CHAPTER FOUR

A California Nitrogen Mass Balance for 2005

Appendix 4.1 Supplemental data tables for Chapters 3, 4, and 5

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This is an appendix to Chapter 4 of *The California Nitrogen Assessment: Challenges and Solutions for People, Agriculture, and the Environment*. Additional information about the California Nitrogen Assessment (CNA) and appendices for other chapters are available at the Agricultural Sustainability Institute website: asi.ucdavis.edu/nitrogen

Suggested citation:

D Liptzin, RA Dahlgren, and T Harter. "Appendix 4.1: Supplemental data tables for Chapters 3, 4, and 5." Online appendices for California Nitrogen Assessment: Challenges and Solutions for People, Agriculture, and the Environment. TP Tomich, SB Brodt, RA Dahlgren, and KM Scow, eds. Agricultural Sustainability Institute at UC Davis. (2016). asi.ucdavis.edu/nitrogen.

4.1 Supplemental Data Tables

The data tables demonstrate that the amount and quality of available information on the causes, states, and consequences of nitrogen (N) cycling in California varies. Multiple data sources or methods were available in some cases. However, often conclusions had to be made based on limited and incomplete information. Improvements to the following areas would greatly advance our ability to track N flows and better understand the historical and future impacts of a changing N cycle on California.

1) Collect inorganic and organic N fertilizer application rates systematically. Use of N fertilizer represents the largest flow of new N into the environment, but the system of reporting is flawed and incomplete. In addition, application of organic N sources is not tracked (except for the San Joaquin Valley dairies). One opportunity may be to couple or model a N fertilizer reporting system based on the pesticide reporting system. The cost of compliance and burden of reporting needs to be considered if enhanced reporting is implemented.

2) Create a real-time updating system to integrate data collected and monitor changes. Many of the state agencies (Air Resources Board, California Department of Food and Agriculture, State Water Resources Control Board) collect data relevant to understanding the N challenge in California. However, the data are either buried on their websites, on the hard drives of a single employee, or only available as hard copies in their regional offices. A system that compiles data from various agencies and tracks changes in patterns would serve as a foundation for integrated cross media (air, soil, and water) responses.

3) Emissions, and the factors controlling their variability, need to be better established. In particular, information on leaching from croplands under current conditions, ammonia emissions from tailpipes, biological N fixation in crop and natural lands, and nitrous oxide emissions present significant uncertainty. Additional research to better characterize emissions from these sources will help researchers, farmers, and policy makers devise more targeted solutions.

4) Ground level concentrations of NO_x, NH_3, O_3 and PM are detectable by satellites, which are being used in conjunction with surface data and meteorological models to give a more complete assessment of spatial trends. Despite the advantages of better geographic coverage, the main limitation of remotely sensed data is that they lack the continuous temporal resolution. The value of remote sensed data for monitoring and regulatory compliance is expected to increase as long-term satellite records accumulate over time and more sophisticated air quality models for integrating these data with surface measurements are developed.

Introduction

The following data tables supplement and support the statements and conclusions in the body of the assessment report. The data tables are not summaries of findings, but rather summaries of what is known and available to evaluate the causes, states, and consequences of nitrogen (N) cycling in California. To this end, the data tables have two primary purposes: (1) summarize the sources of data and approaches used in the assessment, and (2) systematically evaluate the quality of available data. The data tables are organized by broad categories and each includes the indicators used in the assessment related to that topic. Relevant sections of the assessment are noted for each indicator in the table to track information and show linkages across chapters.

The following topics are covered in the data tables.

Table 1: Synthetic fertilizer use
Table 2: Industrial synthetic nitrogen
Table 3: Biological nitrogen fixation: natural lands
Table 4: Biological nitrogen fixation: cropland
Table 5: Nitrous oxide (N_2O) and dinitrogen (N_2) gas
Table 6: Nitric oxide (NO) + nitrogen dioxide (NO_2) and ammonia (NH_3)
Table 7: Area burned by wildfire
Table 8: Land use
Table 9: Nitrogen storage
Table 10: Harvested nitrogen
Table 11: Animal production
Table 12: Organic nitrogen reuse
Table 13: Agronomic nitrogen use efficiency of crops
Table 14: Solid waste
Table 15: Manure
Table 16: Groundwater nitrogen
Table 17: Surface water nitrogen
Table 18: Dissolved nitrogen in waste discharge
Table 20: Nitrogen in drinking water
Table 21: Nitrous oxide emissions from agricultural soils
Table 22: Nitrogen-related air pollutants

Following the models of other assessments, "reserved wording" was used to quantify areas of uncertainty (Box 1; modified from (Ash et al., 2010)), providing a more consistent analysis across chapters. This approach takes into account both the level of scientific agreement and amount of available evidence.

Box 1 Communicating uncertainty (Source: Ash et al. 2010)

Quantitative Analyses – the following reserved wording was used for statements that lent themselves to formal statistical treatment, or for judgments where broad probability ranges could be assigned:

Virtually certain	Greater than 99% chance of being true or occurring
Very likely	90-99% chance of being true or occurring
Likely	66-90% chance of being true or occurring
Medium likelihood	33-66% chance of being true or occurring
Very unlikely	1-33% chance of being true or occurring
Exceptionally unlikely	Less than 1% chance of being true or occurring

Qualitative Analyses – the following reserved wording was used for more qualitative statements:

Level of Agreement	Amount of Evidence: *Limited*	*Medium*	*High*
High	Agreed but unproven	Agreed but incompletely documented	Well-established
Medium	Tentatively agreed by most	Provisionally agreed by most	Generally accepted
Low	Suggested but unproven	Speculative	Alternate explanations

Table 1. Synthetic fertilizer use

<table>
<tr><th>Indicator</th><th>Data sources and approach</th></tr>
<tr><td>Statewide nitrogen (N) fertilizer use

(Sections 3.2, 4.1.2; Appendix 4.2.4; Figure 3.2; Box 4.3)</td><td>Compilation of fertilizer sales data from annual tonnage reports for 2002-2007 (California Department of Food and Agriculture). Sales data for years following 2002 were deemed unreliable due to unexplainable 50% increase in sales. Mass balance calculations used mean value for 1980-2001.</td></tr>
<tr><td>Fertilizer use by crop

(Sections 3.2.1, Appendix 4.2.2,; Table 3.1; Figures 5.1.3, 5.1.5; Appendix 3.1)</td><td>Estimated fertilizer use for the known land cover types receiving fertilizer was summed. With the exception of turfgrass, fertilization rate was multiplied by the acreage.
• The acreage of cultivated crops was calculated as the mean acreage reported in the USDA National Agriculture Statistics Service (NASS), California County Agricultural Commissioners' Data (2002-2007) annual summary of statewide data. The crops were aggregated to match the categories used by the California Department of Water Resources (DWR) land use surveys. The fertilization rates were calculated as the average of the recommended rates across all regions and management practices in the recent (1999-2010) UC Davis Cost Studies and the grower reported rates for California in the USDA Chemical Use Surveys.
• The acreage of environmental horticulture crops was based on the average of the 2002 and 2007 USDA Agricultural Census. Fertilization rates were calculated based on expert opinion (R. Evans, UC Davis) of irrigation rates and fertilizer concentrations.
• Turfgrass fertilizer use was based on expert opinion (B. Augustin, Scotts-Miracle Gro Company) and was scaled down from the national estimate of fertilizer use on turfgrass and the fraction of national turfgrass in California reported by Milesi et al. (2005).</td></tr>
<tr><th colspan="2">Uncertainty and information status</th></tr>
<tr><td colspan="2">♦ Statewide fertilizer use is not directly measured, so fertilizer sales are the best available proxy. There was high agreement between the top-down approach based on fertilizer sales data, compared to the bottom-up approach which calculated fertilizer usage by land cover type (e.g., cultivated crops, environmental horticulture, and turfgrass). At the statewide level, these resulted in estimates of fertilizer use within 5% of each other (ignoring the large reported increase in N fertilizer sales starting in 2002).</td></tr>
<tr><td colspan="2">♦ For the top-down approach, the CDFA's annual tonnage reports provide a better estimate of the tonnage of fertilizing materials sold than of the tonnage of N sold (see Box 4.3 in CNA). It appears that problems in the reporting system may explain the puzzling 50% increase in reported sales from 2001 to 2002.
• There are potentially double counting problems in the accounting methodology. The reporting system is designed to track the amount of fertilizing materials sold by licensed</td></tr>
</table>

