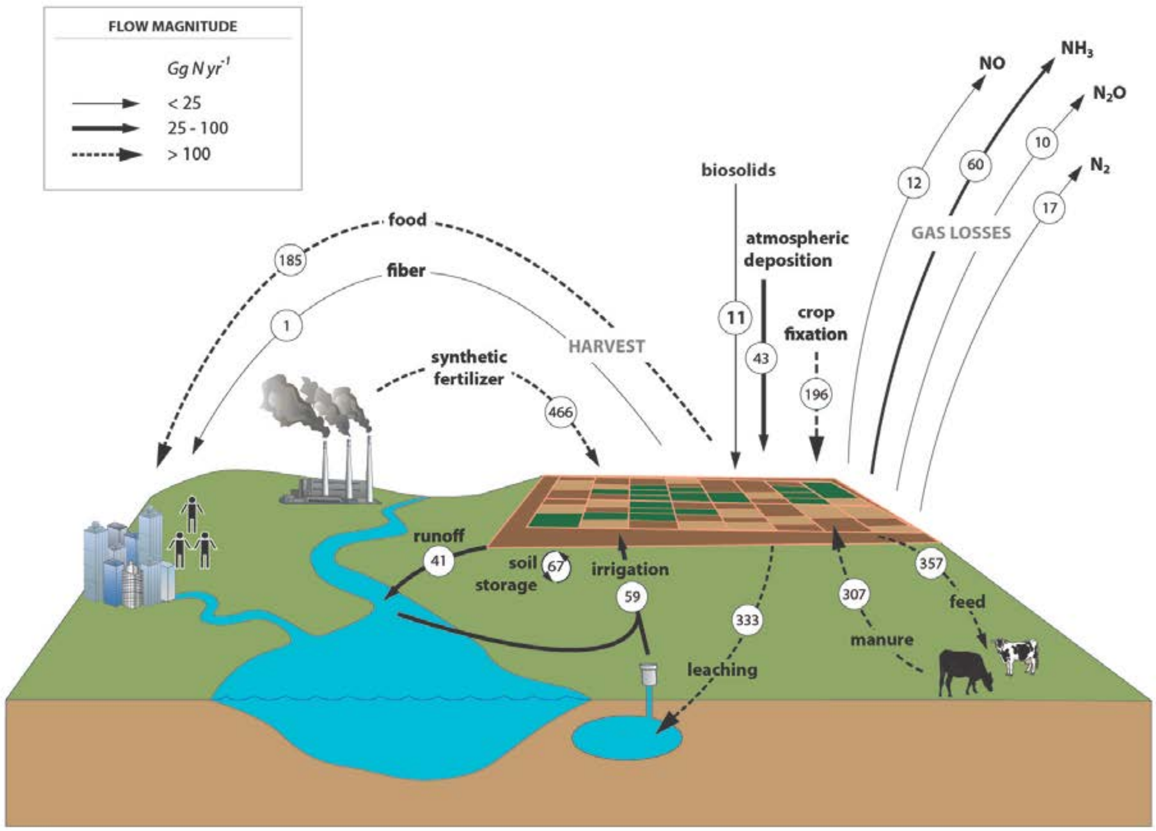


Figure 4.7. Flows of nitrogen in California urban land in 2005. The circled values indicate the absolute magnitude of the flow in Gg N yr^{-1} with arrow thickness specifying the relative magnitude of the flow. Storage terms are indicated with arrows on the circled values.

