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Connecting nitrate concentrations in shallow groundwater to nitrogen mass balances in California dairy farms

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Submitted by
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Abstract

High nitrate concentrations in groundwater in the Central Valley (CV) in California, US, present a risk for human health and the environment. An approach to understand and investigate nitrogen fluxes are mass balances. This work assesses the suitability of mass balances to estimate nitrate concentrations in groundwater based on farm reports in comparison to monitoring well samples.

Dairy farms in the CV are required to report the amount of nitrogen applied and harvested for each field. This data was used to create mass balances and estimate nitrate leakage to groundwater. Long-term groundwater samples from eight dairy farms with shallow groundwater table in the CV were compared to the estimated leakage from mass balances. Statistical methods and a linear mixed model were applied. Additionally, data from the entire CV area was tested for a shorter time period.

The leakages estimated by the mass balances are within the range of the groundwater samples in most cases but vary significantly for each dairy farm. Additional parameters such as depth to ground water table, concentrations of Manganese, Dissolved Oxygen and texture were analyzed as potential influencing factors but show no significant impact on farm level. However, on higher level, e.g. for the entire CV, the analyzed factors show some significance.

Possible reasons for the identified discrepancies are measurement uncertainties, inconsistencies of reported data from the farmers and the assumptions made to the mass balances such as ammonia emissions. Furthermore, the mass balance approach integrates the nitrogen flux spatially while the monitoring wells provide only point data.

Keywords: nitrate leaching, groundwater, mass balance, dairy farms, Central Valley

Zusammenfassung

Hohe Nitratkonzentrationen im Grundwasser im Central Valley (CV) in Kalifornien stellen ein Risiko für die menschliche Gesundheit und die Umwelt dar. Ein Ansatz zum Verständnis und zur Untersuchung von Stickstoffflüssen sind Massenbilanzen. Diese Arbeit untersucht die Eignung von Massenbilanzen zur Abschätzung der Nitratkonzentration im Grundwasser auf Grundlage von Betriebsberichten im Vergleich zu Grundwasserproben.

Milchviehbetriebe in Kalifornien sind verpflichtet, die Menge an Stickstoff zu melden, die auf jedes Feld aufgebracht und geerntet wird. Diese Daten wurden verwendet, um Massenbilanzen zu erstellen und die Nitratauswaschungen ins Grundwasser abzuschätzen. Grundwasserproben aus mehreren Jahre von acht Milchviehbetrieben mit flachem Grundwasserspiegel wurden mit Schätzdaten aus Massenbilanzen verglichen. Dafür wurden verschiedene statistische Methoden und ein Linear Mixed Modell angewandt. Zusätzlich wurden Daten aus dem ganzen Central Valley über einen kürzeren Zeitraum analysiert.

Die durch die Massenbilanzen geschätzten Auswaschungen liegen in den meisten Fällen auf ähnlichem Niveau wie die Grundwasserproben, variieren aber je nach Milchviehbetrieb stark. Zusätzliche Parameter wie Tiefe des Grundwasserspiegels, Mangankonzentrationen, gelöster Sauerstoff oder Textur wurden als mögliche Einflussfaktoren analysiert, zeigten aber keine signifikanten Auswirkungen auf Betriebsebene. Im größeren Maßstab, z.B. für das gesamte Central Valley, zeigen die Faktoren jedoch einen gewissen Einfluss.

Mögliche Gründe für die festgestellten Abweichungen sind Messunsicherheiten, Inkonsistenzen der von den Landwirten berichteten Daten sowie die getroffenen Annahmen zu den Massenbilanzen wie z.B. Ammoniakemissionen. Darüber hinaus integriert der Massenbilanzansatz den Stickstofffluss räumlich, während die Grundwassermessstellen nur Punktdaten liefern.

Stichworte: Nitratauswaschung, Grundwasser, Massenbilanz, Milchviehbetriebe, Central Valley

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List of Abbreviations

BNF	Biological nitrogen Fixation
CA	California
CV	Central Valley
CVDRMP	Central Valley Dairy Representative Monitoring Program
DO	Dissolved Oxygen
DTW	Depth to water level
GIS	Geographical Information System
GW	Groundwater
KS-Test	Kolmogorov-Smirnov-Test
MB	Mass Balance
MB A	Mass Balance A
MB B	Mass Balance B
MCL	Maximum Contaminant Level
MDL	Minimum Detection Limit
MW	Monitoring Well
N	Nitrogen
SJV	San Joaquin Valley
UC Davis	University of California, Davis
US	United States
WHO	World Health Organization

1. Introduction

1.1. Nitrate in groundwater – general problem

Nitrogen gas (N_2) makes up about 78% of the atmosphere. For plant and animal use the N_2 has to be in the form of reactive nitrogen. Reactive nitrogen includes active nitrogen compounds in inorganic reduced forms (e.g. NH_3, NH_4^+), inorganic oxidized forms (e.g. NO_x, HNO_3, N_2O, NO_3^-) and organic compounds e.g. urea (Galloway and Cowling 2002). Nitrogen (N) is an important nutrient for plant growth. Plant uptake of N depends on various factors such as climate, the type of crop, the actual yield or the amount of other nutrients available in the soil (Powell et al. 2010). The supply of N to the soil used to be based mainly on biological nitrogen fixation and applying manure until the invention of the Haber-Bosch process. This process produces N fertilizer for the food production for the majority of the world's population. However, some of the N fertilizer applied gets lost to the atmosphere as NH_3, NO or N_2O or leaks beyond the root zone and the vadose zone to groundwater as NO_3^- (Galloway and Cowling 2002). Before reaching groundwater processes like denitrification, exchange reactions and dilution change the concentration of N (Blume et al. 2010).

High leakage rates can contaminate groundwater with high nitrate concentrations. Contaminated groundwater might be used for drinking water and can cause human harm like methemoglobinemia for infants and other health issues (Comly 1945; Ward et al. 2005). The drinking water guideline in the Unites States defines a Maximum Contaminant Level Goal of 10 mg/l (EPA 2018). The World Health Organization defines 50 mg/l NO_3 as a limit (WHO 2017). Nitrate (NO_3) is often measured as nitrate-N (NO_3-N). The conversion factor is 1 mg/l as nitrate is equal to 0.226 mg/l as nitrate-nitrogen.

Besides leaching to groundwater an excess of N can have impacts on other parts of the environment. In surface water N can lead to eutrophication. It can impact the climate change as NO_2 and ammonia volatilization can cause soil acidification (Buczko et al. 2010). Therefore it is aimed to diminish the N loss and the nitrate concentration in groundwater to achieve a sustainable use of groundwater (Gorelick and Zheng 2015).

1.2. Problem in the Central Valley

Nitrate leaching to groundwater from agriculture is a problem in many regions worldwide (Gutiérrez et al. 2018). Agricultural areas are non-point sources for elevated nitrate concentrations (Burkart and Stoner 2002).

Increased nitrate concentrations in groundwater in the Central Valley (CV) have been found and investigated for a long time, starting in the 1950s (State Water Resources Control Board 1988; Burow et al. 1998; Harter et al. 2002; Burow et al. 2008; Viers et al. 2012). Long-term impact of agricultural activity and permeable sediments increase the risk in the CV for high levels of nitrate in groundwater (Burow et al. 1998). Lower nitrate concentrations with increasing depth show that the contamination originated from the surface (Ransom et al. 2017). Samples showing high nitrate concentrations had recent recharge, high Dissolved Oxygen (DO) in groundwater and agricultural impact (Burow et al. 1998). Besides agricultural activities as non-point sources there also exist point sources. These can be septic tanks, dairy farms or feed lots which can cause high nitrate-N concentrations (Bertoldi et al. 1991). In the CV groundwater is used mainly for irrigation and provides drinking water. High nitrate concentrations found in shallower groundwater contaminate drinking water taken of domestic wells which are usually screened in these parts (Burow et al. 2008).

1.3. Objective

This work is part of assessing the actual nitrate leakage from dairy farms in the CV. The objective of this work is to assess the connection between the estimated nitrate leakage from the reported N mass balance of nine dairy farms and the observed NO_3-N concentrations in their groundwater. This work uses a simple approach both on a field and a farm scale to determine whether obtained mass balances can be connected to the observed data.

2. Literature Review

2.1. Nitrogen mass balance

A mass balance includes different fluxes and changes in storage within a defined system. It is useful to quantify one unknown term if all other variables are known. A nitrogen mass balance can be used to estimate the unknown amount of leakage of nitrogen as nitrate as a contaminator in groundwater (Carey et al. 2017). It is important to manage N use so that less losses occur to the environment (Rotz 2004). This means optimizing N use to prevent harm for human health and for the environment (Galloway 2003).

A nitrogen mass balance can help to understand the behavior of nitrogen in different phases and reservoirs like the soil, the ocean and the atmosphere. Here the focus lies on the soil as it is connected to the groundwater. Important fluxes in the soil are atmospheric deposition, biological N fixation, organic and inorganic fertilizer as inputs and volatilization and plant uptake as outputs (Gutiérrez et al. 2018). In recent years the amount of available N from chemical processes has increased which led to a higher amount of N in reservoirs (Siebert 2005).There is an increase of nitrogen emission and therefore an increase of atmospheric deposition (Kanakidou et al. 2016). Climate change might also influence the distribution of N (Tomich et al. 2015). These developments make it even more important to quantify the amount of nitrogen in each reservoir to be able to prepare for future challenges caused by too much nitrogen.

In terms of spatial scale a mass balance is often calculated as farm-gate balance or a smaller unit which can be sub-system within the farm (Ruijter et al. 2007). These systems can be further divided up into soil surface or soil system budgets (Carey et al. 2017). Depending on the scale and the object of research different inputs and outputs are taken into account. The spatial scale can also be extended to a bigger unit then a farm such as a region, an industry or a state. An example for a mass balance of the state of California is given by Liptzin et al. 2016. In terms of time period mass balances are usually calculated on an annual base as this is the relevant scale for groundwater data. The annual approach of the mass balance data means a simplification of reality (Einarsson et al. 2018). Statistical data such crop data or harvest results are usually available on annual base, too.

The input data of a mass balance cannot be based exclusively on sampled data due to measurement restrictions and high cost. That is why models can give important insights into the N fluxes. Models identify and quantify N fluxes in order to reduce N leakage (Botros et al. 2012; Gutiérrez et al. 2018). A review on existing N models regarding N in soil-plant systems was done by Cannavo et al. 2008.