	dealers to unlicensed purchasers by county. However, it is possible that some dealers are reporting all sales. • The largest source of error is likely the conversion of the tonnage of materials to tonnage of N for farm use fertilizers. While the common fertilizers have a specific grade (e.g., the grade of anhydrous ammonia is 82-0-0 or 82% N, 0% phosphorus and 0% potassium), in California there is a large tonnage of specialty fertilizers that are lumped together as “other.” In older tonnage reports the “other” category was assumed to have a grade of 10-3-3, but the current tonnage reports do not state this explicitly. • Reporting of tonnage of non-farm fertilizing materials is also inadequate as there is no way to report the grade of this material. The tonnage reports do not indicate how the tonnage of non-farm N is calculated, although it can be assumed the grade for these materials is also 10-3-3.
♦	For the bottom-up approach, there is uncertainty in both the acreage and the fertilization rates, with the level of uncertainty dependent on the crop. • There is high agreement on the acreage of most crops in the various data sources. Acreage reported by the NASS California Agricultural Commissioners’ Data is very similar to the acreage reported in the USDA Agricultural Census. • However, calculations of fertilization rates are hindered by limited and inconsistent data. Fertilization rates were estimated as the average of the recommended rates reported in the UC Davis Cost Study reports and fertilization rates reported by growers as part of the USDA Chemical Use Surveys. While the rates in these two sources across all crops are highly correlated, they can disagree by 50% for a given crop. • Turfgrass acreage is calculated based on the empirical relationship observed between impervious surface area and turfgrass from remote sensing imagery. There are no other reliable quantitative estimates of turfgrass acreage for California. • There is limited evidence for fertilization rates in turfgrass. Our estimate of fertilizer use is based on scaling down the Scotts Company national estimate of fertilizer use on turfgrass. While the Scotts Company does extensive research on the “Do it yourself” homeowners market to evaluate its market share, the total use of fertilizer on turfgrass is suggested but unproven. • There is medium agreement on the acreage of environmental horticulture crops, but there is limited evidence for the fertilization rates of these crops. This category comprises a variety of crops ranging from woody perennials to annual bedding plants to cut flowers grown in the open. While these highly productive crops very likely receive the highest fertilization rates of any crop in the state, there are no available recommendations or surveys on fertilization rates for any of these crops in California. Further, it is unknown how much recycling of N in the irrigation water occurs.
♦	Estimating fertilization rates is complicated by the large amount of manure produced in the state. More likely than not, manure N replaces synthetic fertilizer as the source of nutrients for many acres of forage crops near dairies. However, it is not clear if this replacement is complete or if these crops still receive some inorganic fertilizer. Further, a large fraction of solid manure appears to be composted to some degree and applied as an organic amendment to soils and not included as part of nutrient management plans.

♦ *See also* manure (Table 15)

Table 2. Industrial synthetic nitrogen

Indicator	Data sources and approach
Ammonia consumption for industrial uses *(Sections 3.5, 4.1.1, 4.1.4; Appendix 4.2.4)*	Industrial nitrogen (N) consumption is only reported at the national level for the United States. To estimate levels for California, the national estimates by Domene and Ayers (2001), Kramer (2004) , and FAOSTAT (2002) were scaled down based on California's population reported in the US Census.

Uncertainty and information status
♦ Both the total ammonia (NH_3) consumption and synthetic fertilizer N use at the national level are agreed but unproven. Therefore, there should be high agreement on the total consumption of NH_3 in forms other than fertilizer calculated by difference. However, there is low agreement, in part due to annual variation.
♦ Disagreement also arises from a lack of publically available data. Domene and Ayres (2001) attempt to track all of the major industrial end uses of NH_3 in the United States. However, this information is derived from private industry sources which are compiled by consulting companies. Individual reports are available for most industrial N-containing compounds, but they cost hundreds to thousands of dollars each and are not typically available in libraries. Thus, it is difficult to assess the quality of these data.
♦ Information on the ultimate fate of these materials after they are produced is scarce. Some of the materials, like nylon carpets, acrylonitrile butadiene styrene (ABS) in automobiles and electronic equipment, are increasingly being recycled. However, the majority of these materials likely still end up in landfills where they decompose slowly.
♦ The available information on NH_3 consumption is somewhat dated. This is important because unlike fertilizer consumption which has leveled off recently, the use of NH_3 has been growing and continues to grow rapidly (International Fertilizer Institute cited in European N Assessment (2011)).
♦ *See also* solid waste (Table 14).

Table 3. Biological nitrogen fixation: natural lands

<table>
<tr><th>Indicator</th><th>Data sources and approach</th></tr>
<tr><td>Biome specific N fixation rates

(Sections 3.2.2.3, 4.1.2, 4.1.6; Appendix 4.2.3)</td><td>Estimation of natural land nitrogen (N) fixation was based on the dataset presented in Cleveland et al. (1999). The low percent cover estimate for biome specific N fixation rates was used and biome areas were derived from our land cover map (see Table 8).

Semi-quantitative estimates of species-specific rates of N fixation are available in the USDA PLANTS database, but there are limited data on the areal extent of these species precluding usage of this approach.</td></tr>
<tr><td>Empirical relationship with actual evapotranspiration

(Sections 4.1.6; Appendix 4.2.3)</td><td>The statewide average evapotranspiration (ET) was calculated from MODIS data (provided by Qiaozhen Mu, University of Montana) and the empirical relationship between actual ET and N fixation as described in Cleveland et al. (1999).</td></tr>
<tr><th colspan="2">Uncertainty and information status</th></tr>
<tr><td colspan="2">♦ Biological N fixation is the largest source of N to natural ecosystems, but magnitude of the rates is speculative. Two main approaches have been used for symbiotic N fixation: (1) biome specific rates based on Cleveland et al. (1999) and (2) species specific rates. Sobota et al. (2009) used both methods for Central Valley watersheds and found the latter to be 50% less than the former assuming that Ceanothus spp. were the only N fixers.</td></tr>
<tr><td colspan="2">♦ Biome specific N fixation rates are the most common approach for mass balance studies, but the rates are speculative.
The biome-specific rates reported in the global data in Cleveland et al. (1999) are likely biased upwards because studies of N fixation are more likely to occur in areas with higher N fixation rates. While these authors report estimates of rates across a range of percent cover for the N fixing species, even the lowest coverage may overestimate fixation rates. For example, two of the seven reported rates of symbiotic N fixation are for Alnus (alder) forests which have very high rates of N fixation.
The biome-specific estimates of N fixation varied by a factor of three and the estimate based on ET varied by a factor of six, depending on the assumption of percent cover of N fixing species. There was considerable overlap in the range of N fixation estimates between the two methods, but the lower bound for the ET-based estimate was considerably lower. Perhaps because of the Mediterranean climate, the ET for the biomes in California is lower than the global average ET for these biomes. The mass balance approach (subtracting all known outputs from atmospheric deposition) was also on the low end of the range. Because the biome-level estimates do not take into account the quantity of N deposition, this approach assumes that atmospheric N deposition is largely replacing N fixation as a source of new reactive N. One problem with this approach is that the distribution of N fixing species may not align with the distribution of N deposition. That is, regions with high N deposition may be regions that previously had modest rates of N fixation.</td></tr>
<tr><td colspan="2">♦ Calculations using a species-based approach are currently difficult because of lack of data on the</td></tr>
</table>

coverage of individual species. • Plants with symbiotic N-fixing associations are concentrated in a few families and genera: *Fabaceae*, *Alnus* (Betulaceae), *Ceanothus* (Rhamnaceae), *Purshia* and *Cercocarpus* (Rosaceae). While these species have the potential to fix N, relatively few field measurements have been made. • Very high rates (100 - 200 kg N ha^{-1} yr^{-1}) have been estimated for pure stands of red alder (*Alnus rubra*) in the Pacific Northwest, but pure red alder stands are limited in California. • Many understory species in forests and shrubs in dryland ecosystems are capable of N fixation, but the rates may be low because of moisture and light limitation and low primary productivity. However, one shrub species, *Ceanothus velutinus*, has been measured to have relatively high fixation rates (>10 kg N ha^{-1} yr^{-1}) at moderate cover in the forest understory (Busse, 2000) or in the understory of drier coniferous forests (Johnson, 1995). Other *Ceanothus* species have been measured to fix N at rates up to 100 kg N ha^{-1} yr^{-1} in pure stands as well (Conard et al., 1985). Little is known about fixation rates for many of the other shrub species or the predominantly herbaceous, but widely distributed, *Fabaceae* species in California.
♦ Using the biome-specific rates requires a measure of the areal extent of the biomes. While there are several potential data sources, there is generally high agreement once the detailed vegetation communities are lumped into biomes.
♦ There is limited evidence for the percent cover of most N fixing species. There are vegetation plots which have been inventoried by state and federal agencies or non-governmental organizations that are representative of large areas of the state. However, extracting the appropriate cover data for this analysis was beyond the scope of the assessment.
♦ There is a high degree of uncertainty on the effect of atmospheric N deposition on the rates of N fixation. It is tentatively agreed by most that increasing N deposition will decrease the competitive advantage of symbiotic N fixing species. Fertilization experiments have shown that increased N availability is associated with decreased N fixer abundance (e.g., (Suding et al., 2005)). However, there is limited evidence that N deposition has caused changes in the abundance of N-fixing plant species. Based on the mass balance, we estimate that N deposition is now similar in magnitude to natural lands N fixation. If this increased deposition has resulted in a decrease of N fixation, either by decreasing the abundance of N fixing plants or decreasing the fixation rate without altering abundance, then N fixation would be significantly lower than our estimate.
♦ The presence of non-native species is another factor that may affect natural lands N fixation rates. Some of the plants included in the USDA PLANTS database are crop species (e.g., *Medicago sativa* and *Trifolium spp.*) and most others were deliberately introduced for various reasons (e.g., *Vicia spp.* and *Eleagnus angustifolia, Cytisus scoparium*). These species tend to fix at high rates with twelve in the "high fixer group" and eighteen in the "medium fixer group," out of thirty-four species total. There is limited evidence for the magnitude of N fixed by these species, but they are widespread in many ecosystems and especially in human disturbed ecosystems. While these species may change local ecosystem nutrient cycling, they likely do not change the statewide N balance. For example, if we assume a medium fixation rate (120 kg N ha^{-1} yr^{-1}) and 5% cover of non-native N fixers on 1 million ha, the statewide total would only be 6 Gg N yr^{-1}.