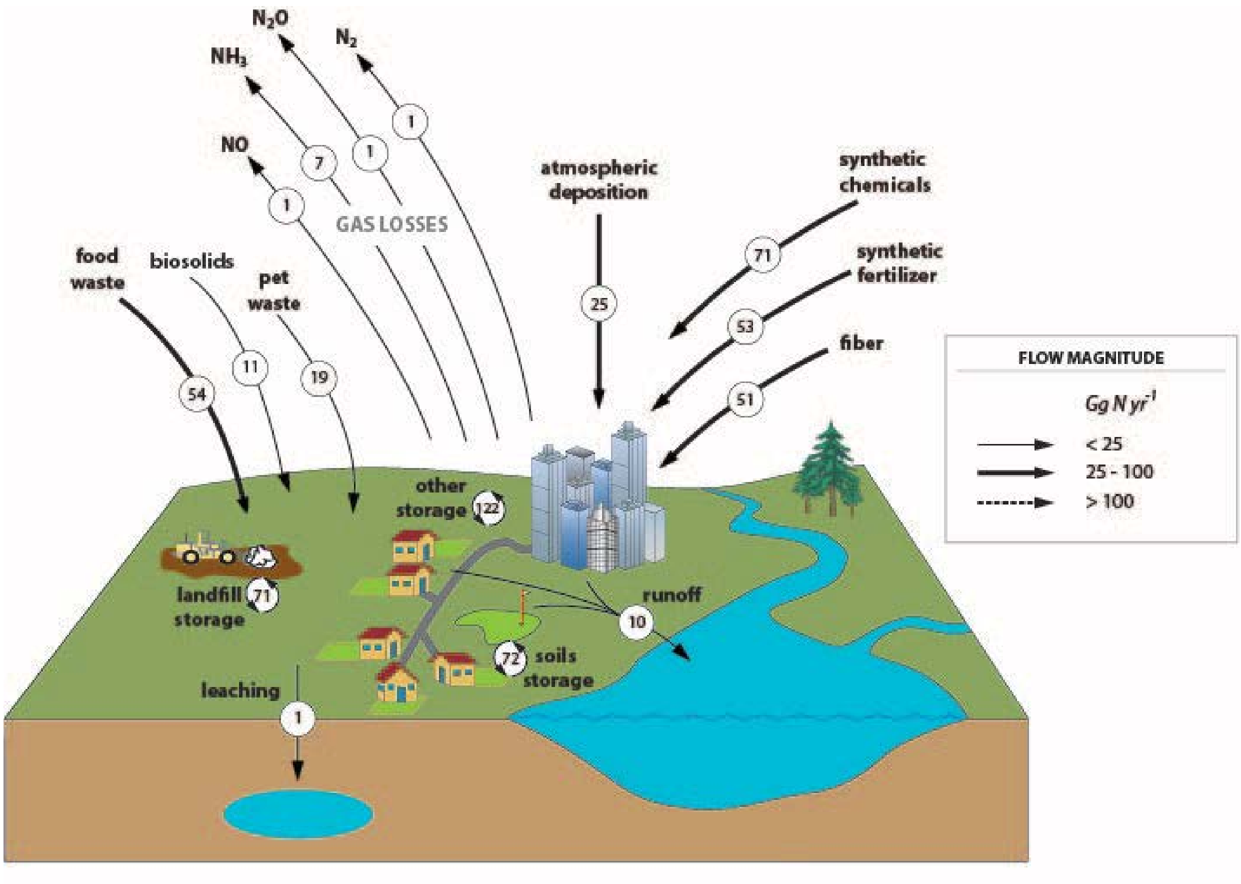


Figure 4.8. Flows of nitrogen in California natural land in 2005. The circled values indicate the absolute magnitude of the flow in Gg N yr^{-1} with arrow thickness specifying the relative magnitude of the flow. Storage terms are indicated with arrows on the circled values. To distinguish it from other gaseous emissions, there is a separate arrow for wildland forest fires, representing the total amount of N volatilized (predominantly N_2).

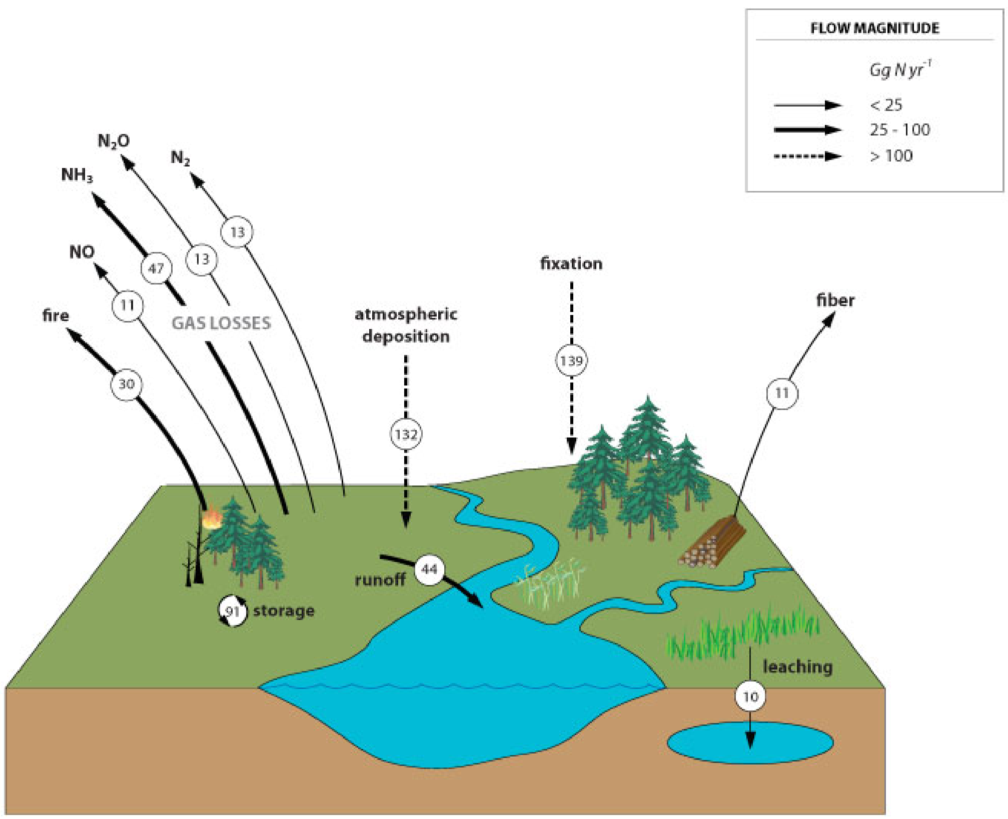


Figure 4.9. Relationship between wastewater treatment plant design flow and nitrogen discharge in California. Design flow was chosen as the predictor because it is reported by essentially all facilities to the State Water Resources Control Board. Population served is also a strong predictor of N discharge, but is not necessarily reported as part of the Waste Discharge Requirements. The data points represent the mean value calculated from monthly data for each facility the years in which data were available between 2002-2007. The facilities chosen for this analysis included all of the large treatment plants in the state (population served > 100,000) as well as all of the treatment plants in Region 2 because it is the only region with an electronic database of monitoring data.