Instead of using various input variables for a model there is also the option to use indicators. An indicator is a variable which gives information about other variables which are harder to access. Indicators can help to estimate nitrogen losses (Delgado et al. 2008). Bockstaller et al. 2008 reviewed various indicators to assess water pollution and other environmental effects of agriculture on the environment. They distinguish indicators derived from management practice, simulation models and measured indicators.

2.2. Nitrogen mass balance on a dairy farm

2.2.1. General

Mass balances can help to optimize nutrient use on dairy farm and help to understand the different fluxes. Studies of the N mass balance on dairy farms in different regions have been done by several authors (Rankinen et al. 2007; Schröder et al. 2007; Cherry et al. 2008; van der Schans et al. 2009; Burchill et al. 2016; Carey et al. 2017). There is a need to optimize N intake for crops and for animals to decrease potential leakage to groundwater (Galloway et al. 2008). A N mass balance on a dairy farm can be useful to optimize the amount of N applied as fertilizer and manure to crops and diminish losses (Gutiérrez et al. 2018). Quantifying N losses on dairy farms can help to change management practices to diminish N emissions (Powell and Rotz 2015). This can include maximizing the conversion of N in forage to usage as manure on fields and optimizing storage efficiency (Spears et al. 2003).

Van der Schans et al. (2009) developed a N mass balance for a dairy farm in the CV including the different areas of a dairy (Figure 1).

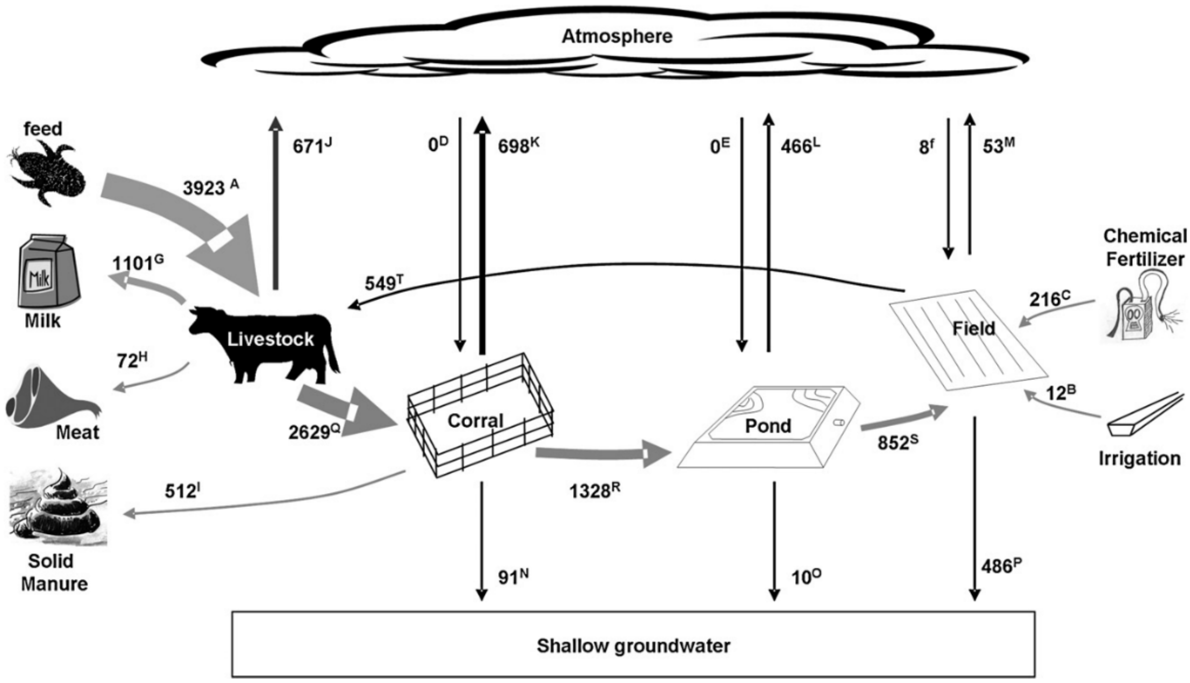

Figure 1: Nitrogen mass balance for a dairy farm in kg N/year/ha-forage field (van der Schans et al. 2009).

A nitrogen mass balance on a dairy farm can be seen as a closed system inside the farm gates (dairy farm gate mass balance). Forage, fertilizer and animals bought are inputs, milk, animals sold, manure exported and losses to the environment are outputs. Soil, land surface, storage of forage and numbers of animals constitute changes in N storage. In the CV cows are milked throughout the year and there are about 15% dry cow at all times. Important fluxes are the uptake of forage by cows and the N output as excretion. Manure is collected from the corral area and stored, usually in lagoons (in Figure 1 shown as pond). After a certain storage period manure and liquid manure is then applied to fields. Part of it gets lost to the atmosphere as gases (ammonia) before it is applied to the fields where it can be transformed to gases or found as nitrite or nitrate. Part of the N is taken up by plants and harvested and used again as forage for the dairy farm cows. Another part of N accumulates in soil. There are three different forms on N in soil, organic N, ammonium (NH_4^+) and nitrate (NO_3^-) (Gutiérrez et al. 2018). Most N in soil is part of soil organic matter. The amount of soil organic matter changes according to factors like soil type and texture, hydrological soil properties, climate and land-use (Chang et al. 2005). Another part of the surplus N leaches through the vadose zone to the groundwater. A detailed description of processes on a dairy farm in the CV can be found in Harter et al. 2002; van der Schans et al. 2009.

The leakage of N varies for each management area on a dairy farm. When looking for leakage to groundwater it is useful to divide the dairy farm in different management units to easier quantify potential N losses and assess how to reduce them (Lockhart et al. 2013). The management units used here are corrals, lagoons and fields (see Figure 1). Corrals are the areas where the cows spend most of their time. Lagoons are used for manure storage. On field crops are grown. Main N losses on dairy farms take place as ammonia in corrals (up to 50%), in the lagoon (up to 70% without cover) and during field application (Rotz 2004). For mass balances management units can be used to identify the sources of nitrate in groundwater.

2.2.2. Regulation 'General Order for existing Milk Cow Dairies'

Dairy farms as part of the intensive agriculture in a highly vulnerable region of the CV in California (CA) impact nitrate concentrations in groundwater (Harter et al. 2002). Dairy farmers in CA are requested to do a nutrient mass balance per field and harvest to be in accordance with the Waste Discharge Requirements by the California Regional Water Quality Control Board (CRWQCB 2013). They submit this information as an Annual Report to the Regional Water Board. In 2007 the Regional Water Board issued the first General Order for existing Milk Cow Dairies (CRWQCB 2007). Like in other countries regulations on N have the objective to force farmers to apply the fertilizer and manure in a way and quantity to meet crop's needs but to prevent nitrate leaking to groundwater (Miller et al. 2017).

The following section provides a more detailed description of the individual components of the Annual Report of dairy farms which can be used to calculate a field N mass balance.

2.2.3. Parts of the nitrogen mass balance

Various input and output variables are described in the Annual Reports. The data can be used to create a N mass balance to assess the potential nitrate leakage to groundwater. On field level data are total N applied and total N harvested. On a dairy farm level there are additional components such as imports and exports of N and atmospheric volatilization. Processes such as biological nitrogen fixation and denitrification are explained separately even though they are included in other parts of the mass balance in the Annual Reports.

Total N applied to fields is measured as the amount of N in fertilizer, manure and irrigation water. The quantity of N in fertilizer is known as it is purchased. The amount of excreted manure is usually estimated based on herd size (Nennich et al. 2005). Irrigation water which was pumped from groundwater or taken from a stream is tested on N concentration (Viers et al. 2012). Mineralization by tillage and atmospheric deposition of N to fields are usually estimated. Tillage increases the amount of mineral N available in soil by decomposition of soil organic matter. Atmospheric deposition is estimated to be about 70kg/ha/y (Harter 2012a). Other estimations range between 4 to 75 kg/ha/y (Körschens et al. 1998; Sainju 2017).

The Total N harvested is measured as the amount of N in harvested crops.

N imports of dairy farms are measured and include waste water, fertilizer and dry manure from other dairy farms which is used for bedding or other bedding material. Other nutrient imports are requested to be reported as well. Some dairy farms export manure.

Atmospheric volatilization describes the ammonia emissions from dairy farms. N from manure is converted to ammonium and lost as ammonia to the atmosphere. It depends on factors like management type, temperature, wind speed, the original N amount in the manure and its pH value and therefore is extremely variable (Hristov et al. 2011). Manure collection and storage and all management parts which include air exposure influence the loss of ammonia (Aguerre et al. 2012; Kohn 2015). Measurement of ammonia emissions can be done as a ratio of N to non-volatile minerals or as N isotopes ratio. For dairy farms the amount lost as ammonia is estimated to be about 35 - 50% (Hristov et al. 2011). For dairy farms in the CV a loss of 20 - 40% is estimated which includes a low amount of denitrification (Chang et al. 2005). Viers et al. 2012 estimate a loss of about 38% from manure prior to land application. Nitrous oxide emissions from soil are estimated to account for up to a third of the greenhouse gas emissions from agriculture in California (Burger et al. 2013). Here they are neglected in the mass balances as they are not affecting groundwater (Burchill et al. 2016).

Biological nitrogen fixation (BNF) is an important part for a sustainable and productive agriculture instead of only using synthetic fertilizer (Peoples et al. 1995). Legumes and rhizobia are responsible for most N_2 fixing processes (Herridge et al. 2008). Factors influencing BNF include amount of N in soil, legume crops in the fields and yield (Ledgard and Steele 1992).

Denitrification is the reduction of nitrate to any gaseous nitrogen compound, usually NO_2 and N_2 (Galloway 2003). The process depends mainly on Dissolved Oxygen (DO) availability (Rivett et al. 2008; Yuan et al. 2017). In soil it can occur in unsaturated soils and below the water table when nitrate and denitrifying bacteria exist (Singleton et al. 2007). Denitrification is happening more at lower depth because of the lack of oxygen and can be affected by vertical groundwater movement due to pumping (Almasri and Kaluarachchi 2004). Denitrification highly varies with site. Uncertainties in estimating denitrification arise from identifying the spatial extent of anaerobic conditions under heterogeneous hydrogeological settings (Singleton et al. 2007).

Often, in shallow groundwater denitrification is not large enough to have a large impact on nitrate concentrations (Green et al. 2008). In the CV low denitrification rates are suggested

(Liptzin et al. 2016). Loss of N due to denitrification is estimated to be 8 - 28% in the CV (Miller et al. 2017).