Table 4. Biological nitrogen fixation: cropland

<table>
<tr><th>Indicator</th><th>Data sources and approach</th></tr>
<tr><td>Crop specific nitrogen (N) fixation rates

(Sections 3.2.2.3, 4.1.2; Appendix 4.2.3; Figure 3.5)</td><td>The N fixation rates were multiplied by the mean crop acreage for 2002-2007 reported in the USDA National Agricultural Statistics Service (NASS), California Agricultural Commissioners' Data.
For alfalfa, the empirical relationship reported by Unkovich et al. (2010) between N fixation rates and plant productivity was used.
For all other crops, the standard literature value of N fixation rates was used (Smil, 1999).</td></tr>
<tr><th colspan="2">Uncertainty and information status</th></tr>
<tr><td colspan="2">♦ N fixation has not been quantified in California alfalfa for several decades. However, the reported relationship between N fixation rate and dry matter production reported in Unkovich et al. (2010) is quite robust. While the rates of productivity are significantly higher in California (i.e. the statewide mean productivity is higher than the highest value reported by Unkovich et al.), there is no reason to think that the relationship between dry matter production and N fixation would differ at higher productivity levels. This relationship, however, is only for aboveground biomass.</td></tr>
<tr><td colspan="2">♦ For alfalfa, the most important source of uncertainty is the amount of fixed N in belowground biomass. Unkovich et al. (2010) suggest that 50% of total N fixation has been reported to be in belowground biomass. Because of the frequent number of cuttings (up to 12 in the Imperial Valley), root production likely lags behind aboveground production. Thus, we assumed that only 25% of total fixation would be in belowground biomass. The difference in assumptions about fixed N in roots represents a difference of 83 Gg N yr^{-1}.</td></tr>
<tr><td colspan="2">♦ While there is limited evidence for the fixation rates of leguminous crops other than alfalfa, they cover such small acreages that total crop fixation rates are not affected. Two possible exceptions include:
Irrigated pasture used to be managed to have high clover cover. Based on expert opinion (M. George, UC Davis), we assumed a value of 10% clover cover in irrigated pasture, a value which is suggested but unproven.
The growing conditions for rice also favor the growth of several taxa of blue-green algae. Based on Smil (1999), N fixation rates by these free living N fixers (e.g., Nostoc and Anabaena) are 20-30 kg N ha^{-1} yr^{-1}. However, N fixation has not been measured in rice in California in recent decades. While these taxa occur, in some cases they are managed because they compete with rice seedlings. Even though there is limited evidence to support both rice and pasture N fixation, the maximum error is likely less than 10 Gg N yr^{-1} combined.</td></tr>
</table>

Table 5. Nitrous oxide (N_2O) and dinitrogen (N_2) gas

Indicator	Data sources and approach
Fossil fuel combustion N_2O: emissions inventory *(Sections 3.4, 4.1.1, 4.1.7; Tables 4.1A, 4.13; Appendix 4.2.1)*	All fossil fuel combustion related emissions of N_2O were based on the average of the 2002-2007 California Air Resources Board (ARB) Greenhouse Gas Emission Inventories.
Natural land soils N_2O: biome-specific rates *(Sections 4.1.1, 4.1.6; Table 4.5; Appendix 4.2.8)*	For natural land emissions, the biome-specific rates from each published source (see Table 4.5 in CNA) were multiplied by the biome areas in the land cover map (see Table 8 below). The mean of the estimates from all sources was calculated.
Cropland soils N_2O: literature compilation *(Sections 4.1.1, 4.1.2, 4.2.8; Table 4.5; Appendix 4.2.8)*	For cropland emissions, the mean was calculated for the product of the area of cultivated cropland in the land cover map (see Table 8) and published global estimates of cropland rates (see Table 4.5 in CNA) as well as the median rate for California (see Appendix 4.2.8).
Soil N_2 emissions: N_2:N_2O ratios *(Sections 4.1.1, 4.1.7; Appendix 4.2.8)*	The reported N_2:N_2O ratios for cropland and natural land in Schlesinger (Schlesinger, 2009) were used to estimate N_2 emissions.
Aquatic ecosystems N_2O and N_2 *(Section 4.1.8; Appendix 4.2.9)*	In aquatic systems, both N_2O and N_2 were estimated independently based on published estimates in Beaulieu et al. (2011) and Mulholland et al. (2009).
Groundwater denitrification (*Section 4.1.9; Appendix 4.2.10)*	Denitrification was estimated with three approaches: (1) assuming a half-life of nitrate of 31 years (Green et al., 2008) and historical estimates of N inputs to groundwater, (2) multiplying estimates of the volume of groundwater (CA DWR 2003) by an estimated denitrification rate (Liao et al., 2012), and (3) assuming a fixed fraction of N inputs to groundwater is denitrified (Leip et al., 2011; Seitzinger et al., 2006).

Uncertainty and information status
♦ Emissions of N_2O from fossil fuel combustion are tentatively agreed upon by most. Emissions are largely derived from fuel use which is well established, but there is limited evidence for the magnitude of the emission factors used.
♦ It is suggested but unproven that N_2O emissions from natural land soils are of similar magnitude to cropland soils in California. We rely on several global estimates of N_2O emissions for our

calculations, as there are very few field-based estimates across the wide range of ecosystems in the state. Emissions could be higher in California because of the higher amounts of N deposition in many natural land regions. For example, Fenn et al. (1996) report rates almost an order of magnitude higher at a high N deposition site compared to a low deposition site.
♦ Rates of nitrous oxide emissions from soils are provisionally agreed upon by most. Of the four calculated estimates, the median value of California field data was more than double the other estimates, but may be high for two reasons: • First, the crops that were examined may be fertilized at higher rates than the average crop in the state. • Second, in many cases, the timing of the measurements may not have been ideal for scaling up to an annual scale. Stehfest and Bouwman (2006) note that the length of the study is negatively related to N_2O fluxes. That is, the longer the time span that was included in the study, the lower the reported N_2O emissions. ♦ Ongoing research in California as part of a concerted effort funded by the California Air Resources Board, California Department of Food and Agriculture, the California Energy Commission, and CalRecycle suggests that with proper management, N_2O emissions from well-managed California crops can be significantly lower than the global averages. In addition, this project is helping to develop California-specific parameters to improve the DeNitrification-DeComposition (DNDC) model used by Li et al. (1996). Decreasing this uncertainty is potentially important for estimating greenhouse gas emissions, but is a minor source of absolute uncertainty in the N mass balance calculations.
♦ There is limited scientific evidence for dinitrogen (N_2) emissions from soils. This is one of the largest sources of uncertainty in many N budgets for natural lands. Schlesinger (2009) compiled existing data, but there are still relatively few estimates of N_2 emissions and little understanding of what controls the emission rates. There are two main methods for field measurements of N_2: (1) incubations with acetylene, and (2) ^{15}N labeling experiments. In the former, the last step of denitrification, the conversion of N_2O to N_2, is blocked and N_2O is measured. For the latter, the labeled N can be measured directly as N_2. There is a growing consensus that isotopic methods are more robust, but they are more time consuming and expensive to use. Ecosystems models like DAYCENT and DNDC can estimate N_2 emissions, but need to be validated with field measurements. ♦ Pioneering work on denitrification using the acetylene method was conducted in agricultural soils in California in the 1970s and 1980s although denitrification in soils was studied even earlier by Broadbent (1951). The Schlesinger (2009) database included three of the published studies, but excluded Ryden and Lund (1980). These four works found higher denitrification rates as well as a lower ratio of N_2O to total denitrification. However, the N input rates in these studies were relatively high (300 - 680 kg N ha^{-1} yr^{-1}). Even using the higher N_2:N_2O ratio from the average of these four California studies, the amount of N emitted as N_2 from cropland soils would only increase from 17 to 52 Gg N yr^{-1}, suggesting that leaching still dominates over gaseous emissions for N outputs from cropland soils.
♦ N_2O and N_2 emissions might differ in California's Mediterranean climate due to timing of N availability compared to many other temperate ecosystems. During the hottest months of the years, biotic gas fluxes are minimal as the soils are dry and there is little biological activity. N availability in soils and N concentrations in surface water in natural areas tend to be highest in the fall at the time of