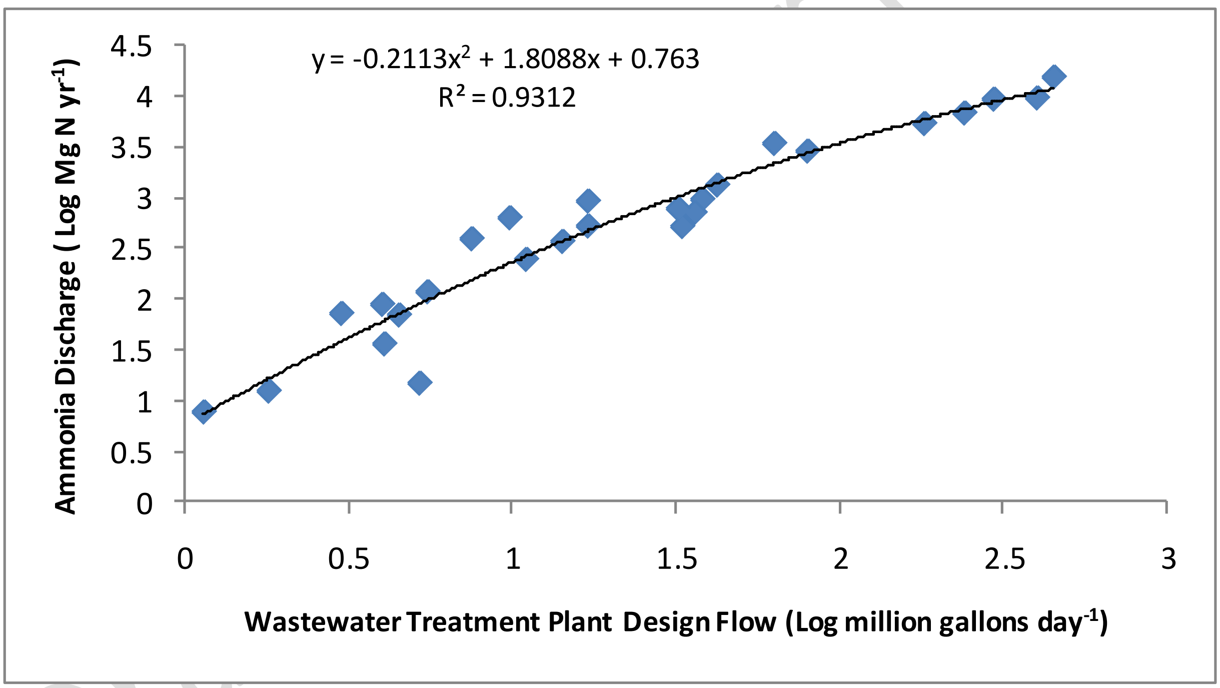


Figure 4.10. N imports and exports/storage per capita (kg N person^{-1} yr^{-1}). Comparison of N flows on a per capita basis for the California N Assessment (CNA) to six representative comprehensive N mass balance studies at various spatial scales around the world. Data for the Netherlands and Europe are from Leip et al. (2011), data for the US are from EPA (2011), data for China are from Gu et al. (2009), data for Korea are from Kim et al. (2008), and data for Phoenix are from Baker et al. (2001).

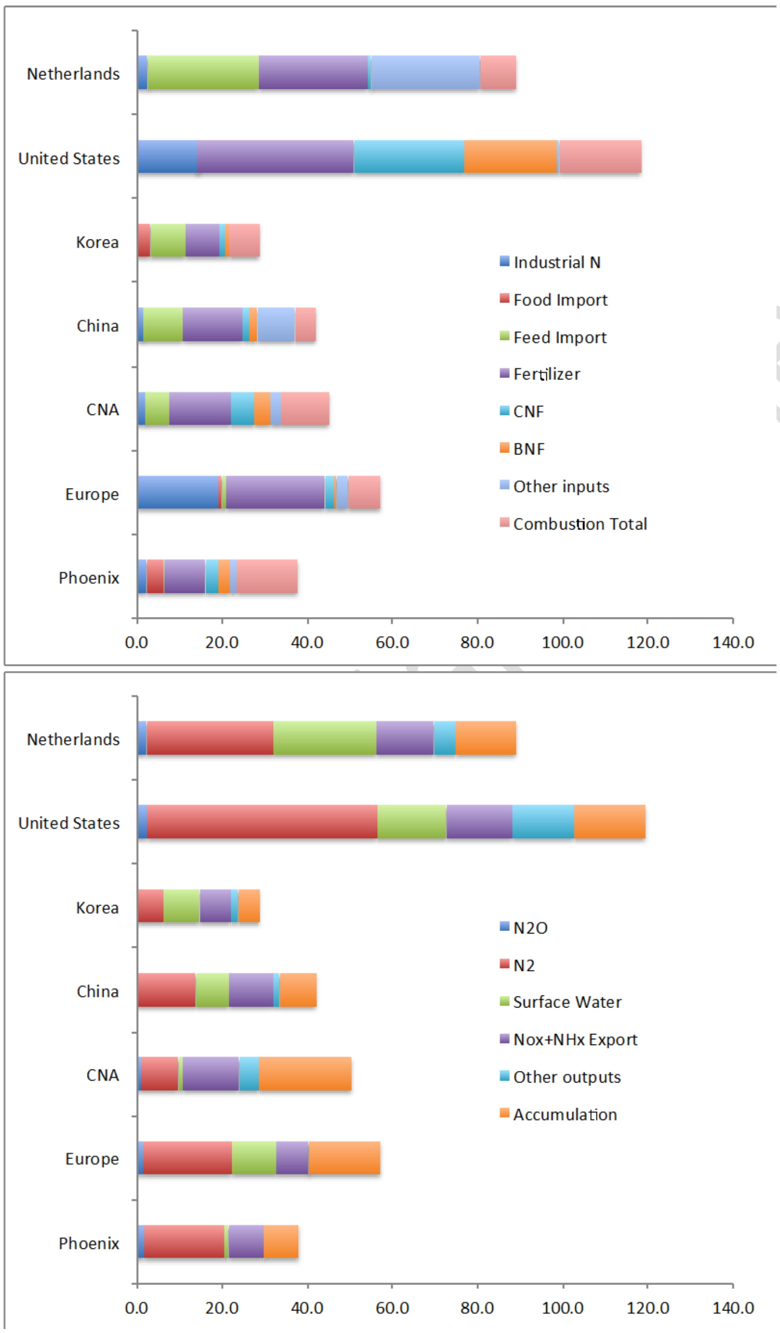


Figure 4.11. N imports and exports/storage per unit area (kg N ha^{-1} yr^{-1}). Comparison of N flows on an areal basis for the California N Assessment (CNA) to six representative comprehensive N mass balance studies at various spatial scales around the world. Data for the Netherlands and Europe are from Leip et al. (2011), data for the US are from EPA (2011), data for China are from Gu et al. (2009), data for Korea are from Kim et al. (2008), and data for Phoenix are from Baker et al. (2001).