Nitrate leakage to groundwater is defined as the nitrate which percolates to the groundwater. It depends on various factors like texture, soil type, geology, hydrology, geochemistry, agricultural practices and land use (Stenberg et al. 1999; Boumans et al. 2005; Collins et al. 2017; Ransom et al. 2018). All factors which affect infiltration rates and denitrification like DO and groundwater table are important for estimating nitrate concentrations in groundwater (Gurdak and Qi 2012). Various management practices e.g. timing and rate of N application and frequent manure removal from corrals have been identified to reduce potential N leakage (Rotz 2004; Di and Cameron 2016).

N loading sources in the CV are mainly cropland (96%) with more than half being mineral fertilizer and about a third animal manure (Harter et al. 2013). N loading rates on dairy farms in the CV were estimated to range from 280 to 480kg N/ha/y (Harter et al. 2002; van der Schans et al. 2009). Rosenstock et al. 2014 found an increase in groundwater N loading in recent decades in the CV when using a modeled mass balance. However, as there are so many different and strongly localized factors influencing nitrate leakage it is hard to quantify and predict groundwater concentration.

A summary of all measured and estimated parts of the N mass balance is given in Table 1.

Table 1: Measured and estimated parts of the N mass balance.

Part of N mass balance	Measured	Estimated
Total N Applied to Field	Manure applied	Atmospheric deposition
	Fertilizer	Tillage
	Irrigation water	
Total N Harvested	Crop Harvest	
Imports to Farm	Imported Dry Manure	
	Imported Waste Water	
	Imported Fertilizer	
	Other nutrient imports	
Exports from Farm	Manure	
Atmospheric volatilization		Ammonia volatilization
		Nitrogen gas
Denitrification		Denitrification
Groundwater Leakage		From N balance

2.3. Estimating groundwater N leaching using dairy field N mass balances

The nitrogen mass balance is one way to estimate potential nitrate concentrations in groundwater. Comparing it to observed nitrate concentrations can be helpful to assess the original mass balance approach. Additional factors can be used to identify their impact on the nitrate concentrations. However, the mass balance is an integrative approach so it can be difficult to identify one single important factor in the results (Buczko et al. 2010).

Usually, models are used to estimate the N loading and their potential leakage to the actual nitrate concentrations in groundwater. The models include a conceptual idea of processes in soil e.g. mineralization, denitrification (Carey et al. 2017; Ransom et al. 2018; Rodriguez-Galiano et al. 2018). However these processes are very hard to quantify as discussed above and might even be possibly neglected in shallow groundwater.

Some challenges have been found when using mass balances. N mass balances usually do not account for the time nitrate needs to leak to the groundwater (Cherry et al. 2008). Some studies show different results when using a mass balance on a farm level or on a field level (Ruijter et al. 2007). A study on dairy farms in the Netherlands investigated N leakage derived from mass balances on field level and showed that the variability on fields was larger than between farms and hence N leakage can be underestimated when looking on farm level only (van Beek et al. 2003). A study in the UK showed a link between N balance and nitrate leaching only in specific areas depending on climate, land use and soil (Lord et al. 2002). A field study in northwestern Germany investigated N leaching to groundwater and also found a poor correlation and suggests that several years data are needed for a reliable estimate of N leakage (Sieling and Kage 2006).

Possible bias and errors of the mass balance input data are often unknown and lead to high uncertainty, especially when quantifying leakage and denitrification (Oenema et al. 2003; Cherry et al. 2008). In spite of these limitations, the mass balance is a good indicator to predict nitrate concentrations in groundwater (Korevaar 1992; Wick et al. 2012; Miller et al. 2017). A big advantage of the mass balance approach is that experimental methods are often too costly for a broad application in practice and therefore restricted in use (Buczko et al. 2010).

3. Study area

3.1. Central Valley

The Central Valley (CV) is a topographic basin in California. The climate is Mediterranean with an annual precipitation of about 290 mm which takes place between October and April (Watanabe et al. 2008). Potential evapotranspiration is about 1200 mm which is more than the precipitation rate (Bertoldi et al. 1991). The CV has a flat topography with a slope less than 0.2 % (Harter et al. 2002). It mostly contains sediments from Jurassic to Holocene with a thickness of up to 9 km in the southern part of the CV, known as the San Joaquin Valley (SJV) (Bertoldi et al. 1991). The aquifer pumped by the wells are mainly of Late Tertiary and Quaternary (Croft 1972; Burow et al. 2004). Groundwater generally flows from the mountain ranges surrounding the CV to its axis and then to the Delta area (Page 1986). Groundwater flow rate is about 5 $x10^{-7}$ m $s^{-}1$ on average (Watanabe et al. 2008).

The agriculture is the most important land use in the CV. A large part of this are dairy farms. Dairy farms use irrigated fields to grow forage crops. About 1600 dairy farms fell under the regulation of the General Order on Dairy Farms in 2007. However, the number is declined to about 1300 due to economic reasons until 2013 (CRWQCB 2013). Five counties producing nearly 75% of the Californian milk are located in the South of the CV. In recent years the total milk production declined (CDFA, USDA 2017).

Textures are mainly sand or sandy-loam for the dairy farms, having sand for the dairy farms of the SJV and sandy-loamy soils in the southern part of the CV. Soil types include Entisols, Inceptisols, Alfisols, Mollisols for the SJV and Entisols, Inceptisols, Mollisols for the southern part of the CV. Most of the soils are alluvium and well drained or moderately well drained to excessively drained (Soils Resource Lab 2018).

The average depth to groundwater on the dairy farms in the SJV is less than 10 m, in the southern part it can be up to 50 m. Shallow in this context means that the first encountered groundwater is close to the first sandy layer in the sediment. On dairy farms in the CV the groundwater is mainly recharged by ‘percolation of excess irrigation water’ (Harter et al. 2001). Recharge is the amount of water which percolates to groundwater annually. Due to the climatic conditions all fields in the CV are irrigated which means a relatively homogeneous recharge. Recharge rates were estimated to be 610 mm/a (Harter 2012a).

3.2. Selected dairy farms

Nine dairy farms with long-term data from groundwater monitoring wells were selected for analysis. All had shallow groundwater and high nitrate concentrations in groundwater. They are located in the central and southern part of the CV (Figure 2).

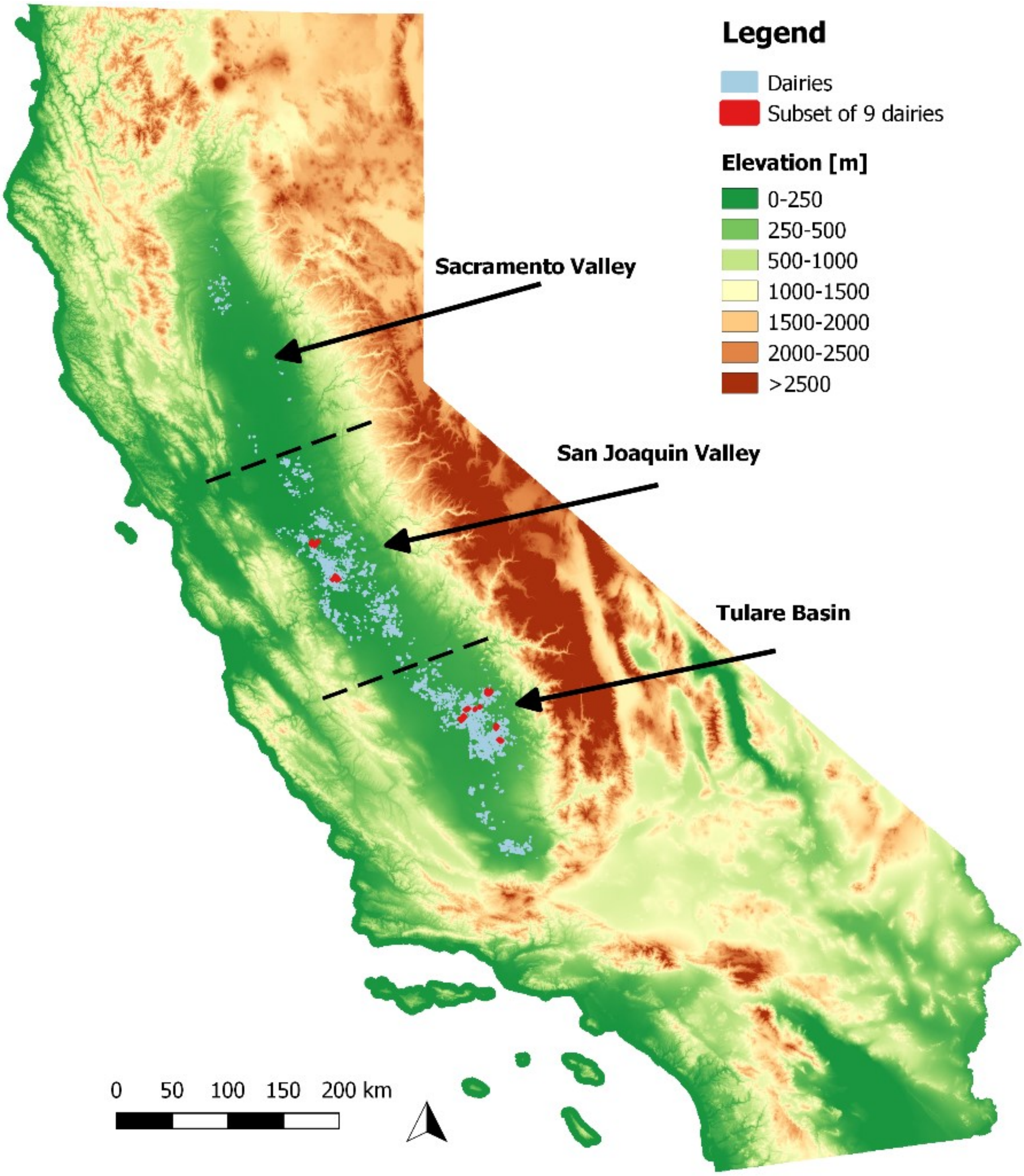

Figure 2: Location of the dairy farms in the Central Valley (based on Harter et al. 2002) .

All dairy farms were part in previous studies of the UC Davis. Dairy farms with shallow groundwater wells were chosen because travel times in the unsaturated zones are short, wells were drilled at lower cost originally and long-term fluctuations were short (Harter et al. 2002). Various studies of the dairy farms described the high groundwater vulnerability in the area (Harter et al. 2002; van der Schans et al. 2009; Harter 2012c; Young et al. 2013; LSCE 2018). All dairy farms use flood irrigation and put manure on fields on which usually forage crops for the dairy cows are grown. Common crops include corn, oats, wheat, grain and Sudan grass. The typical crop rotation is summer corn and winter cereals (van der Schans et al. 2009). Livestock housing is either free-stall or dry-lot. According to the Regional Water Board the dairies in the Central Valley either report to the responsible office in Sacramento (San Joaquin Valley) or Fresno (Tulare Basin) (Table 2).