	the first rain (Ahearn et al., 2004). This is a time of year when many plants are relatively inactive because of hot and dry conditions.
♦	Estimates of statewide wastewater N_2O emissions are speculative due to: (1) a lack of compiled data on the level of treatment, and (2) a wide range of values dependent on the processes used at each facility. • The State Water Resources Control Board conducts a wastewater user charge survey annually, which asks about treatment level. However, this database is collected by the wastewater agency rather than the facility, making it difficult to assign a treatment level and thus the N_2O emissions for each facility. • One study, Czepiel et al. (1995), conducted for one spring and summer at one treatment plant in Durham, New Hampshire, forms the basis of the emission factor used by the ARB for the California Greenhouse Gas Emission Inventory as well as the EPA's National Greenhouse Gas Inventory, as well as one option for Tier I estimates for the International Panel on Climate Change. • Foley and Lant (2008) compiled the few literature values reporting the fraction of influent N released as N_2O. They report a range spanning two orders of magnitude and a median value of 0.01 kg N_2O- kg $^{-1}$ influent N. That is, 1% of influent N is converted to N_2O. For California, the per capita and influent concentration approaches both result in 2 Gg N_2O-N emitted per year.
♦	N gas emissions from denitrification in wastewater are not monitored and can only be estimated by difference. Our calculations suggest a N_2:N_2O ratio of ~17.
♦	N concentration of surface waters varies considerably in space and time (e.g., (Sobota et al., 2009)), making gaseous emissions highly spatially variable. Nitrous oxide emissions from rivers, while relatively low, are related non-linearly to NO_3^- concentrations (Beaulieu et al. 2011). Below a threshold concentration of 95 μg N L^{-1}, N_2O production was low and insensitive to NO_3^- concentrations. However, some rivers in the Central Valley, like the San Joaquin River, have NO_3^- concentrations greater than 1 mg NO_3^--N L^{-1} and would be expected to have higher N_2O emissions. Thus, using average NO_3^- concentrations may underestimate N_2O emissions at high NO_3^- levels and overestimate N_2O emissions at low NO_3^- levels.
♦	Partitioning the water pixels in land-use maps is difficult because there is no spatially explicit data on the location and size of reservoirs and lakes in California. The Department of Water Resources catalogs the latitude/longitude of dams and the United States Geological Survey maps all water bodies, but these datasets are not always consistent, especially for smaller water bodies.
♦	There is limited evidence for how gas losses differ among rivers, natural lakes, and reservoirs. • Harrison et al. (2008) show that reservoirs differ by an order of magnitude in N retention calculated as the difference between N inputs and N outputs. By this definition both denitrification and sedimentation are included in retention. • The total denitrification rates estimated by Seitzinger et al. (2006) were similar between rivers and lakes, but their lakes category included both natural lakes and reservoirs. • The majority of the lake acreage, and most of the large natural lakes in California, are saline; however, there is limited evidence for whether denitrification rates in saline lakes are similar to either freshwater lakes or coastal areas.
♦	Groundwater denitrification is suggested but unproven. Chemical tracers show that denitrification is

widespread even in portions of the aquifer that are oxygenated. However, calculating rates of denitrification over large areas is very difficult because of heterogeneity in N inputs, geochemistry, and hydrology. The approaches vary in their scale, but there is limited evidence, but high agreement, when applied to California.

- Techniques such as measuring N_2: Argon ratios and dual isotopes of NO_3^- can be used to estimate the fraction of initial NO_3^- that has been denitrified. Combined with measurements of water age, the half-life of N can be estimated; this can be converted into an annual rate. A relatively small number of sites have been sampled with this approach. Further, a historical estimate of N inputs to groundwater is necessary. We assumed a linear increase since 1940 just before synthetic fertilizer use became widely commercially available.
- Transport models can estimate rates of denitrification in mg N L^{-1}. In addition to estimates of N and water dynamics, this approach also requires an estimate of the volume of groundwater.
- The less complex IMAGE model of N dynamics (Van Drecht et al., 2003) applied at the global (Seitzinger et al., 2006) and continental (Leip et al., 2011) scales both suggest that 40% - 50% of N inputs are denitrified.
- Validation of these approaches at the scale of California or even just the Central Valley is not currently possible.

Table 6. Nitric oxide + nitrogen dioxide (NO_2) and ammonia (NH_3)

Indicator	Data sources and approach
Fossil fuel combustion: emissions inventory *(Sections 3.4, 4.1.1, 4.1.7; Tables 4.1, 4.12; Appendix 4.2.1)*	The 2002 United States EPA National Emission Inventory (NEI) for criteria pollutants was used to determine emissions of NO_x and NH_3 related to fossil fuel combustion. While NH_3 is not regulated as a criteria pollutant, it is monitored and reported in the same inventory because it is a precursor to $PM_{2.5}$. The California ARB also creates an inventory, but we rely on the EPA data because it was used for modeling N deposition.
Soil emissions: biome specific rates *(Sections 4.1.2, 4.1.6, 4.1.7,; Table 4.5; Appendix 4.2.8)*	Emissions from natural land and cropland soils were based on the product of published rates (see Table 4.5 in CNA) and biome areas. The NH_3 emissions were based on data from Potter et al. (2003). The biome areas were derived from the land cover map (see Table 8 below).
Livestock emissions *(Sections 3.3.3, 4.1.3, 4.1.7; Figure 3.6; Appendix 4.2.6)*	Livestock NH_3 emissions were based on livestock populations reported in the USDA Agricultural Census and emission rates in EPA (2004).

Uncertainty and information status

- ♦ Ammonia and NO_x are both estimated largely based on indirect measures (with the exception of stationary source NO_x emissions which are actually monitored at the point of release from the facility) and compiled as part of an emission inventory by the ARB and the US EPA National Emissions Inventory. Uncertainties in these inventories can be due to either uncertainties in the general approach or in the parameter values.
    - For example, the ARB and EPA model emissions as the product of an activity level and an emissions factor. Thus, there are uncertainties both in terms of the activity levels (e.g., kilometers traveled per day) as well as the emissions factors (i.e. emissions per unit activity).
    - There is also uncertainty associated with choosing which emission processes to include in the model (e.g., running exhaust, idle exhaust, starting exhaust and resting exhaust).
- ♦ Uncertainties in the NO_x inventory vary by sector because of different methodologies.
    - In many cases, stationary sources, like power plants, are based on actual stack emissions and are thus the most certain.
    - Mobile source emissions are agreed but incompletely documented. In general, there is more evidence for emissions from gasoline vehicles than diesel vehicles.
    - There is limited evidence for area-wide sources and emissions from natural sources like wildfires.
- ♦ It is more difficult to assess uncertainty in NH_3 emissions. The ARB methodology has not been approved for public release yet. The EPA NEI does not use the draft calculations done by EPA for livestock emissions as they have not been formally approved yet either. In general, the relative certainty for NH_3 emissions is similar to NO_x across the sectors, but overall, NH_3 emissions are less certain than NO_x emissions.

• For cropland NO_x emissions (Matson et al., 1997) and cropland NH_3 emissions (Krauter and Blake, 2009; Krauter et al., 2006), the calculations are based on a single study of field measurements conducted over a relatively small area over a short period of time. Similarly, the natural land NH_3 measurements (Potter et al., 2003) are based on a single modeling study with limited validation. • Ammonia measurements are taken infrequently from soils. In addition, they are often measured or modeled from bare soil. However, it is likely that NH_3 uptake occurs in plant canopies. Thus, the estimated emissions may be overestimates of the net flux of NH_3 to the atmosphere above the boundary layer. • The livestock NH_3 emissions are based on livestock populations and livestock or facility-type specific volatilization rates. While there is high evidence for the populations, there is limited evidence for the NH_3 emissions from the various types of animals and types of manure management at facilities. While EPA (2004) methodology attempts to estimate emission rates for the various types of manure management systems, there is limited data on the number of each type of facility in California. Furthermore, because of the variability in emissions rates due to operational processes (e.g., frequency of manure collection) it is insufficient to simply know the type of facility or manure management processes used. • In the Central Valley, where the Regional Water Quality Control Board regulates almost all dairies, the type of facility can be inferred from the N management plans that are currently submitted to comply with the 2007 Waste Discharge Requirements General Order for Existing Milk Cow Dairies. For example, corral dairies would be expected to differ substantially from freestall dairies in emissions from the amounts of liquid and solid manure that they produced. • In the ARB inventory for criteria pollutants, it is unclear why there is a large increase in livestock NH_3 emissions during the 2000s as the animal populations have changed only slightly over this time period. • There is limited evidence for emissions of NO from hot desert soils (McCalley and Sparks, 2009). However, this flow is unlikely to be of significant magnitude.
♦ *See also* manure (Table 15)

Table 7. Area burned by wildfire

Indicator	Data sources and approach
Total nitrogen (N) volatilization: land based approach *(Sections 3.7.3; 4.1.1, 4.1.6, 4.1.7; Figure 4.7; Appendix 4.2.8)*	Annual estimates of acreage burned in California, subdivided by vegetation type (e.g., forest, grassland, etc.) (California Department of Forestry and Fire Protection). The typical N volatilization per unit area was based on Johnson et al. (1998).
Emissions of NO_x, NH_3, and N_2O): emissions inventory *(Sections 4.1.1, 4.1.6, 4.1.7; Appendix 4.2.8)*	Wildfire as a source of NO_x and NH_3 was estimated from the EPA 2002 National Emissions Inventory of criteria pollutants. Wildfire as a source of N_2O was based on the California Air Resources Board Greenhouse Gas Emission Inventory.

Uncertainty and information status
♦ The land area burned by wildfire is agreed but incompletely documented. The database from which the estimates are derived is compiled from various sources of inconsistent quality. This, however, does not detract from their overall value; the California Department of Forestry and Fire Protection considers these data of "high quality" (FRAP, 2010). The questions of quality only affect variables not of interest in this assessment.
♦ The nitrogenous products of wildfire include NO_x, N_2O, NH_3, and N_2. The relative amounts depend on the burn conditions, but the predominant product is N_2, which is determined by difference. That is, most sources focus either on a particular gas or on the total N volatilized. The emissions of the inventoried gases are tentatively agreed by most. ♦ Using the estimate of Johnson et al. (1998) for total N volatilization on an areal basis during wildfire, the difference of the total N loss and the sum of the three other gaseous products is N_2. In terms of N mass balance, the areal rate of N_2 emissions is the crucial term, but is suggested but unproven.
♦ *See also* nitric oxide + nitrogen dioxide and ammonia (Table 6).