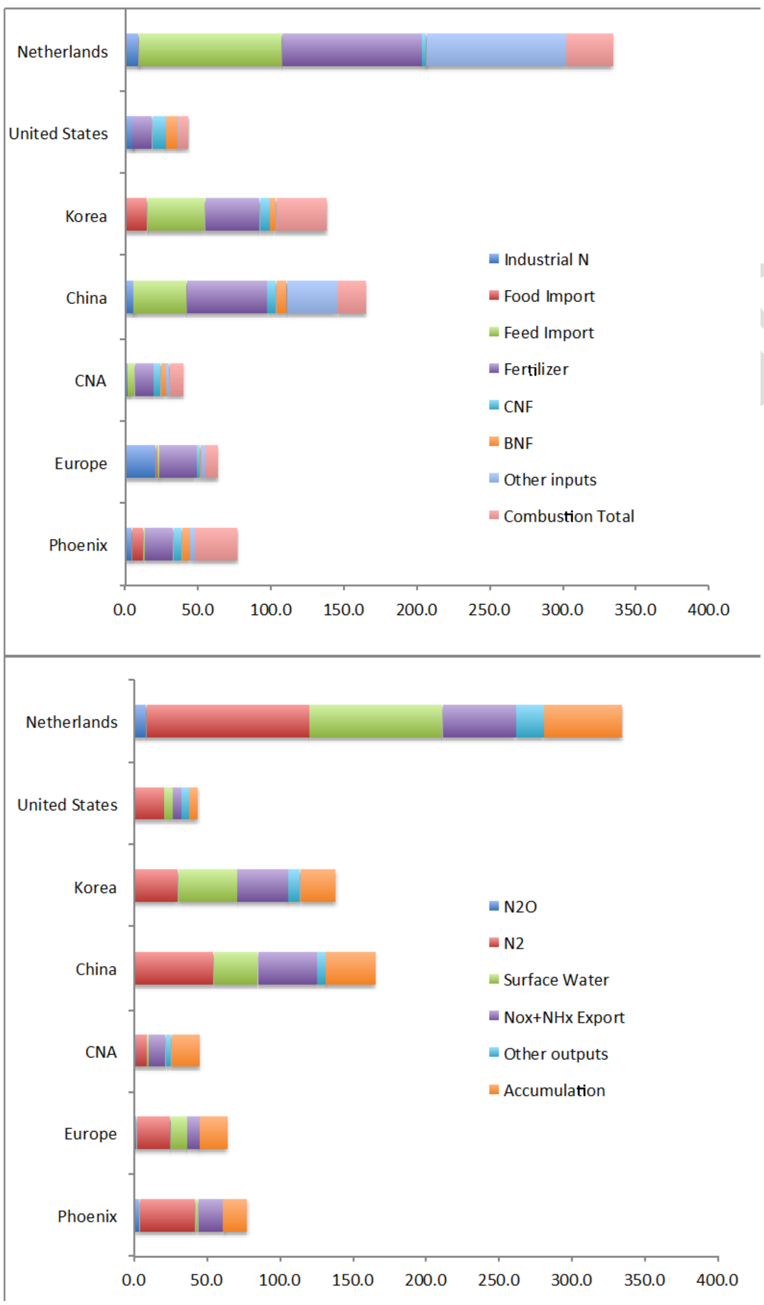


Figure 4.12. Relative contribution of N imports and exports/storage. Data for the Netherlands and Europe are from Leip et al. (2011), data for the US are from EPA (2011), data for China are from Gu et al. (2009), data for Korea are from Kim et al. (2008), and data for Phoenix are from Baker et al. (2001).