Table 2: Selected dairy farms, year built, dairy farm type, soil type, and responsible office of the Regional Water Board and Depth to water table.

Data was taken from UC Davis 1994; Harter 2012b, 2012d, 2012a, 2012e, 2012f.

Dairy ID	**Year built**	**Housing type**	**Dominant texture**	**Responsible office**	**DTW [m]**
DUR	1978	Free-stall	Sand	Sacramento	<12
GEN	1950	Free-stall	Sand	Sacramento	<12
FIS	1917	Free-stall	Sand	Sacramento	<12
CLA	1930	Free-stall	Sand	Sacramento	<12
DLF	2002	Free-stall	Sandy-loam	Fresno	>12
ZZI	1893	Dry-lot	Sandy-loam	Fresno	>12
ELK	2002	Free-stall	Sandy-loam	Fresno	>12
SIE	1990	Dry-lot	Sandy-loam	Fresno	>12
LON	1950	Free-stall	Sandy-loam	Fresno	>12

The total herd size includes milk cows, dry cows and heifers. The mean number of herd size is about 2900 for all dairy farms, varying from 760 to 7700 within the years and dairy farms. Herd size has increased at some dairies in recent years but this is not a consistent finding for all of the dairies (Figure 3). Farm DLF and farm ELK had an increase of herd size in recent years. Farm GEN, farm DUR and farm ZZI show a relatively constant size of manure. This probably means no large changes in management areas. For farms CLA and LON the total herd size shows some year-to-year variation. This might be due to adapting to the economic situation for dairy farms. Farm FIS and farm SIE show a small increase of herd size in recent years. The herd size is important for because it can be used to estimate the amount of excreted manure for a nitrogen mass balance.

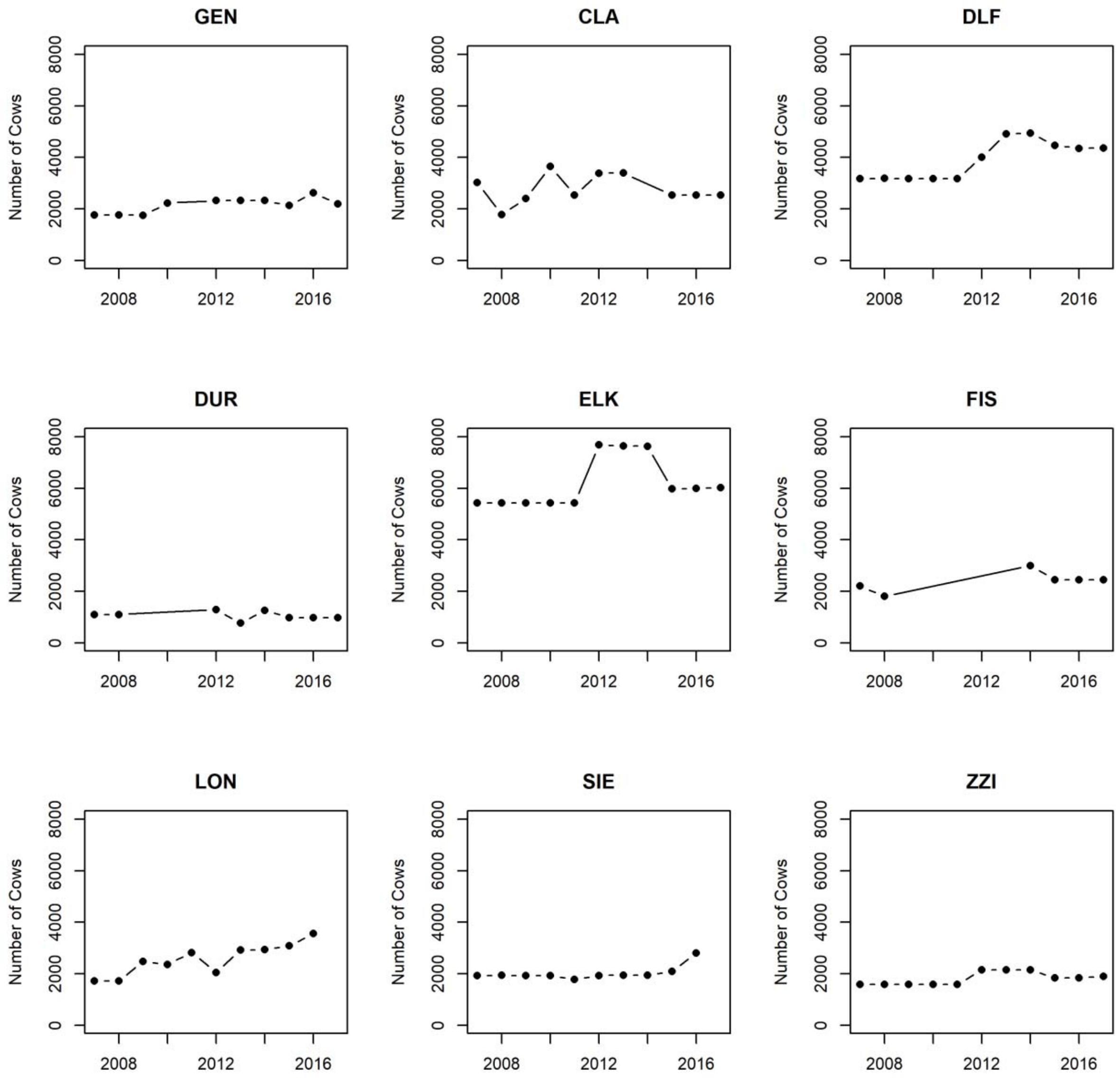

Figure 3: Herd size per dairy per year.

Imperial units used for reporting in the Annual Dairy Report were converted to ISO units, e.g. acres were converted to hectares dividing by 2.471. As most of the dairy farms grow their own forage for their cows a constant ratio between herd size and field size is found for most of the farms in recent years. For farms ELK and DLF an increase of herd size has been shown above. A decrease in the ratio of cows per ha suggests that the amount of area needed to grow forage crops has not been expanded at the same rate as the herd size. Buying or selling forage crops off the dairy farm might therefore be a reason for variations in the values (Figure 4). For farms CLA and ZZI there is a large variability which might be due to the variation in herd size or takeover of additional land.

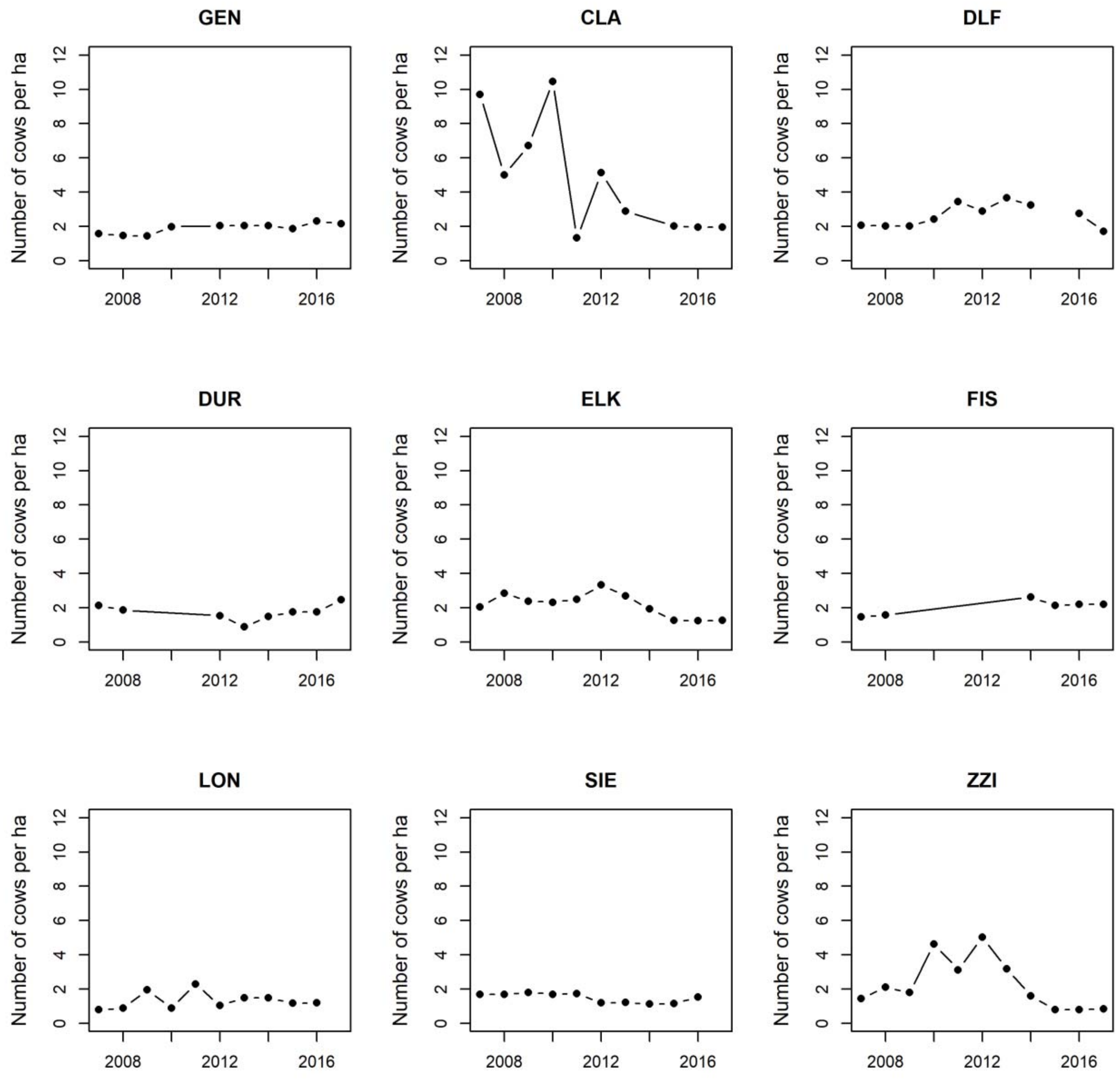

Figure 4: Ratio of herd size to planted field area in ha per year per dairy farm.