Table 8. Land use

Indicator	**Data sources and approach**
Historic land cover and use change: urbanization, agricultural relocation, intensification *(Section 3.7; Figure 3.4)*	Department of Conservation Farmland Mapping and Monitoring Program (http://www.conservation.ca.gov/dlrp/fmmp), Sleeter et al (2008; Sleeter et al., 2010), and USDA Agricultural Census (1977-2007) were used to determine the extent of agricultural land use change.
Current land use map *(Map 4.1)*	The mapping was an amalgam of data sources for years ranging from 1997 to 2007 for different land cover types. The natural lands component was based on the vegetation mapping by the California Department of Forestry and Fire Protection. The cropland was based on the land surveys of the California Department of Water Resources surveys, supplemented where necessary with data from the Department of Pesticide Regulation. The urban boundaries were based on the Department of Conservation Farmland Mapping and Monitoring Program.
Uncertainty and information status	
The extent of land use change is speculative. Multiple efforts document land use change, including: The Department of Conservation's Farmland Mapping and Monitoring Program, the USDA Agricultural Census, and independent primary research. Each uses a different method of calculating land use – ranging from visual surveys to mail-in surveys and remote sensing – and the conclusions derived from the various data sources differ as well. It appears that the major source of uncertainty arises from collection and categorization errors, as sources categorize land use in various ways and to differential levels of specificity. Identification of trends thus depends on nonstandard categorization of land use that is asymmetrical. The USDA Agricultural Census and the California Department of Conservation Farmland Mapping and Monitoring Program (FMMP) use the National Resource Conservation Service's farmland categories. However, even when the same categorization is used, a misunderstanding of the categories can lead to erroneous conclusions (Hart, 2003). A second source of uncertainty is that the geographic scale sampled is not uniform across data sources. Notably, the Department of Conservation's FMMP only surveys approximately 50% of California's land area.	
♦ An important source of uncertainty in land use change for understanding N is the fact that only new remote sensing data are explicitly spatial. The impact of land use change on California's N cycle will largely reflect climate, soils, and changes which are site specific. Without spatially explicit information on land use change and the new and previous management regimes, the consequences of land use changes are difficult to accurately predict. ♦ A source of uncertainty in the land use map is the timescale. Because the DWR has only surveyed some counties infrequently, there is more than a decade difference between counties in the survey year. Both inter-annual variability in annual crops as well as long-term trends in annual and perennial crops are sources of uncertainty in creating a land use map for a single year.	

Table 9. Nitrogen storage

Indicator	Data sources and approach
Repeat sampling *(Section 4.1.2; Appendix 4.2.11)*	DeClerck et al. (2003) report changes in total soil nitrogen (N) in cropland over a 55 year period; this was converted to an annual basis assuming a bulk density of 1 g soil cm^{-3}.
Mass balance *(Sections 4.1.1, 4.1.2, 4.1.4, 4.1.6, 4.1.8, 4.1.9; Appendix 4.2.7, 4.2.9, 4.2.10, 4.2.11)*	N storage in the three land subsystems (cropland, natural land, and urban land) as well as the two water subsystems (surface water and groundwater) was calculated as the difference between inputs and outputs.

Uncertainty and information status
♦ Because of the large stocks of N in soils and vegetation, it is difficult to measure changes in N storage over short periods of time. However, with repeated sampling over decades, trends in storage can be detected. • It is provisionally agreed by most that N storage is occurring in cropland ecosystems in California. It is likely that N has been stored in cropland because of measured increases in soil N (e.g., DeClerck et al. 2003). • While no data have been collected in California, it is well established that turfgrass soils have the capacity to increase N storage for decades (e.g., Raciti et al., 2011). Research in California has demonstrated carbon storage in turfgrass soils though they did not measure N (Townsend-Small and Czimczik, 2010).
♦ For the three land-based subsystems, N storage is determined by mass balance. However, there are several lines of evidence that are consistent with increasing N storage. • Because of the increased acreage of perennial crops (e.g., Kroodsma and Field, 2006), there is likely N storage occurring in the aboveground biomass in cropland as well. • Based on ecosystem models, there is limited evidence that carbon is accumulating in natural land ecosystems (Potter, 2010). Because of the strong link between carbon and N, it is very likely that N is being stored as well.
♦ *See also* solid waste (Table 14), groundwater N (Table 16), and surface water N (Table 17).

Table 10. Harvested nitrogen

Indicator	Data sources and approach
Crop production *(Sections 3.2, 4.1.2, 5.1.1.1; Table 4.4; Figure 5.1.4; Appendix 4.2.5)*	Annual surveys of crop acreage and production in California are conducted at the county level by the California County Agricultural Commissioners. These data are compiled at the statewide level by the California office of the USDA National Agricultural Statistics Service (NASS). The USDA NASS also conducts an annual survey of major crops in every state. The former was used in the assessment since it includes all crops, while the latter only includes ~50 commodities. Both the NASS Agricultural Census and California Department of Water Resources (DWR) are additional sources of data for crop acreages, but neither provides crop production data for the majority of California crops.
Crop nutrient content *(Sections 3.2.3, 4.1.2, 5.1.1.1; Table 3.1; Figure 5.1.4; Appendix 4.2.5)*	Crop nutrient and moisture content are not measured in any comprehensive way in California. The most complete database is the United States Department of Agriculture Crop Nutrient Tool. The tonnage of nitrogen (N) harvested is calculated as the product of tonnage harvested, N content, and dry matter content.

Uncertainty and information status
♦ The NASS annual surveys and NASS statewide compilation of California County Agricultural Commissioners' reports are the major sources of information on crop acreage. The two sources show a high level of agreement (R^2 = 0.99) when crops are clearly identified. However, there are inconsistencies for several important commodities. • NASS also conducts a more detailed 5 year Agricultural Census. While this source is considered the most reliable for crop acreage, it does not include crop production statistics for most crops in California. • A large fraction of the acreage, especially of crops grown for livestock feed, is not clearly identified. For example, the categories used by the NASS statewide compilation of California County Agricultural Commissioners' reports do not specify the type of hay. In some cases, a more detailed description of hay is provided at the individual county level, however, this information is lost when the data are aggregated at the state level. • In the annual surveys conducted by NASS all non-alfalfa hay is lumped together, while in the more detailed Agricultural Census that NASS conducts every five years, the non-alfalfa hay is partitioned into tame hay and small grain hay. Because these crops cover such large acreages and production, and N management practices differ among types of hay, it is important to distinguish between types of hay. • In some cases, there is also a discrepancy between the reported acreage and production. For example, there are more than 60,000 ha in the category "Field Crops, Unspecified," but only about 10,000 Mg of productivity reported on this acreage which is too low for any harvested crop.
♦ The most comprehensive source of crop nutrient and dry matter content is the USDA Crop Nutrient

Tool. This database is a compilation of many published sources (33 for N and 12 for moisture) and contains information on a wide variety of food and forage crops. While this dataset is fairly comprehensive in the crops included, the data are somewhat dated as the median age of the references is 1984. For grain crops the nutrient and moisture content are well established, but for many fruits and vegetables the data are speculative.

- Changes in nutrient content over time are speculative. For example, Davis et al. (2004) reported a small (6%), but significant, decline in protein content in vegetable crops between the 1950s and the 1990s. It is unclear how the dramatic changes in cultivars and management in the last few decades may have altered crop nutrient and dry matter content.
- The N content of some crops is highly elastic and depends on growing conditions. Luxury consumers will increase uptake when it is available (e.g., at higher rates of N fertilization). Greater uptake can translate into greater concentrations of N plant parts.
- For fresh fruits and vegetables (as well as silage), a bigger source of error may be the dry matter content. For example, the dry matter content of lettuce in the database varies from 4% - 6% which represents a difference of 50%.
- Dry matter content in grain and hay crops is well established. One potential source of error is the stage at which hay crops are harvested. We assumed that all crops were harvested at the mature stage when N content is lowest. For small grain hays like oats and wheat, the database reports values 25% lower at the mature stage compared to earlier cuts, with even larger differences reported for some tame grass hays. The timing of the harvest presents a tradeoff between yield and quality with yield increasing and N content decreasing with maturity. The timing of the harvest may also depend on climate as late spring or early fall rains can push the harvest earlier or later.

♦ The Department of Water Resources land use surveys, used to develop the land use map, do not clearly distinguish among feed crops. For example, over 100,000 ha of field crops and almost 500,000 ha of grain and hay crops are not identified as a particular crop. The lack of specificity in these forage crops makes it difficult to calculate N harvest in the crops, as well as to estimate fertilization rates and other processes on large acreages of California cropland.

♦ Pasture is an agricultural land use whose definition varies by source and it is not always clearly distinguished from rangeland. However, we assume that there is no plant product harvested from pasture.

- For the NASS Agricultural Census, pasture is agricultural land that is managed but could not be planted with crops without improvements. It can support livestock, but is not necessarily grazed at any particular frequency.
- According to the NASS Agricultural Census, approximately 300,000 ha, or 5%, of the 5.5 million ha of pastureland in California is irrigated. This compares to the 376,000 ha of pasture based on our land use map using data from the Department of Water Resources.
- Currently, it is likely that most pastureland is minimally managed, with limited seeding of desirable species like clover and little fertilizer applied.

♦ It is likely that commodity boards and some processors take measurements of their crops, but these data are not publically available. The California Department of Food and Agriculture regularly measures contaminants, like pesticides, on produce, but not nutrient or moisture content.