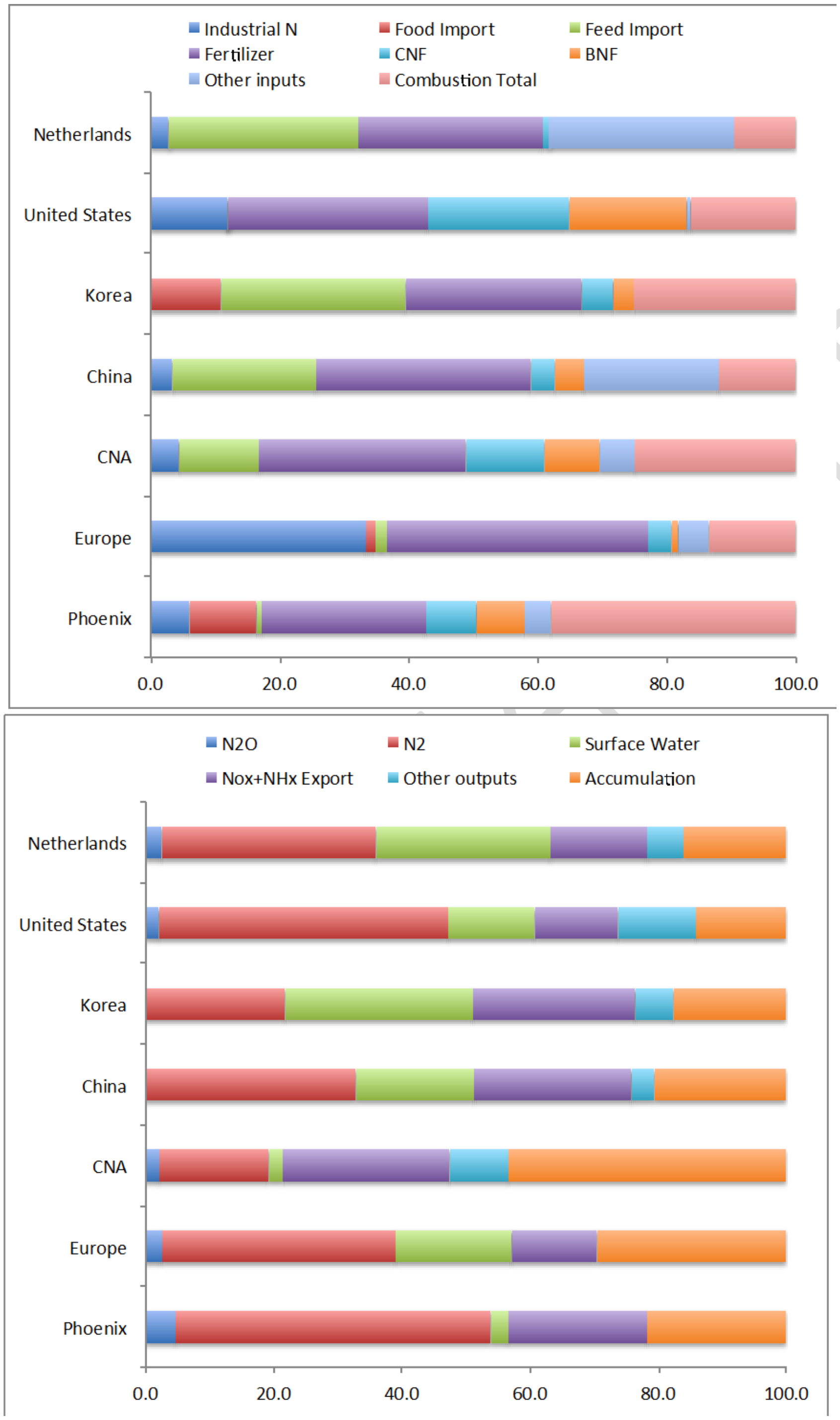


Table 4.1a. California statewide nitrogen mass balance for 2005: imports

Nitrogen flow	Methods section	Flow direction	Flow (Gg N yr^{-1})	Evidence	Agreement
Fossil fuel combustion					
NO_x	4.2.1	Import	359	High	High
NH_3	4.2.1	Import	36	Medium	Medium
N_2O	4.2.1	Import	9	Medium	High
Atmospheric import	4.2.1	Import	40	Limited	Low
Biological N fixation					
Natural lands	4.2.3	Import	139	Medium	Low
Cropland	4.2.3	Import	196	Medium	Low
Synthetic N fixation					
Fertilizer	4.2.4	Import	519	High	Medium
Chemicals	4.2.4	Import	71	Medium	Low
Feed	4.2.5	Import	200	Medium	Low
Fiber	4.2.5	Import	40	Limited	Low
Delta water imports	4.2.9	Import	8	High	Low

Table 4.1b. California statewide nitrogen mass balance for 2005: exports and storage

Nitrogen flow	Methods section	Flow direction	Flow (Gg N yr^{-1})	Evidence	Agreement
Food	4.2.5	Export	79	Medium	Low
Gas export					
NO_x	4.2.2	Export	270	Medium	Low
NH_3	4.2.2	Export	206	Limited	Low
N_2O	4.2.2	Export	38	Medium	Medium
N_2	4.2.2	Export	204	Limited	Medium
Discharge to Ocean					
River	4.2.9	Export	39	High	High
Sewage	4.2.7	Export	82	High	Medium
Storage					
Groundwater	4.2.10	Storage	258	Limited	Medium
Other storage	4.2.11	Storage	443	Medium	Medium

Table 4.2. California cropland nitrogen mass balance in 2005. All flows were calculated independently except soil storage which was calculated by difference. However, there is independent evidence suggesting increases in cropland soil storage. This term may also include storage in perennial crops.

Nitrogen flow	Methods section	Flow direction	Flow (Gg N yr^{-1})	Evidence	Agreement
Biological N fixation	4.2.3	Import	196	Medium	Low
Deposition	4.2.2	Input	43	Medium	Low
Synthetic fertilizer	4.2.4	Import	466	High	Medium
Manure application	4.2.6	Input	307	Medium	Low
Biosolids	4.2.7	Input	11	Medium	Low
Irrigation					
Groundwater	4.2.9	Input	33	Medium	Low
Surface water	4.2.9	Input	18	Medium	Low
Delta	4.2.9	Import	8	High	Low
Gas emissions					
NO	4.2.8	Output	12	Limited	Medium
NH_3	4.2.8	Output	60	Limited	Low
N_2O	4.2.8	Output	10	Medium	Medium
N_2	4.2.8	Output	17	Limited	Low
Feed	4.2.5	Output	357	Medium	High
Fiber	4.2.5	Output	1	Medium	High
Food	4.2.5	Output	185	Medium	High
Runoff	4.2.9	Output	41	Medium	High
Leaching	4.2.10	Output	333	Medium	Medium
Soils	4.2.11	Storage	65	Medium	Low

Table 4.3. Biological nitrogen fixation for agricultural crops in California in 2005

Crop	Acreage (1000s ha)	Fixation rate (kg N ha^{-1})	Fixed N (Gg N)	Fixation rate reference
Alfalfa	457	393	180	Unkovich et al. 2010
Dry beans[1]	83	40	3	Smil 1999
Fresh beans[2]	11	40	0.4	Smil 1999
Rice	226	25	6	Smil 1999
Pasture (clover)	434	15	7	Smil 1999
Total			196	

[1] Includes all dry beans including dry lima beans

[2] Includes snap beans and green lima beans

Table 4.4. Harvested N by crop. The production (Gg N yr^{-1}) and acreage (ha) and N yield (kg N ha^{-1} yr^{-1}) of the top twenty crops in terms of harvested N.

Crop	Harvested N (Gg N yr^{-1})	Cumulative production (%)	Harvested acreage (ha)	Percent of acreage (%)	N yield (kg N ha^{-1} yr^{-1})
Alfalfa hay	187	39.0	457467	12.5	410
Corn silage	41	8.6	179382	4.9	230
Haylage, non-alfalfa	28	5.8	161289	4.4	172
Wheat	27	5.6	205956	5.6	131
Rice	26	5.4	226499	6.2	114
Cotton[1]	23	4.9	264060	7.2	89
Almonds[2]	23	4.7	254527	7.0	89
Tomatoes, processing	16	3.4	125420	3.4	131
Corn grain	9	1.9	56737	1.6	161
Walnuts	8	1.6	94943	2.6	83
Lettuce	7	1.5	99584	2.7	73
Sudan hay	7	1.4	34201	0.9	197
Small grain hay	6	1.3	86360	2.4	73
Grapes	6	1.2	335890	9.2	17
Broccoli	5	1.0	48070	1.3	98
Pistachios	5	1.0	43963	1.2	106
Oranges	4	0.7	78441	2.1	46
Sugar beets	4	0.7	18617	0.5	190
Potatoes	3	0.6	16912	0.5	173
Carrots	3	0.6	22159	0.6	121
Other crops	44	9.2	848788	23.2	52
Total	481	100	3659264	100	132

[1]Includes lint and seed
[2]Includes kernels and hulls

Table 4.5. Sources of data for biome-specific NO and N_2O fluxes. Biome-specific NO and N_2O fluxes were calculated as the average of several published sources for cropland and natural lands. For the published studies with areal rates by biome (cropland, desert, coniferous forest, hardwood forest, grassland, shrubland) we used the biome areas from CAML. For the emissions factor approach we assumed 1% of fertilizer (both synthetic and manure) were converted to N_2O like the California Air Resources Board. However, we also included a background cropland emission of 1 kg N_2O-N ha^{-1} based on Stehfest 1996 to calculate total, not just anthropogenic N_2O emissions. We also compiled published estimates of NO and N_2O for California cropland. In the case of N_2O we used the median flux across all crops and management practices while for NO we calculated the mean of the daily flux estimates for the crops measured by Matson et al. (1997).