4. Methods

This chapter gives an overview of the data sources, the data assessment and the data analysis. Data of nine dairy farms in the CV was analyzed. The groundwater data was selected with a focus on monitoring wells which represent the impact of fields. This made it comparable to the mass balance data which was calculated on a field scale and a farm scale. Both the mass balance data and the groundwater data were compared to each other for the selected dairies. In a second part a short-term data set of the whole CV was analyzed.

Analysis was done in R (R Core Team 2018) using R Studio (RStudio Team 2016). GIS Data was processed using QGIS (QGIS Development Team 2018).

4.1. Data sources

The groundwater data was collected by various UC Davis studies and newer data was available from the Central Valley Dairy Representative Monitoring Program (CVDRMP). The mass balance data used was extracted from the Annual Dairy Reports, made available by the Regional Water Board and the CVDRMP to UC Davis. All data for well drilling logs and GIS data was provided by UC Davis. GIS data was imported from the California Department of Water Resources 2018 for the CV. A detailed overview of all sources is given in Table A 1.

4.2. Data assessment

This chapter gives an overview on how data was sampled, preprocessed and prepared for analysis of groundwater data, N mass balance data, impacting factors and the regional analysis.

4.2.1. Groundwater data

All samples were taken from monitoring wells on dairy farms or dairy farm fields. The data was sampled during four periods from 1993 to 2017. There are some years without groundwater data (Figure 5). There is only one dairy farm (farm GEN) with data available for all four phases, i.e. this means a total of 20 years sampled within a 25 years' time period from 1993 to 2017. For farm CLA there is data available for the first two phases only. For farms FIS and DUR there is data for the first two phases and then for one additional phase. For farms DLF, ELK, LON, SIE and ZZI there is data for the last two phases which means eight years sampled within an eleven years' time period from 2007 to 2017.

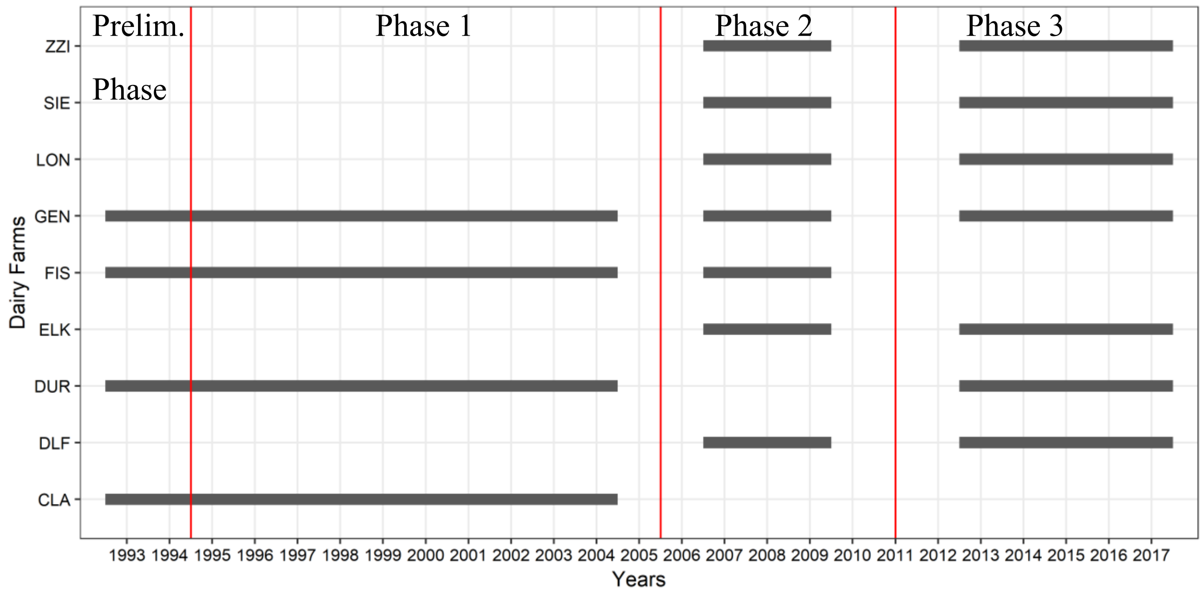

Figure 5: Data availability per dairy farm.

In the Preliminary Phase samples were taken quarterly between summer 1993 and 1994 at five dairy farms with a total of 44 wells. In Phase 1 from 1995 to 2004 samples were taken more frequently than before (Harter et al. 2002). One dairy farms with observation data from Preliminary Phase and Phase 1 was excluded from further analysis since no mass balance were available. During Phase 2 seven other dairy farms were monitored from 2007 to 2009 (Harter 2012a). This phase included nested wells, which have at one location different screens in different depths installed. This helps to identify nitrate concentrations in different depths and in different groundwater layers of sand even when the water tables vary highly. This way, the variance of water quality within the aquifer can be evaluated (Rudolph et al. 1998). For all nested wells the first encountered groundwater and the available nitrate concentration was identified for each sampling date. For nested wells only identified measurements was used per date. In 2010 the CVDRMP, a Non-Profit Group of dairy farm owners and operators was founded to monitor groundwater quality at 42 dairy farms in the CV (LSCE 2018). This data was used for Phase 3, i.e. 2012 to 2017.

Wells were sampled at different frequency in each period. Wells in the Preliminary Phase in 1993 to 1994 were sampled quarterly, in Phase 1 each five to six weeks. Since then wells are usually sampled quarterly again. Sampling protocols include measurement of groundwater levels and pumping a certain amount of water before taking a sample to ensure stability of water quality. Water samples are collected, cooled and stored for analysis. 'Control, blank, duplicated and diluted duplicate' samples are taken (Harter et al. 2001). NO_3-N is measured using diffusion-conductivity analyzer (Harter et al. 2001). Later field studies followed the same procedure (van der Schans et al. 2009; Young et al. 2013; LSCE 2018).

Apart from nitrate-N different water quality parameters were measured. During 1995 to 2003 and 2007 to 2009 Dissolved Oxygen (DO) was measured among other. Between 2008 and 2009 further water quality parameters e.g. Manganese (Mn) were sampled. Both DO and Mn were taken into account in this analysis. The reason for this was a previous study which showed a correlation between nitrate concentrations in groundwater and the probability for Mn and DO occurrence (Ransom et al. 2017).

Water quality data was left censored. All samples with only a Minimum Detection Limit (MDL) given were replaced with half the detection limit (Helsel 2005). The number of NO_3-N values of non-detects were low (29 samples). For the nine dairy farms there were a total of 5254 NO_3-N samples.

Each well was assigned a well source area in Phase 1 based on estimates of recharge, hydraulic gradient data and conductivity. Well source areas are divided into five classes. Three classes are the same as the management units of a dairy (see also 2.2.1): *corral*, *lagoon* and *field*. Wells with a source area located on a boundary of these management units were identified as *multiple*. One additional class is *up gradient* where the well source area of a well is located up gradient of the groundwater flow of the dairy farms (Harter et al. 2002). Van der Schans et al. 2009 estimated the N leakage for the three management units on one dairy farm using well source areas.

Groundwater data includes a mix of water age (Horn and Harter 2009). Monitoring wells capture mainly recent groundwater which is a few weeks old until less than two years old (Watanabe et al. 2008). Non-steady groundwater flow directions can therefore lead to mix source areas over time. Other management units may have zero recharge e.g. plastic lined lagoons (LSCE 2018).

For some wells the well source area was assigned differently in later phases. It was assumed that the most recent analysis identified the most reliable well source area and this was assigned to the well for all years. For some wells the source area is undetermined. For the analysis only wells with an identified well source area were taken into account (Table 3).

Table 3: Number of wells per well source area per dairy farm.

	CLA	**DLF**	**DUR**	**ELK**	**FIS**	**ZZI**	**SIE**	**LON**	**GEN**	**TOTAL**
Field	12	2	4	1	11	3	1	4	1	39
Lagoon	0	0	3	1	1	1	0	0	2	8
Corral	4	0	2	1	2	2	0	0	2	13
Up gradient	6	0	0	0	2	0	1	1	3	13
Multiple	2	4	1	1	2	1	2	2	4	19
TOTAL	24	6	10	4	18	7	4	7	12	92

All wells with fields as an assigned source area were selected (39 wells on nine dairy farms). For nested wells only first-encountered groundwater nitrate concentrations were selected. A mean value for each well per dairy farm for each year was calculated. For some comparisons with the mass balance data only the aggregated data was used.

4.2.2. Nitrogen mass balance

In this work an extended dairy field mass balance approach is used. N applied to fields is estimated based on excretion rates and estimated atmospheric losses between manure excretion and land application. The output of the field mass balance is the harvested N in crops. The amount of N left is used to estimate groundwater leakage.

The reported values from the mass balances are mainly designed to evaluate the N leakage from fields. The focus was on manure irrigated fields.

N data was sampled according to the requirements of the General Order (CRWQCB 2007). The frequency of sampling is regulated (overview in Miller et al. 2017). UC Davis has developed instructions on how to sample the different parts of the N mass balance (Meyer 2008; Meyer and Mullinax 2008). Farmers use estimation formulas to calculate the total weight of N in manure applied or manure exported. The estimations are usually based on measurements of the moisture percentage and weight of the sample.

There are several assumptions made in order to calculate the mass balances and in a second step to compare them to nitrate in groundwater. Alfalfa (*Medicago sativa*) fields were excluded for analysis because alfalfa plants fix N from the atmosphere and therefore alfalfa fields usually do not receive any manure or fertilizer (Viers et al. 2012). For the dairy farms monitored by CVDRMP only fields close or within the source area of the monitoring wells were included for mass balance A

Figure 6). For mass balance A (MB A) the difference between N applied and N harvested is already reported in lbs/ac.

Denitrification and other processes within the soil and the vadose zone are neglected. It is assumed that denitrification in the shallow groundwater has a minor impact (Liptzin et al. 2016). To create a mass balance the N organic content in soil is considered as constant although this is not necessarily the case in reality (Buczko et al. 2010). Reported data and assigned well source area are assumed to be correct.

Two different kinds of mass balances were calculated, each of them with different data from the Annual Reports (Figure 6 and 7). For recharge an annual amount of 610 mm/a was assumed (Harter 2012a). The output of both mass balances was the annual potential N leakage to the groundwater. This was later directly compared to the observed values in groundwater.

MB A is based on land applied N on a field scale without alfalfa fields, the mean is calculated for the whole dairy farm (Figure 6). MB A only takes into account the reported N applied to the fields. Then the amount of N in the harvest is subtracted. The remaining amount of N is understood as potential loss to the groundwater. Processes in the soil and the vadose zone are not taken into account.