Table 11. Animal production

Indicator	**Data sources and approach**
Animal populations *(Sections 3.3.1, 4.1.3, Figure 3.6; Appendix 4.2.5)*	The National Agriculture Statistics Service (NASS) Agricultural Census from 2002 and 2007 was used to calculate annual production data for meat producing animals. For dairy cattle and layers, inventory data from the NASS annual surveys were used. Cattle populations are also inventoried at the county level by the California Department of Food and Agriculture (CDFA) and at individual dairy facilities by the Regional Water Quality Control Boards, as well as the CDFA Milk Pooling Branch. Horses are included in the NASS Agricultural Census, but the population very likely only includes working animals. Surveys conducted by the American Veterinary Medical Association (AVMA, 2007) were deemed a better source.
Nutrient content *(Section 4.1.3; Appendix 4.2.5)*	With the exception of milk, there is no agreed upon nitrogen content values for most animal products; the most comprehensive source is NRC (2003). Another often cited source for animal products in watershed nitrogen (N) budgets is from a conference proceedings (Van Horn, 1998).

Uncertainty and information status
♦ Livestock populations, with the exception of horses, are well established. • Both the NASS Agricultural Census and the CDFA report cattle populations and the statewide herd size differ by less than 10%. • In the Central Valley, where more than 90% of the dairy cows are located, the herd size at every regulated dairy is also reported to the Region 5 Water Quality Control Board. Similarly, in Region 8, the Water Quality Control Board collects herd size information by dairy facility. • Outside these regions, the only source for dairy facility locations (but not herd size by dairy) is from the Department of Food and Agriculture Milk Pooling Branch.
♦ The N content of milk is well established.
♦ The N content of other animal products is tentatively agreed by most. While the N content of food products is readily available, the N content of the entire animal product, including the egg shell and other inedible portions, are needed. Because of limited evidence, it is difficult to evaluate how much uncertainty there is in N content.
♦ We have assumed that there is no spoilage of livestock feed in California. Therefore, all of the imported grain and harvested feed crops are consumed by animals. There is limited evidence for spoilage rates. A widely cited value is 10% of non-hay, non-silage crops in Jordan and Weller (1996). However, it is not clear how this value was estimated. Because most of the feed crops grown in California are hay or silage crops, only the imported grain corn would be subject to spoilage. However, a 10% spoilage loss of imported feed would represent ~20 Gg N. Further, there is limited evidence for the fate of spoiled livestock feed.

Table 12. Organic nitrogen reuse

Indicator	Data sources and approach
Manure sales *(Section 4.1.3; Appendix 4.2.6)*	The tonnage of manure sales from 2002-2007 is included in the annual surveys at the county level by the California County Agricultural Commissioners. These data are compiled at the statewide level by the USDA National Agricultural Statistics Service (NASS). The manure N and moisture content was based on Pettygrove (2010).
Manure composting *(Sections 3.2.2, 3.3.3; Table 3.3)*	The CalRecycle Solid Waste Information System provides information on the location and types of materials used at composting facilities, but not information on tonnages of materials actually composted.

Uncertainty and information status
♦ The extent of organic nitrogen (N) use as a primary fertilizing material or as a soil amendment is largely speculative. Sales of organic N products, with the exception of manure, are not tracked and data on distribution and rates of use for all organic N sources are largely unavailable. • Manure sales are tracked as part of the NASS statewide compilation of California County Agricultural Commissioners' reports. While the type of manure is not reported, based on location and the close relationship between milk production and manure production, it was assumed that this was solid manure similar to corral scrapings sold from dairy farms. The ultimate fate of this dairy manure is unknown, but it is likely composted to some degree either before or after sale and used as an organic amendment. • Manure from beef feedlots (Harris Ranch and Imperial County) is very likely composted and sold as fertilizer. Composting facilities require permits from CalRecycle and the facility locations and maximum tonnages of materials are available in the Solid Waste Information System. However, the actual amounts and types of materials passing through these facilities are not tracked. Nor is the destination or use of the composted product tracked. • Manure applications on cropland, managed as part of Central Valley Dairy is limited to between 1.4 and 1.65 times crop uptake. The amount of manure applied is collected by each dairy for regulatory compliance, but the data are not currently available to the public.
♦ Indirect indicators support the conclusion that organic N is increasingly demanded and available in California. Increased acreage in organic farms, urban waste diversion programs, and biosolids production suggest that organic N materials are more available than ever. Understanding where and at what rate they are applied is, however, speculative for the most part.
♦ *See also* solid waste (Table 14) and manure (Table 15)

Table 13. Agronomic nitrogen use efficiency of crops

Indicator	Data sources and approach
N use efficiency (*Section 3.2.3; Table 3.1; Appendix 3.1*)	Compilation of peer reviewed literature (Table 3.1)
Uncertainty and information status	
♦ Measures of agronomic nutrient use efficiency (NUE) are ratios of plant nutrient uptake to nutrients applied. Sophisticated methods have been developed, including using isotopes, to precisely determine how much of the applied nitrogen (N) gets into the plant. However, methods that are able to differentiate between the sources of N have to be performed under controlled conditions in a research plot. How closely these values reflect NUE in field conditions is uncertain.	
♦ Comparatively few controlled experiments of NUE have been performed on the breadth of California crops under irrigated Mediterranean conditions (Table 3.1). • Historically, NUE has been the focus of agronomists and there are good data measuring NUE in cereals, especially rice, dating back into the 1960s. • Although there have been a significant number of N rate trials on other crops, often the methods are inadequate to determine fertilizer NUE. For example, some trials for tree crops do not include a zero-N plot. Without a zero-N plot to compare yields and N harvested, it is impossible to differentiate between yield derived from N mineralized from the soil or fertilizer N applied.	
♦ There is uncertainty about the carryover and availability of N not assimilated from one season to another. A fraction of fertilizer N applied is sequestered by the soil and may become plant available in subsequent seasons. However, studies using isotopic methods capable of measuring uptake over multiple seasons are rare. In high rainfall areas, the excess N may be leached. But in low-rainfall areas with efficient irrigation and deep-rooted trees, the fate of N is more uncertain.	

Table 14. Solid waste

Indicator	Data sources and approach
Landfill surveys *(Section 4.1.4; Table 4.10; Appendix 4.2.7)*	CalRecycle conducts surveys of materials disposed of in landfills every three years. Nitrogen (N) tonnage was calculated based on the typical N content of organic materials (see Table 4.10). There are no data sources for the disposal of synthetic N in landfills.
Biosolids *(Section 4.1.5; Appendix 4.2.7)*	CalRecycle reports the tonnage of biosolids based on the estimates of the California Association of Sanitation Agencies. The N content was based on Metcalf and Eddy (2003).

Uncertainty and information status
♦ There is limited evidence on the ultimate fate of products containing synthetic N. Both nylon and acrylonitrile butadiene styrene (ABS) plastic are recyclable, but the rate of recycling is unknown. Recycling rates are likely higher in particular sectors, like automobiles and electronic waste. Some products, like polyurethane, are incorporated with other materials and are difficult to recycle. The lifespan of most synthetic N products is years to decades, with the non-recycled waste disposed of in landfills.
♦ The wet tonnage of green waste disposed in landfills is reported by CalRecycle based on surveys of arriving materials. • There is medium evidence for the dry tonnage of N in green waste. • Food waste has been well characterized. Food waste can occur in many ways, but there is no standard definition or accounting system other than measuring what arrives in the landfill. Thus, food waste is a mixture of inedible materials (e.g., watermelon rinds, bones. etc.), processing waste, spoilage or food in retail settings past its due date, and uneaten food. • Yard waste is composed of materials like grass clippings, senesced leaves and wood which differ by more than an order of magnitude in N content. Because there is not a breakdown of yard waste into its various constituents, it is difficult to assign a typical N content. • There is limited evidence for the N content of wood products other than lumber. While derived from wood, there is limited evidence of whether N is removed during the manufacturing process for these products.
♦ It is tentatively agreed by most that a growing number of waste agencies are diverting green waste, including both yard waste and food waste, from landfills to composting operations in California. However, the magnitude of N diverted and the fate of this compost is suggested but unproven. In addition, there may be some issues with the quality of the ultimate product as there can be other materials (e.g., plastics) or chemicals mixed in during the collection of the organic materials.
♦ The tonnage of biosolids is tentatively agreed by most. The statewide tonnage is reported by CalRecycle based on data from the California Association of Sanitation Agencies. However, the reported N content can vary widely. The fate of these materials is also tracked and the vast majority is land applied with alternative daily cover at landfills a secondary use. While these materials are tested for nine regulated pollutants and pathogens, there is some concern about using biosolids as a nutrient

	amendment on cropland, especially food crops.
♦	It is agreed but incompletely documented that emissions from landfills is an insignificant flow of N. Landfills are permitted to be lined such that leaching is minimized. However, landfill liners degrade over time and may leak N-rich effluent into groundwater. Because liner leaks form thin plumes of NO_3^-, they are often difficult to detect with monitoring equipment. It is well established that emissions of N_2O are fairly insignificant. However, the magnitude will depend on the type of cover used to control nuisance. Therefore, the most likely fates of N in a landfill should be storage or denitrification to N_2. There is limited evidence for N_2 emissions, although in their compilation of Air Pollution Emission Factors (AP42), the EPA suggests as much as 5% of landfill gas is N_2. Based on the reported amount of landfill gas in the California Air Resources Board Greenhouse Gas Emission Inventory, landfill N_2 emissions would be over 200 Gg N yr^{-1} at 5% N_2 emissions, significantly higher than our estimate of landfill storage.