Source	**NO ($Gg\ N\ yr^{-1}$)**		**N_2O ($Gg\ N\ yr^{-1}$)**		**Type of data**	**Spatial extent**
	Cropland	**Natural land**	**Cropland**	**Natural land**		
Dalal and Allen (2008)				19	Field	Global
Davidson and Kingerlee (1997)	18	8.9			Field	Global
Li et al. (1996)			6.9		Model	California
Potter et al. (1996)	7.4	12		7.9	Model	Global
Stehfest and Bouwman (2006)	4.9	13	5.9	11	Field	Global
Emissions factor			9		Field	Global
California literature	9		14		Field	California
Average estimate	12	11	10	13		

Table 4.6. California livestock nitrogen mass balance in 2005. The total amount of feed was calculated as the sum of manure production based on livestock population and the amount of animal food products. Imported feed was calculated as the difference between feed crops harvested in California and the total amount of feed.

Nitrogen flow	Methods section	Flow direction	Flow (Gg N yr^{-1})	Evidence	Agreement
Feed					
California feed	4.2.5	Input	357	Medium	High
Imported feed	4.2.5	Import	200	Limited	Low
Manure	4.2.6	Output	416	High	High
Food	4.2.5	Output	141	Medium	Medium

Table 4.7. Confined livestock populations and manure and animal food products in California in 2005. The total N requirement and manure production are population based estimates based on inventory or sales data. The calculated food produced column is the independent estimate of food N based on the tonnage of animal food products and their N content. For comparison "Food produced as feed - manure" is calculated as the difference between the N requirement and manure production.

Class	Inventory (1000 head)	Annual sales (1000 head)	Total N requirement (Gg N)	Manure production (Gg N)	Calculated food produced (Gg N)	Food produced as feed - manure (Gg N)
Dairy cow	1,715		351	266	85	86
Dairy heifer	772		42	33		
Dairy calf	772		25	18		
Layers	21,115		12	6	6	7
Beef steer	644		43	32	18	11
Horses	876		32	35		
Turkeys		6,327	4	7	4	-3
Broilers		270,480	35	19	15	15
Pigs		303	3	1	1	2

Table 4.8. Fate of manure nitrogen from confined livestock in California in 2005. Manure production was calculated based on livestock populations as were ammonia (NH_3) emissions. Nitrous oxide (N_2O) emissions were direct emissions from manure prior to land application from the California Air Resources Board greenhouse gas inventory. All manure except dairy manure was assumed to be utilized as a solid. Leaching was calculated based on the fraction leached from dairy facilities reported in van der Schans et al. (2009).

Nitrogen flow	**Methods section**	**Flow direction**	**Flow (Gg N yr^{-1})**	**Evidence**	**Agreement**
Manure production	4.2.6	Input	416	High	High
Gas emissions					
NH_3	4.2.6	Output	97	Medium	Low
N_2O	4.2.6	Output	2	Medium	Low
Leaching	4.2.6	Output	10	Medium	Low
Cropland	4.2.6	Output	307	Medium	Low

Table 4.9. California urban land nitrogen mass balance in 2005. All terms except soil storage and other storage were calculated independently. Soil storage was calculated as the difference between the inputs of deposition, synthetic fertilizer, and dog waste and the outputs of gases and runoff to surface water. This storage term may also include storage in perennial vegetation in urban landscapes. Other storage includes the materials that cannot be tracked to landfills. This includes synthetic chemicals and some fiber products.

Nitrogen flow	Methods section	Flow direction	Flow (Gg N yr^{-1})	Evidence	Agreement
Deposition	4.2.2	Input	25	Medium	Low
Synthetic fertilizer	4.2.4	Import	53	Limited	Low
Synthetic chemicals	4.2.4	Import	71	Medium	Low
Fiber	4.2.5	Import	51	Limited	Low
Food waste to landfill	4.2.7	Input	54	Medium	Medium
Pet waste	4.2.7	Input	16	Limited	Low
Biosolids	4.2.7	Input	11	Medium	Low
Gas emissions					
NO	4.2.8	Output	1	Limited	Medium
NH_3	4.2.8	Output	7	Limited	Low
N_2O	4.2.8	Output	1	Medium	Medium
N_2	4.2.8	Output	1	Limited	Low
Runoff	4.2.9	Output	10	Medium	High
Leaching	4.2.10	Output	1	Medium	Low
Landfill	4.2.7	Storage	71	Medium	Medium
Soils	4.2.11	Storage	72	Medium	Low
Other	4.2.11	Storage	122	Limited	Low

Table 4.10. Sources of nitrogen to landfills in California in 2005. With the exception of cat waste and biosolids, which are based on the mass balance, the tonnage of materials sent to the landfill is based on CIWMB (2004). All moisture and N contents are from Cornell (1992) with the exception of food waste (Zhang et al. 2007). The category including leaves and grass was assumed to be equally composed of these two materials. Only food waste and cat waste are considered a new input to urban land while the other organic materials were already considered part of the urban landscape.