MB A focuses on the field only. It is assumed that 30% of the N of excreted is lost in the corrals and in the lagoons due to ammonia emissions. This is a fixed factor used in the Annual Dairy Reports and does not account for individual management features on the dairy in terms of corrals and lagoons.

The MB A for dairies within the CVDRMP (farms DLF, DUR, ELK, LON, SIE and ZZI) is calculated only on fields which are within the well source area of the monitoring wells. For the two remaining farms CLA and FIS all fields were used.

Mass Balance A

Potential Leakage to groundwater = (N applied – N harvested) / recharge

N applied:	Includes all N applied to field (sum of atmospheric deposition, manure, fertilizer, process wastewater and fresh water)
N harvested:	N harvested from crops

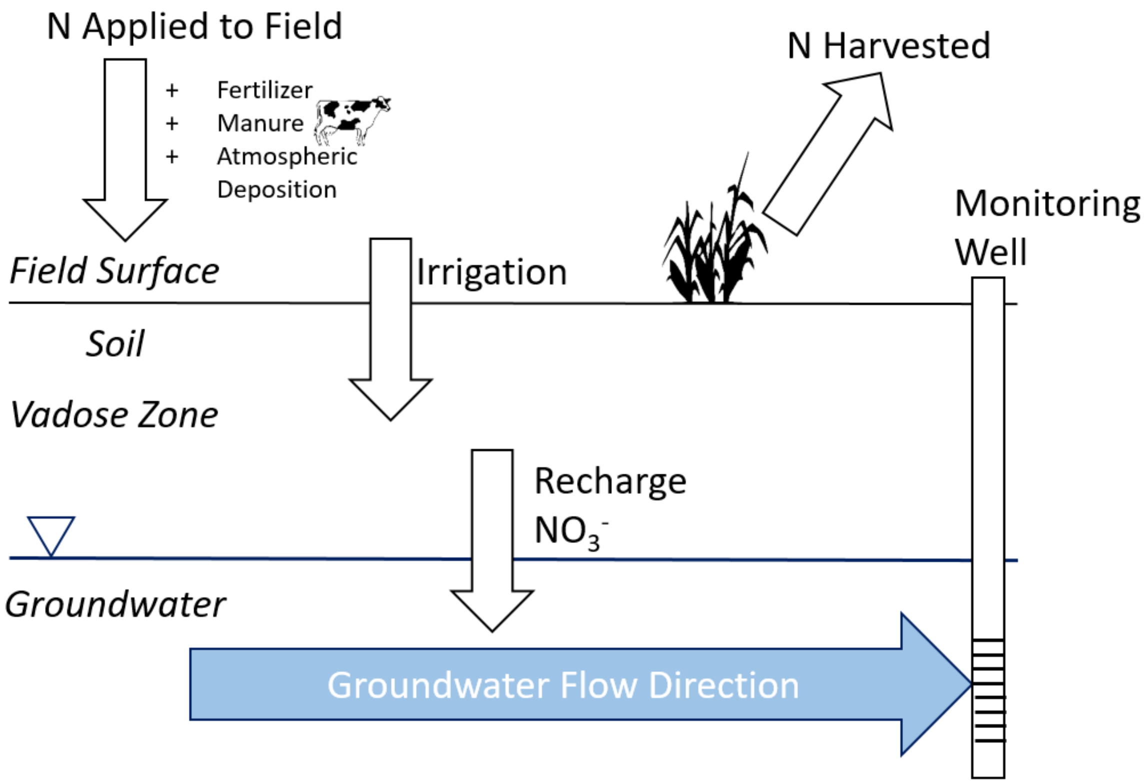

Figure 6: Schematic representation of mass balance A.

Mass balance B (MB B) is based on the amount of excretion on a dairy farm level (Figure 7). The parameters are described below. This mass balance is based on the amount of excreted manure. As in MB A 30% of ammonia emissions are subtracted from the amount of N in excreted manure. This time the calculation is based on a dairy farm level which means that all imported and exported N in the form of manure or fertilizer is included in the calculation. An additional loss of 10% N (factor 0.9) in this mass balance accounts for further N losses due to ammonia emissions, transportation losses and other losses. The final amount of N applied to all fields is subtracted by the amount of N in harvested crops. The amount of N left is divided by the hectares planted on the dairy farm fields. This amount of N is assumed to represent the potential N loss to groundwater. As in MB A processes in soil and the vadose zone are not taken into account.

Mass Balance B:

*Potential Leakage to groundwater = [(N Excreted *0.7 volatilization losses + N imported – N exported)*0.9 - N harvested] / hectares planted / recharge*

N excreted:	N in manure
Volatilization losses:	mainly ammonia losses
N imported:	Includes all N from imported manure and fertilizer
N exported:	Includes all N exported from the dairy farm, usually manure
Factor 0.9:	Accounts for additional losses of N before field application
N harvested:	N harvested from crops
hectares planted:	All hectares without alfalfa fields

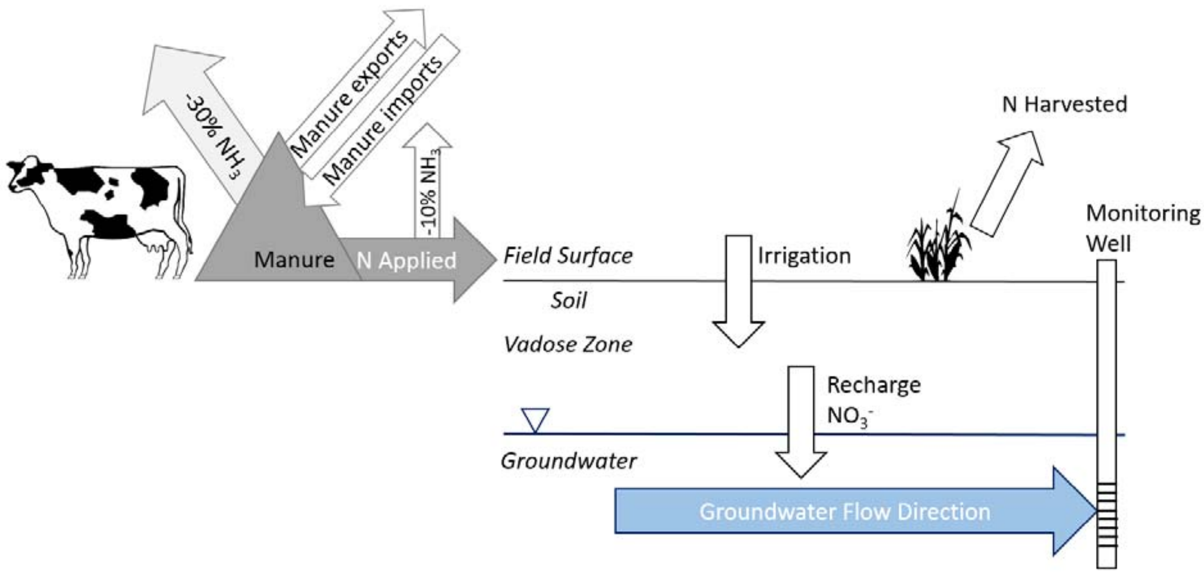

Figure 7: Schematic representation of mass balance B.

For the mass balances data from 2012 and onwards have been used (Miller et al. 2017). The data can be easily extracted from the reports or are already available in the database of CVDRMP (LSCE 2018).

4.2.3. Additional data

Additional data included drill logs from monitoring wells, location of the dairy farms, dairy farm age and type of corral, i.e. free stall or open lot. These were used to assess the changes in groundwater data and nitrate mass balance.

4.2.4. Data for the Central Valley

For an additional analysis all available data of dairy farms in the CV was taken into account. This included the mass balances from all dairy farms in the CV for the years 2012-2014 and groundwater quality data from 2007-2009. Data for depth to water table was imported for spring 2011. Dairy farm locations are shown in light blue in Figure 2.

Well data was imported in a Geographical Information System (GIS) (QGIS, Version 2.18.24) and values for the probability of occurrence of Mn and DO were included from Ransom et al. 2017. This data was chosen because Ransom et al. found these among 145 variables as one of the most important variables to predict nitrate concentrations in groundwater.

All wells were clustered into two classes with a probability of more than 50% high Mn (>50 mg/l) and low DO (<5 mg/l) or below. DTW of spring 2011 was linked to the dairy farm layer using NNJOIN extension in QGIS.

Wells providing ground water quality data were directly related to specific dairy farms. Hence wells have been assigned to the nearest dairy farm provided the well is less than 2 km away from the farm. In case two or more wells are assigned to a farm the mean value of nitrate content was calculated. Both the data set for the mass balance and the groundwater data were aggregated for the available period of time. Censored data was substituted with half the MDL.

4.3. Data analysis and statistical methods

The objective of the data analysis was to identify a relationship between the groundwater data and the calculated leakage data from the mass balances. The potential nitrate leakage of the mass balances and the observed nitrate concentrations in groundwater are directly compared. Processes in soil and the vadose zone are not considered in this analysis due to limited impact in shallow groundwater (see 2.2.3).

Since the data sets differed in time period and sample size additional analyses have been conducted. First the groundwater data were analyzed by itself, looking at distributions and trends. Second, the groundwater data was compared to the estimated mass balance data. Additional factors were analyzed to identify possible variations in the data sets. Third, a comprehensive data set of the CV was analyzed. Each part is described below in detail.

4.3.1. Groundwater analysis

The groundwater data was tested for normal distribution using the Shapiro-Wilk-Test (Shapiro and Wilk 1965). The Kolmogorov-Smirnov-Test (KS-Test) was used to test for other distributions. The KS-Test compares the empirical distribution function with the theoretical one and gives a value for the fit (Massey 1951).

For simple statistical tests and graphical comparisons the original data was used. For further analysis the data was log-transformed. No negative values exist in the original data set. '1' was added to all values to prevent negative values as a result of the log-transformation.

For each dairy farm and the entire data set the data was tested for trends using the Mann-Kendall test, which is based on the Kendall rank correlation. It is used for non-parametric data (Mann 1945; McLeod 2005).

Trends for individual wells were calculated for the available period of time. The results were compared to the study by LSCE 2018.

Since the data sets of monitoring wells covered not always each year a linear regression was used to fill the gaps in order to be able to compare well data to the N balance data by year.

4.3.2. Comparing groundwater and mass balances

Observed NO_3-N values in groundwater were compared with the calculated leakage from the mass balance. Aggregated values for the whole time period were compared. This was done by taking the mean of the groundwater values for each year. A ratio was calculated to compare the two mass balances for all the dairy farms.