Table 15. Manure

Indicator	Data sources and approach
Manure production *(Sections 3.2.2, 4.1.3; Appendix 4.2.6)*	Manure production can be estimated directly based on standard values from the American Society of Agricultural Engineers (ASAE) or as the difference between estimated feed demand from ASAE and the measured production of animal products (see Table 4.7).
Manure composting *(Section 3.2.2)*	The CalRecycle Solid Waste Information System provides information on the location and types of materials used at composting facilities, but not information on tonnages of materials actually composted.
Gaseous emissions *(Sections 4.1.3, 4.1.7; Appendix 4.2.6)*	Livestock NH_3 emissions were based on livestock populations reported in the USDA Agricultural Census and emission rates (EPA, 2004).
Fertilization with manure (*Sections 3.2.2, 4.1.2)*	There are no data sources for the actual use of manure as fertilizer.
Uncertainty and information status	
♦ Because of new regulations taking effect in the Central Valley, every regulated dairy will be completing a nutrient management plan (NMP) which aims to track nitrogen (N) across the entire dairy operation. While it is still not clear in what form these data will be publically available, in theory, the NMPs will be an extremely valuable source of information about N. While all flows of N will be quantified, some will be more reliable than others.	
♦ Manure N production rates depend on the breed of cattle and the efficiency of milk production. • There is no comprehensive population numbers by breed. However, in the Central Valley, the predominant breed is reported as part of nutrient management plans to comply with the 2007 Waste Discharge Requirements General Order for Existing Milk Cow Dairies. • Using the standard values from the American Society of Agricultural Engineers, the efficiency of dairy production is ~25%. However, if the efficiency were 30%, there would be 20 Gg N more in milk and less manure N produced annually with the same feed intake.	
♦ The livestock NH_3 emissions are based on livestock populations and livestock or facility-type specific volatilization rates. While there is high evidence for the populations, there is limited evidence for the NH_3 emissions from the various types of animals and types of manure management at facilities. While the EPA (2004) methodology attempts to estimate emission rates for the various types of manure management systems, there is limited data on the number of each type of facility in California.	
♦ The extent of organic N use as a primary fertilizing material or as a soil amendment is largely speculative. Sales of organic N products are not tracked and data on distribution and rates of use for all organic N sources are largely unavailable.	

	• Potential manure production is calculated based on dairy herd sizes for several counties as part of their annual Agricultural Commissioners' report. The ultimate fate of this dairy manure is unknown, but it is likely composted to some degree either before or after sale and used as an organic amendment. • Manure from beef feedlots (Harris Ranch and Imperial County) is very likely composted and sold as fertilizer. Composting facilities require permits from CalRecycle and the facility locations and maximum tonnages of materials are available in the Solid Waste Information System. However, the actual amounts and types of materials passing through these facilities are not tracked, nor is the destination or use of the composted product tracked. • Manure applications on cropland, based on regulations of the Central Valley Regional Water Quality Control Board, are limited to between 1.4 and 1.65 times crop uptake. The amount of manure applied is collected by each dairy for regulatory compliance, but the data are not currently available to the public.
♦	Estimating fertilization rates is complicated by the large amount of manure produced in the state. More likely than not, manure N replaces synthetic fertilizer as the source of nutrients for many of the acres of forage crops near dairies. However, it is not clear if this replacement is complete or if these crops still receive some inorganic fertilizer. Further, a large fraction of solid manure appears to be composted to some degree and applied as an organic amendment to soils. The N embodied in the manure may or may not be accounted for as part of nutrient management plans.

Table 16. Groundwater nitrogen

Indicator	Data sources and approach
Leaching fraction and leaching amount *(Section 4.1.2; Appendix 4.2.10)*	Compiled public data that reported either the fraction of fertilizer applied, or the amount of N leached in irrigated California cropland soils (see Appendix 4.2.10).
Denitrification (Section 4.1.9; Box 4.4; Appendix 4.2.10)	Denitrification was estimated with three approaches: (1) assuming a half-life of nitrate of 80 years (Landon et al., 2011) and historical estimates of nitrogen (N) inputs to groundwater, (2) multiplying estimates of the volume of groundwater recharge (CA DWR, 2003) by a fixed denitrification rate of 0.04 mg N L^{-1} yr^{-1} (Landon et al., 2011), and (3) assuming a fixed fraction of N inputs to groundwater is denitrified (Seitzinger et al., 2006; Leip et al., 2011).

Uncertainty and information status
♦ Leaching of N occurs when excess water transports excess N below the rooting zone. The mass balance calculated the load of N in leaching in two ways: (1) multiplying measured N concentrations in the leachate by the modeled volume of recharge volume, and (2) calculating the mean of the percentage of applied fertilizer that was reported as leaching. These two metrics differed by 120 Gg yr^{-1}, which is one of the largest sources of uncertainty in the mass balance. Assuming only a small soil storage term (5 Gg N yr^{-1}) from repeated sampling of cropland soils 55 years apart and calculating leaching by difference would suggest that the higher estimate calculated with the first method is the better estimate. ♦ There is limited evidence for the fraction of fertilizer that leaches and the N concentration in leachate, but these measurements are typically made completely independent of each other. Both of these measurements vary in time and space based on the crop type, soil characteristics, and agronomic practices. In many mass balances, the leaching term is calculated by difference because of the difficulty in measuring it.
♦ The sampling of groundwater wells for NO_3^- is not a random sample of groundwater basins which could bias the estimates of the total amount of N in groundwater. If the samples were more likely to be taken in areas with NO_3^- contamination or at shallower depths, the estimate of the median groundwater concentration would be higher than the actual median.
♦ While there were multiple approaches to estimating groundwater denitrification, there are relatively few measurements from California to choose which approach is preferable. Therefore, the estimate of this flow is tentatively agreed by most.
♦ Drainage can affect the fate of N leaching through soils. The presence of drainage can divert recharge to surface water instead of groundwater, leading to an overestimate of the N flow to groundwater. However, there is low agreement on how to define and survey drainage.
♦ The most recent national estimate of drained land suggests that over 1 million ha are present in California (Pavelis, 1987); however, it is unclear what the exact definition of "drainage" is. The acreage with subsurface drainage is likely considerably lower than this estimate, largely concentrated

	in Imperial County and in the west side of the San Joaquin Valley. While there is no centralized database mapping the location of drained lands, it is likely that tile drained lands predominantly occur in these closed basins with no drainage to the ocean. With the exception of the Grasslands Bypass project, it is very unlikely that there are any other major sources of NO_3^- to rivers from subsurface tile drainage in California.
♦	It is very likely that surface agricultural drains are a major source of NO_3^- to rivers in California as some of the highest concentrations of NO_3^- (reported in Kratzer et al., 2011, Sobota et al., 2009) were observed in small creeks that are dominated by irrigation return flows during the summer (e.g., Orestimba Creek).
♦	We assumed no transport of N between surface water and groundwater. While it is well established that water flows bi-directionally between rivers and groundwater in California, there is limited evidence for the magnitude of N transport. It is also well established that the hyporheic zone, where groundwater and surface water meet, is a particularly active location for N transformations such as denitrification.
♦	*See also* Nitrous oxide (N_2O) and dinitrogen (N_2) gas (Table 5)

Table 17. Surface water nitrogen

Indicator	Data sources and approach
River discharge N *(Section 4.1.8; Appendix 4.2.9)*	For large rivers in California, nitrogen (N) concentrations and flow data are monitored by the US Geological Survey (USGS). While the flow data are typically measured hourly, the N concentrations are measured weekly to monthly. Thus, the N load is calculated by modeling (e.g., LOADEST) to be able to infer the values in between sampling points. For California, published sources with river N discharge data include Sobota et al., 2009, Schaefer et al., 2009, and Kratzer et al., 2011. N discharge in smaller watersheds is monitored sporadically around the state, but two potential sources of data are the Surface Water Ambient Monitoring Program of the State Water Resources Control Board and the California Water Quality Monitoring Collaboration Network.
N retention *(Section 4.1.8; Appendix 4.2.9)*	Rivers and lakes have the ability to retain N. That is, N flowing in from rivers does not flow back out. Retention can be estimated by mass balance (i.e. the difference in N inputs to rivers and the N load carried to the ocean). Retention can be partitioned into gas losses and burial in sediment based on global estimates of denitrification (Seitzinger et al., 2006).

Uncertainty and information status

- ♦ The N load in major rivers in California is well established.
    - Bias in the LOADEST model used to calculate annual N loading from periodic water samples is a minor source of uncertainty. In general, the model tends to overestimate at low flows and underestimate at high flows.
    - A larger source of uncertainty is inter-annual variability. Unlike agricultural production and fossil fuel combustion which vary by less than 25% from year to year, river N loads fluctuate dramatically; largely related to variability in precipitation. Based on the data for 1975-2004 in Kratzer et al. (2011), there is a five-fold difference in the Sacramento and Santa Ana Rivers and a 10-fold difference in the San Joaquin River between the highest and lowest annual loading value.
- ♦ While the major rivers in California are monitored by the USGS, many of the small coastal watersheds are not. There is no centralized database for water quality monitoring by other agencies or non-governmental organizations. The Surface Water Ambient Monitoring Program at the State Water Resources Control Board and the California Water Quality Monitoring Collaboration Network are potential sources of data, but were not used in the mass balance calculations.
- ♦ There is high potential for N storage in California reservoirs, however information is limited and differences in calculations make broad generalizations difficult. While the buildup of sediment in reservoirs is well established, the fate of N in reservoirs is speculative.
    - The most common approach to examining the effects of reservoirs on N is to calculate N retention as riverine N inputs minus dissolved N outputs. Thus, both sedimentation and denitrification contribute to N retention.
    - Harrison et al (2008) reported N retention an order of magnitude higher in reservoirs

compared to lakes.