Material	Tonnes	Moisture (%)	N (%)	Gg N
Paper	7,678,172	20	0.1	6.1
Lumber	3,528,376	15	0.1	3.0
Prunings	836,687	15	0.1	0.7
Stumps	108,867	15	0.1	0.1
Food	5,322,138	74	3.2	44.3
Leaves and grass	1,541,838			9.0
Manure	33,187	72	1.6	0.1
Cat waste				3
Biosolids				11
Total				68

Table 4.11. Fate of nitrogen in human food in California in 2005. This table does not include the 54 Gg N yr^{-1} of food waste that ends up in landfills or the 79 Gg N yr^{-1} of food exported from California. The difference between inputs and estimated outputs was accounted for as N_2 loss. For comparison, we estimated that N_2 emissions associated with N removal in wastewater facilities was only 14 Gg N yr^{-1}.

Nitrogen flow	Methods section	Flow direction	Flow (Gg N yr^{-1})	Evidence	Agreement
Excretion	4.2.7	Input	174	Medium	Low
Biosolids	4.2.7	Output	22	Medium	Low
Gas emissions					
N_2O	4.2.7	Output	2	Medium	Medium
N_2	4.2.7	Output	29	Limited	Low
Surface water	4.2.7	Output	12	Medium	Medium
Leaching					
Septic	4.2.7	Output	16	Limited	Low
Natural land	4.2.7	Output	11	Limited	Low
Ocean	4.2.7	Output	82	High	Medium

Table 4.12. California natural land nitrogen mass balance in 2005. Storage was estimated as the difference between inputs and outputs and could occur in soils or vegetation.

Nitrogen flow	Methods section	Flow direction	Flow (Gg N yr^{-1})	Evidence	Agreement
Biological N fixation	4.2.3	Import	139	Medium	Low
Deposition	4.2.2	Input	132	Medium	Medium
Gas emissions					
NO	4.2.8	Output	11	Limited	Low
NH_3	4.2.8	Output	47	Limited	Low
N_2O	4.2.8	Output	13	Limited	Medium
N_2	4.2.8	Output	13	Limited	Low
Fire	4.2.8	Output	30	Limited	Low
Runoff	4.2.9	Output	44	Medium	High
Leaching	4.2.10	Output	10	Limited	Low
Fiber	4.2.5	Output	11	Limited	Low
Storage	4.2.11	Storage	91	Limited	Low

Table 4.13. Atmospheric nitrogen balance for California in 2005. Only the fossil fuel combustion and the upwind sources of N were new statewide inputs of N. All N_2 and N_2O emitted were assumed to be an output from the state. For NO_x and NH_3, export beyond the state boundary of these gases was calculated as the difference between emissions and deposition. Because of reactions in the atmosphere, a significant fraction of the export of oxidized and reduced N has been converted to chemical forms (e.g., nitric acid, ammonium nitrate particles, peroxyacetyl nitrate) other than NO_x and NH_3. These oxidized and reduced forms are often summarized as NO_y and NH_x.

N flow	**Methods section**	**Flow direction**	**NO_x (Gg N yr^{-1})**	**NH_3 (Gg N yr^{-1})**	**N_2O (Gg N yr^{-1})**	**N_2 (Gg N yr^{-1})**	**Total (Gg N yr^{-1})**
Fossil fuel combustion	4.2.1	Import	359	36	9		404
Soil	4.2.8	Input	24	110	24	31	188
Manure	4.2.6	Input		97	2		99
Upwind sources	4.2.1	Import	20	20			40
Wastewater	4.2.7	Input			2	29	31
Pet Waste	4.2.7	Input		4			4
Fire	4.2.8	Input	3	3		24	30
Surface water	4.2.9	Input			2	34	31
Groundwater	4.2.10	Input				91	91
Deposition	4.2.2	Output	135	67			202
Export	4.2.2	Export	270	203	38	204	716

Table 4.14. California surface water nitrogen mass balance in 2005. The reservoir storage term was calculated by difference. An independent estimate of N storage in lake and reservoir sediments was 14 Gg N yr^{-1}.

Nitrogen flow	Methods section	Flow direction	Flow (Gg N yr^{-1})	Evidence	Agreement
Runoff to rivers					
Natural land	4.2.9	Input	44	Medium	High
Cropland	4.2.9	Input	41	Medium	High
Urban land	4.2.9	Input	10	Medium	High
Sewage	4.2.7	Input	12	Medium	Medium
Deposition	4.2.2	Input	2	Medium	Low
Irrigation	4.2.9	Output	8	Medium	Low
Gas emissions					
N_2O	4.2.9	Output	2	Medium	High
N_2	4.2.9	Output	28	Medium	Low
Ocean	4.2.9	Export	39	High	High
Lake/Reservoir storage	4.2.9	Storage	32	Limited	Medium

Table 4.15. Estimated annual N discharge to the ocean by watershed for California. For watersheds that were drained by rivers that reach the ocean, we used literature estimates of N loads at the furthest downstream gauge. The three sources of data were Sobota et al. (2009), Schaefer et al. (2009) and Kratzer et al. (2009) with the data representative of the years 2000-2003, 1992 and 2000-2004 respectively. In watersheds where there were no literature values for N discharge, we first calculated the estimated N loading to the watershed based on the export coefficients. We used export coefficients for cropland, urban land, and natural land from two sources: (1) values reported in Wickham et al. (2008) and (2) values calculated for the Central Valley from Kratzer et al. (2011) and multiplied these values by the area of each land cover. We compared the predicted values of annual N loading based on export coefficients to the measured values for the 8 watersheds available in the literature. Based on the log-log regression (R^2 = 0.71) of predicted against measured data, we adjusted the predicted N loading to the watershed from the export coefficients in Wickham et al. (2008) to estimate the N discharged to the ocean for the watersheds . To simplify these calculations we lumped the small (<1000 km^2) coastal watersheds into four basins: 1) the north coast, from the Oregon border to San Francisco Bay, (2) the San Francisco Bay/Delta downstream of the USGS gauges at Vernalis on the San Joaquin River and Freeport on the Sacramento River, (3) the central coast from San Francisco Bay to the Santa Clara River, and (4) the south coast from the Santa Clara river south to the Mexican border. The Oregon watershed includes the N loading from tributaries of the Rogue River that flow from California into Oregon.