To explain the discrepancy different explanatory variables were taken into account. The groundwater data was averaged for all years by monitoring well and divided into two subcategories according to different parameters like depth to water level, DO and Mn concentration, texture, geographical region, age of dairy farm and others. The Wilcoxon Rank Sum Test was used to test the difference between each two categories (Wilcoxon et al. 1970). A variable was considered significant when $p < 0.05$. For more than two categories the Kruskal-Wallis test was used (Lockhart et al. 2013).

A Linear Mixed Model (LMM) was used to explain the variances per dairy farm. LMMs are models with fixed effects (=parameters of the basic population) and random effects (=parameters for individual units). The random effects account for factors which are not explicitly looked at and therefore explains the error term better than a linear model (Pinheiro and Bates 2009):

$$Observation = fixed\ effects + random\ effects + error$$

For the analyzed data set the individual dairy farms are the random effects. It was assumed that each dairy farm can be seen as a separate entity as locally effective environmental factors and management practices are distinct from each other (Rosenstock et al. 2014) even though some dairy farms are located close to each other. Fixed effects are DTW, categories of Mn/DO, texture, age of dairy farms and geographical region. For each analysis a null model was calculated and compared using an ANOVA to see if there is a significant difference between the null model and the actual model. For a direct comparison with the mass balance data the groundwater data was aggregated on a yearly base.

The assumptions for a linear mixed model are the same as for a linear model (Pinheiro and Bates 2009). The log transformed data was used so a linear mixed model could be used instead of a generalized linear mixed model. Random intercepts were used but not random slopes. The Maximum Likelihood Method was used to optimize the model.

4.3.3. Analysis for the CV data set

Values for NO_3-N, DO and Mn were aggregated by dairy farm using the mean value of each well for the whole available period 2007 to 2009. For this data set no well source area was available and all wells were included.

For comparing the aggregated groundwater nitrate concentrations with the mass balance the probability of Mn/DO the data was divided into two categories. One consists of all dairy farms with high Mn and low DO values, the other of the ones with low Mn and high DO. Additionally, farm with shallow DTW and DTW of more than 12 m divided. Finally, the region was segregated into three sub regions using the divisions of the Regional Water Quality Control Boards in California (Region 5: Redding, Sacramento and Fresno).

The mass balance for the CV was calculated using the approach of MB B. MB A was not calculated since field values were not available for all the dairies in the CV. MB B was calculated as shown above for each dairy farm for period 2012 to 2014. The calculation includes only data sets with area data and data of N harvested and the N excreted.

The aggregated results of the mass balance were compared with aggregated groundwater data although different periods were compared. A Shapiro-Test was performed to test for normal distribution. Kendall's-Tau test was used to test for correlation. A Wilcoxon-Rank Test and a Kruskal-Wallis-Test was used to assess the significance of the difference of the values for NO_3-N and the MB B. No log-transformed data was used.

5. Results and Discussion

This chapter is divided into six parts. First, the groundwater data is analyzed and then compared to the estimated leakage derived from the mass balance (2^{nd} part). Possible variables influencing nitrate concentrations in groundwater are looked at in the third part. The fourth part analyzed the groundwater and mass balance data further using a linear mixed model. Then the data set is expanded to the entire CV and again analyzed for discrepancies between the estimated leakage and the mass balance. Finally, possible reasons are presented for the results found.

5.1. Groundwater Analysis

5.1.1. Well source area

Most dairies had not all types of well source areas assigned to their monitoring wells (see 4.2.1). Some of them have been assigned to multiple source areas because the estimated well source area was on the boundary of various management areas. The monitoring wells with multiple source areas were not included in the analysis because the data cannot be linked to management units. The dairy farm ELK was skipped in the analysis as there were only three measurements for field monitoring wells available. So only eight dairy farms were taken into account in the analysis.

The nitrate-N concentrations vary depending on the well source area assigned to the monitoring wells in each dairy farm. There is no clear pattern in distribution (Figure 8).

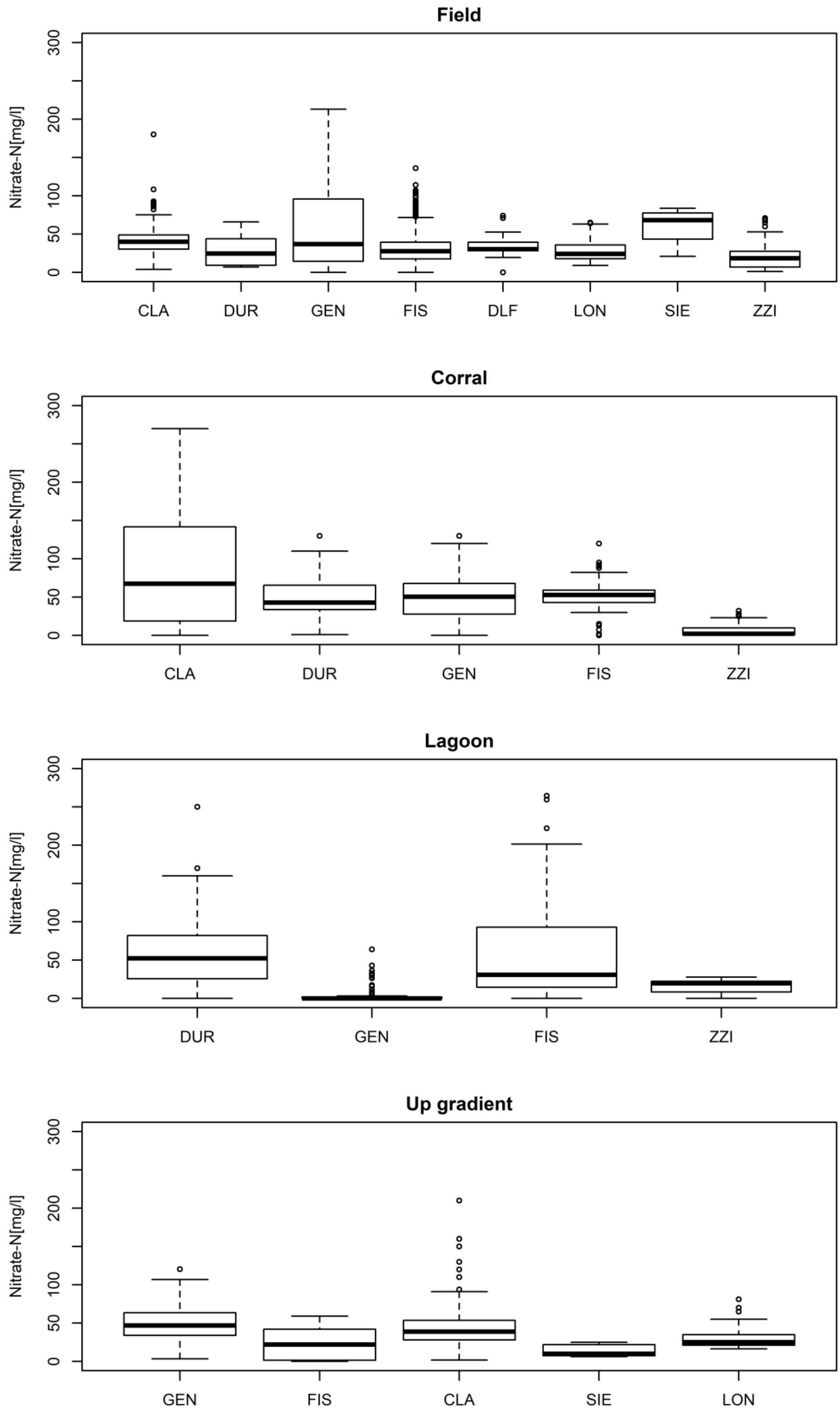

Figure 8: Observed Nitrate-N per well source area and dairy farm.

Nitrate concentrations divided only by the well source areas still vary, however it seems less than for the unique dairies. All median values lie above the MCL of 10 mg/l (Figure 9). Only values below 300 mg/l Nitrate-N are displayed because only data of monitoring wells linked to lagoons have some outliers up to 600 mg/l which might be an indicator for a leaking lagoons. Monitoring wells with corral influence show a higher median nitrate value than the others. Monitoring wells with mainly lagoon influence show the lowest NO_3-N median which indicates low seepage rates of most lagoons (LSCE 2018). Field monitoring wells show an overall similar average mean compared to the other wells but also many outliers.

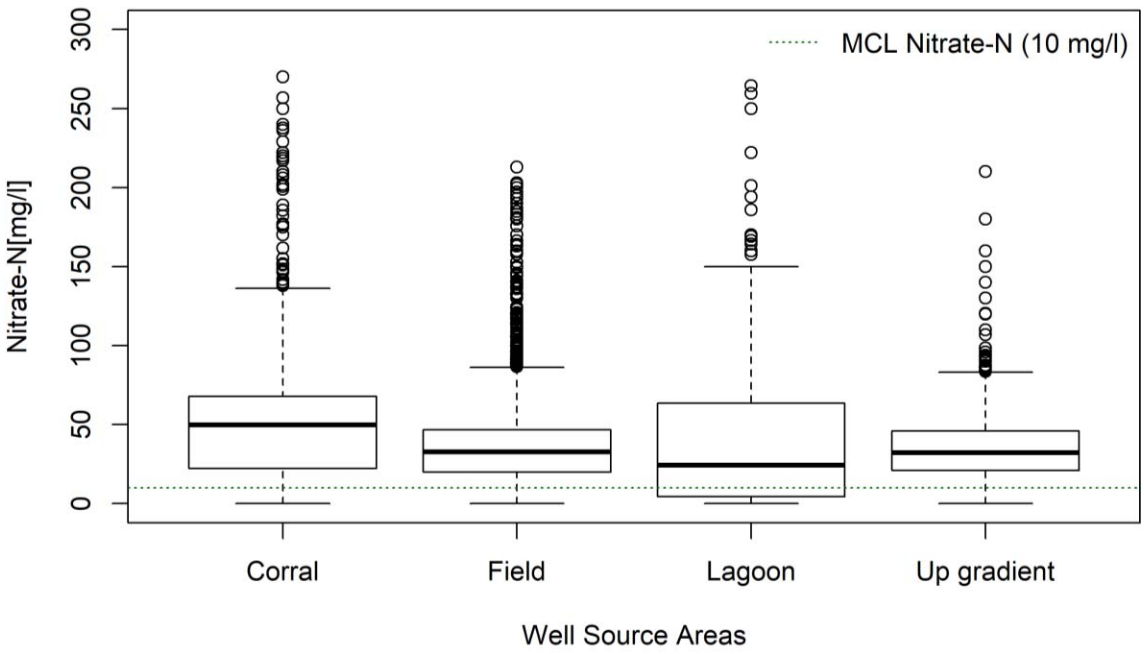

Figure 9: Well source areas and NO_3-N concentrations observed for all monitoring wells.