- There is high potential for denitrification in reservoirs, but there are relatively few empirical studies separating N retention between sediment burial and denitrification. The most thorough review of denitrification (Seitzinger et al. 2006) lumps lakes and reservoirs together. However, if N retention is 10 times higher in reservoirs, it is not clear if denitrification would be similarly higher.

Table 18. Dissolved nitrogen in waste discharge

Indicator	**Data sources and approach**
Nitrogen discharge *(Sections 3.6, 4.1.5; Appendix 4.2.7)*	The flow of effluent and nitrogen (N) concentration are monitored by most regulated dischargers in the state. The data are available from the Regional Water Quality Control Boards, but often only in hard copy at regional offices. For dischargers to surface water the United States EPA should also receive the same data, but access to this information is unclear.

Uncertainty and information status
♦ In California, there are approximately 900 regulated wastewater treatment facilities that discharge to land or surface water. Availability of monitoring data varies and is dependent on the permitting agency. • In practice, the Regional Water Quality Control Boards issue permits regardless of the location of discharge, even though discharge to surface waters is regulated by the Clean Water Act under the authority of the United States EPA. • Surface water permits (i.e. National Pollutant Discharge Elimination System (NPDES)) are renewed every five years and typically have more extensive monitoring compared to the land discharge permits (Waste Discharge Requirement NON15) subject to the California Water Code. • Almost 300 facilities have permits to discharge to surface water (including the Pacific Ocean), but this includes 44 of the 50 largest facilities in the state. As there are typically more stringent regulatory and monitoring requirements for facilities that discharge to surface water, there is more evidence for the N discharge from large facilities compared to small facilities. However, data suggest (see Figure A4.2.1 in Appendix 4.2.7) that there is a strong relationship between size of facility and N discharge across the five order of magnitude range in facility size. • Currently, only Region 2 (San Francisco Bay) has an electronic database that provides easy access to monitoring data for wastewater treatment plants, although most other regions are aiming for this in the near future.
♦ N concentrations in wastewater discharge are well established with ranges of values published in wastewater engineering textbooks. • The frequency of monitoring (monthly) for most facilities is largely sufficient for estimating N loads. San Francisco is the only large city that has mixed stormwater and sewage treatment which results in dramatically different flows in winter and summer. • Most facilities without N removal treatment only measure ammonia, resulting in limited evidence for the concentration of other forms of N. Based on the available data, nitrate and organic N contribute 10% - 20% of the total N discharge. • Facilities with N treatment typically only measure NO_3^-. There is limited evidence for the amount of dissolved N that is actually removed. While the technology exists to remove up to ~80% of the N, in many cases facilities are only converting NH_3 to NO_3^- without converting significant quantities of N to inert N_2 gas. On average, the NO_3^- concentrations at facilities in California with N treatment were 66% less than the NH_3 concentration at facilities without N treatment, but there was high variability among facilities.

- ♦ Food processors also discharge N, predominantly as organic N. Like wastewater treatment plants, these facilities are considered point sources and can be authorized to discharge to surface water with a NPDES permit, to land with a NON15 permit, or through industrial stormwater permits. Unlike wastewater treatment plants where there are predictable N concentration values and discharge, food processing facilities vary by orders of magnitude in N concentrations and can be highly seasonal in the magnitude of discharge. The monitoring data are less accessible for food processing plants, but the limited evidence suggests that some large processors annually discharge as much organic N as a city of 100,000 people.

Table 20. Nitrogen in drinking water

Indicator	Data caveats and sources of uncertainty
Historic trends in groundwater nitrate *(Section 5.2.1.5)*	Despite reporting significant increases in groundwater nitrate over time, Boyle et al. (2012) note that it is difficult to establish accurate historic trends because the data used in their analysis contained a relatively small number of samples prior to 1990 which was comprised mostly of public supply wells, and a large increase in the number of samples from domestic and irrigation wells at dairies beginning in 2007. Since public supply wells tend to be deeper and have somewhat lower nitrate concentrations than the shallow wells used for domestic and agricultural purposes, this change in data sources would tend to exaggerate the increasing trend particularly after 2007 (Figure 5.2.5). Acknowledging this caveat, the overall trend was still increasing throughout the study area prior to 2007.
Future projections of groundwater nitrate *(Section 5.2.1.5)*	The nitrate transport model projections reported by Boyle et al. (2012) suggest that groundwater nitrate concentrations will increase in the future, but the data exhibit significant spatial and temporal uncertainty. This uncertainty is due to inherent variability in nitrogen (N) loading (i.e. N losses to the environment) across different land use and source types (e.g., agricultural crops, septic systems, manure lagoons). But while the model may not forecast future groundwater nitrate levels with a high degree of accuracy, it is still seen as a useful tool for evaluating the impact of alternative land use management scenarios that might be adopted in the future.
Proportion of wells with elevated nitrate *(Section 5.2.2.2)*	Data compiled from the California State Water Resources Control Board suggest that 9.8% of approximately 16,000 wells tested had at least one value greater than the drinking water maximum contaminant levels (MCL = 10 mg nitrate-N L^{-1}), and 5.8% had median levels greater than this value (Figure 5.2.5). The proportion of wells with average and maximum values exceeding the MCL and median values >3 mg nitrate-N L^{-1} also varied across the state. These results should be thought of as general indicators, as the wells in this database included many types of wells, some of which were drilled specifically to characterize areas thought to have high nitrate levels.
Exposure to groundwater nitrate *(Section 5.2.2.2)*	While efforts are underway to compile service maps and information on the number of people served by water systems of various sizes (e.g., self-supplied, public and community water systems, etc.), at present such data are very limited for many counties in the state (C. Wolff, personal communication). As such, accurate estimates of the number of people in each county and statewide that are at risk of exposure to high nitrate drinking water are difficult to make at present.

Table 21. Nitrous oxide emissions from agricultural soils

Indicator	Data sources and approach
IPCC Default Emission Factors (EFs) for direct and indirect N_2O emissions *(Section 5.4.3)*	Reported by IPCC (2006) as part of their guidelines for Tier 1 inventory methods.

Uncertainty and information status
♦ The IPCC's default EFs for direct and indirect N_2O emissions are derived from a large number of field experiments (>100 studies) conducted globally in recent decades. Considerable variation in experimental N_2O flux measurements averaged across many environmental conditions, geographic and temporal scales, and cropping systems introduces a high degree of uncertainty in the IPCC default EFs for N_2O. For example, the uncertainty in direct N_2O emissions from agricultural soils ranges from 0.003 to 0.03 kg N_2O – N per kg N applied. Despite this caveat, emissions calculations based on default EFs remains a useful accounting method for national and regional greenhouse gas

Table 22. Nitrogen-related air pollutants

Indicator	Data sources and approach
Historic trends in NO_x, O_3 and PM2.5 *(Section 5.3.2 and Section 5.3.3)*	Reported by Parrish et al. 2011 using data from monitoring stations in the South Coast Air Basin.
Spatial trends in NH_3 *(Section 5.3.2)*	Reported by Clarisse et al. (2010, 2009) using satellite data retrieved from an infrared atmospheric sounding interferometer (IASI).
Spatial trends in $PM_{2.5}$ *(Section 5.3.2)*	Reported by van Donkelaar et al., 2010 who compared surface measurements of $PM_{2.5}$ with satellite data retrieved from a moderate resolution imaging spectroradiometer (MODIS) and multi-angle imaging spectroradiometer (MISR).
Effects of O_3 on crop yields *(Section 5.3.6.2)*	Reported by Grantz and Shrestha (2005) using data from O_3 dose response models.

Uncertainty and information status
♦ Historic trends in these air pollutants in California are based on data originally reported by Alexis et al., 1999 and Cox et al., 2009. The data for each pollutant are available from the CARB at http://www.arb.ca.gov/aqd/almanac/almanac99/appendix.htm. While the overall decline in criteria air pollutant levels is relatively certain, the rate of decline varies considerably among regions. This spatial variability is influenced by a wide range of factors including emissions sources, economic activities, seasonal and climatic differences, and the relative quantity of each primary
♦ Satellite data on spatial trends in NH_3 were drawn from a dataset with global geographic coverage. The mapping procedure used by van Donkelaar et al., 2006 is based on the linear relationship between the brightness temperature difference and the retrieved total NH_3 column. Their regression analysis on a wide selection of regions at different times of the year showed that 1 K correspond to 15± 7.5 mg m^{-2} of NH_3 with a confidence interval of 80%.
♦ A comparison of measured and satellite-estimated $PM_{2.5}$ indicated a statistically significant relationship with an uncertainty of ± (1 μg/m^3 or 15%).
♦ Uncertainty in yield losses by crops due to O_3 can result from variability in both the level of O_3 exposure and the sensitivity of the crop.

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