	N loading to rivers based on export coefficients (Gg N yr^{-1})		Estimated N discharge to ocean (Gg N yr^{-1})		Measured N discharge to ocean by watershed (Gg N yr^{-1})			
Watershed	**Wickham et al. 2008**	**Central Valley watersheds**	**Wickham et al. 2008**	**Central Valley watersheds**	**Sobota et al. (2009)**	**Schaefer et al. (2009)**	**Kratzer et al. (2011)**	**Best estimate of discharge to ocean**
Bay Delta	8.1	6.9	3.3	3.5				3.3
Central Coast	4.1	3.1	2.3	2.3				2.3
Colorado	2.9	2.0	1.9	1.8				1.9
Cuyama	0.9	0.6	0.9	0.9				0.9
Delta Rivers	4.0	3.7	2.2	2.5	0.2			0.2
Eel	2.5	1.6	1.7	1.5		2.7		2.7
Klamath	7.4	5.0	3.1	2.9		4.6		4.6
North Coast	2.9	1.8	1.8	1.6				1.8
Oregon	0.1	0.1	0.3	0.3				0.3
Pajaro	1.4	1.2	1.2	1.3		1.4		1.4
Russian	1.6	1.4	1.3	1.4		1.1		1.1
Sacramento	28.8	24.7	6.8	7.0	7.8	7.1	6.9	7.3
Salinas	3.4	2.9	2.0	2.1		0.9		0.9
San Joaquin	13.8	12.8	4.5	4.9	2.6		4.9	3.7
Santa Ana	2.4	1.8	1.7	1.7		2.0	1.6	1.8
Santa Clara	1.4	1.0	1.2	1.2				1.2
South Coast	10.8	8.3	3.9	3.9				3.9
California Total	96	79	40	41				39

Table 4.16. California groundwater nitrogen flows in 2005. We assumed no net transport of N between surface water and groundwater. Storage of N in groundwater was calculated as the difference between inputs and outputs.

Nitrogen flow	Methods section	Flow direction	Flow ($Gg\ N\ yr^{-1}$)	Evidence	Agreement
Soils leaching					
Cropland	4.2.10	Input	333	Medium	High
Urban land	4.2.10	Input	1	Medium	Low
Natural land	4.2.10	Input	10	Limited	Low
Manure leaching	4.2.6	Input	10	Medium	Low
Sewage leaching	4.2.7	Input	27	Medium	Medium
Irrigation	4.2.10	Output	33	Medium	Low
Denitrification	4.2.10	Output	91	Limited	Medium
Storage	4.2.10	Storage	258	Medium	Low

Table 4.17. Major non-fertilizer uses of synthetic nitrogen in the United States. Source: Domene and Ayres 2001.

Compound	N (Gg yr^{-1})	End use
Acrylonitrile	173	Acrylonitrile Butadiene Styrene
Caprolactam	86	Nylon
Hexamethylenediamine	203	Nylon
Isocyanates	90	Polyurethane
Melamine	54	Laminates and surface coatings
Urea	180	Resins
Adipic Acid[1]	185	Nylon Manufacturing
Methylmethylacrylate[2]	102	Acrylic glass manufacturing

[1]NO_x, N_2O, and N_2 emissions from the reduction of nitric acid are a byproduct of adipic acid synthesis, but N is not a component of the product.

[2]Ammonium sulfate, typically used as fertilizer, is produced as a byproduct of methylmethylacrylate synthesis.

Table 4.18. Synthetic nitrogen consumption (Gg N yr^{-1}) in the United States. Where possible, non-fertilizer consumption was partitioned into explosives, plastics and synthetics, and other uses.

Source	Year	Fertilizer	Non-fertilizer	Explosives	Plastics and synthetics	Other
Kramer 2004	2002	11,636	1,565	998	491	76
FAO (2013)	2002	10,945	4,277			
Domene and Ayres 2001	1996	11,297	3,020	557	786	1677

Table 4.19. Assumed nitrogen content of animal products. Source: NRC 2003.

Product	N content (%)
Hogs, beef	2
Milk	0.5
Eggs	1.8
Broilers, turkeys	2.3

Table 4.20. References for other nitrogen mass balance studies. Types of mass balances include the Net Anthropogenic Nitrogen Inputs (NANI) approach described by Jordan and Weller (1996), comprehensive approaches that include all N flows, and intermediate approaches that examine only a subset of the landscape (e.g., agriculture) or a subset of the flows across the entire landscape.

Author	Year	Type	Spatial Extent
Antikainen	2005	Comprehensive	Country
Baisre	2006	NANI	Country
Baker	2001	Comprehensive	Region
Bormann	1977	NANI	Watershed
Boyer	2002	NANI	Watersheds
Carey	2001	NANI	Watersheds
Castro	2003	NANI	Watersheds
David	2000	NANI	State
Delwiche	1970	Intermediate	Global
EPA	2011	Intermediate	Country
Galloway	2004	Intermediate	Global/Continents
Goolsby	1999	Intermediate	Watershed
Gu	2009	Comprehensive	Region
Han	2011	NANI	Region
Han	2008	NANI	Watersheds
Howarth	1996	NANI	Watersheds
Howarth	2012	NANI	Watersheds
Janzen	2003	Agriculture	Country
Jordan	1996	NANI	Watersheds
Keeney	1979	Intermediate	State
Kim	2008	Comprehensive	Country
Leip	2011	Comprehensive	Country
Messer	1983	Agriculture	State
Miller	1976	Agriculture	Region
NRC	1972	Intermediate	Country
OECD	2001	Agriculture	Country
Parfitt	2006	Intermediate	Country
Prasad	2004	Agriculture	Country
Quynh	2005	Intermediate	Watersheds
Robertson	1986	Intermediate	Countries
Salo	2007	Agriculture	Country
Schaefer	2007	NANI	Watersheds
Schaefer	2009	NANI	Watersheds
Sobota	2009	NANI	Watersheds

Soderlund	1976	Intermediate	Global
Valiela	2002	NANI	Watersheds
van Drecht	2003	Intermediate	Global
Velmuragan	2008	Intermediate	Country