This work focus on monitoring wells with a field source areas because the mass balance data relate to fields.

5.1.2. Descriptive statistics

The number of measurements per field monitoring well and dairy farm differs widely per year. For some dairy farms it increased in recent years (Figure 10). Each row of the plot represents one monitoring well, each column a year and the number of measurements is shown in size and color. One square represents the data of one well for one year. Data from 38 groundwater monitoring wells at eight dairy farms was analyzed. Only one monitoring well is farm GEN and farm SIE respectively. For the farms DLF, DUR, LON and ZZI less than five monitoring wells with fields as a well source area are available. Only farms CLA and FIS provide measurements of more than 10 monitoring wells. In total there are 1099 groundwater NO_3-N samples. There are 29 measurements where non-detects were substituted with half the MDL.

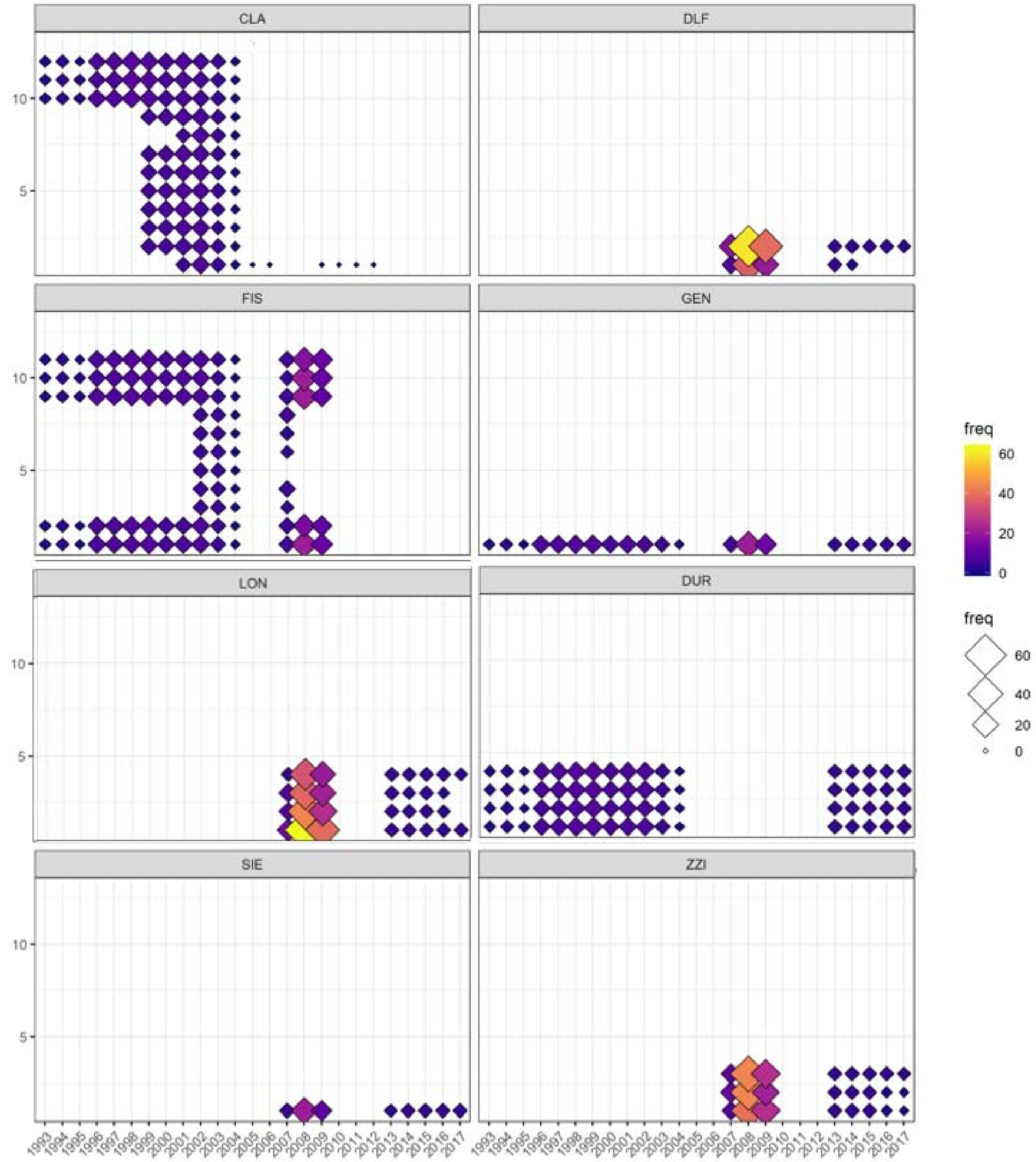

Figure 10: Number of measurements per field monitoring well and dairy farm per year.

The sampled nitrate concentration in the groundwater monitoring wells with field well source area is right-skewed as the mode (30 mg/l) is lower than the mean (35.39 mg/l) (see Figure 11). The amount of skewness is 2.41. About half of the data lies between 18 and 43 mg/l, but there are also many outliers.

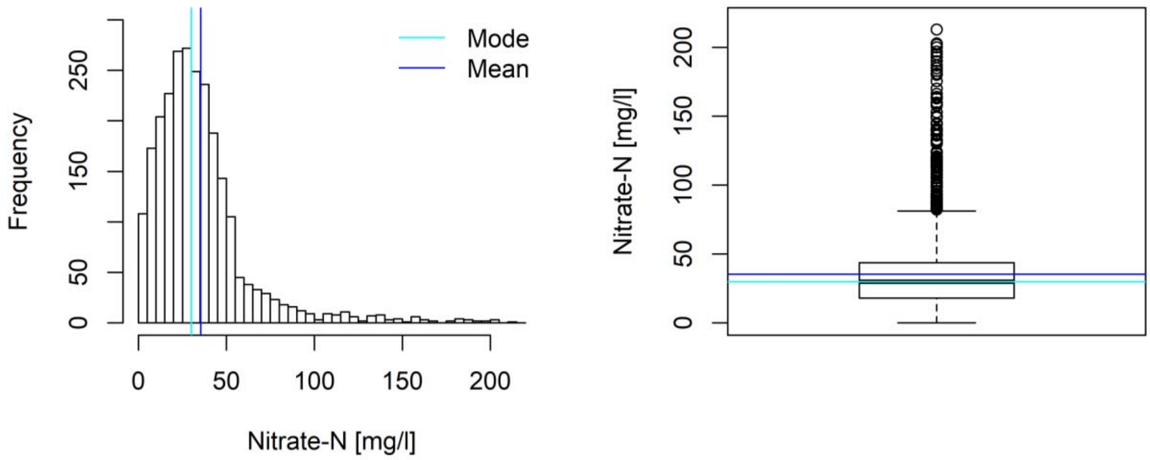

Figure 11: Overview of selected groundwater data from field monitoring wells.

Nitrate-N concentrations for all dairies are significantly above the MCL of 10 mg/l (Figure 12). The variability of data for each individual dairy farm might be partly caused by different numbers of the observations (Figure 10). For farm SIE there is only one monitoring well with a field as source area and the median value is quite high. For farm DUR there is a large range of higher nitrate concentrations in the observed data set. For farms CLA and FIS higher peak nitrate concentrations have been observed. All the other dairy farms range between 0 and 100 mg/l. A statistic summary for each well can be found in Table A 2.

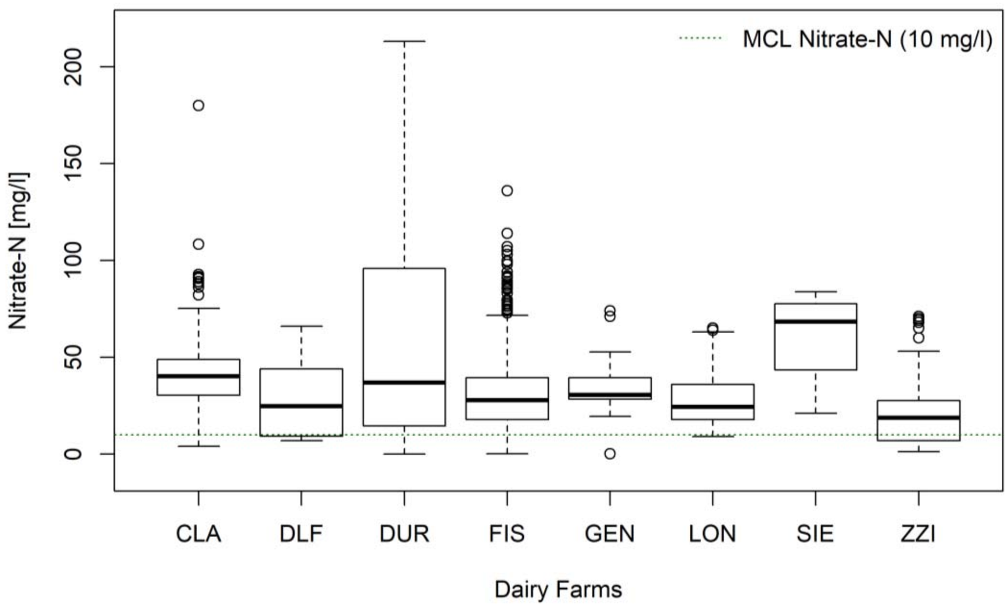

Figure 12: Boxplots of values of NO_3-N in all field monitoring wells per dairy farm.

The Shapiro Test showed that the data was not normal distributed (p-Value <0.00001). Groundwater data was fitted to different distributions and the KS-Test was performed to test if the sample has a certain distribution. Between the Gamma, Weibull and Log-Normal Distribution the data fitted best to the Gamma distribution (d-Value= 0.066049). The same result was shown by the Akaike information criterion (Sakamoto et al. 1986). For lower Nitrate concentrations up to 50 mg/l values the gamma distribution fits quite well. For higher Nitrate concentrations the gamma distribution fits less to the original data and under- or overestimates the Nitrate in groundwater. Most of the data analyzed is below 100 mg/l and seems to be captured well enough by the gamma distribution (Figure 13). It can be assumed that the values estimated by the gamma distribution are within a realistic range.

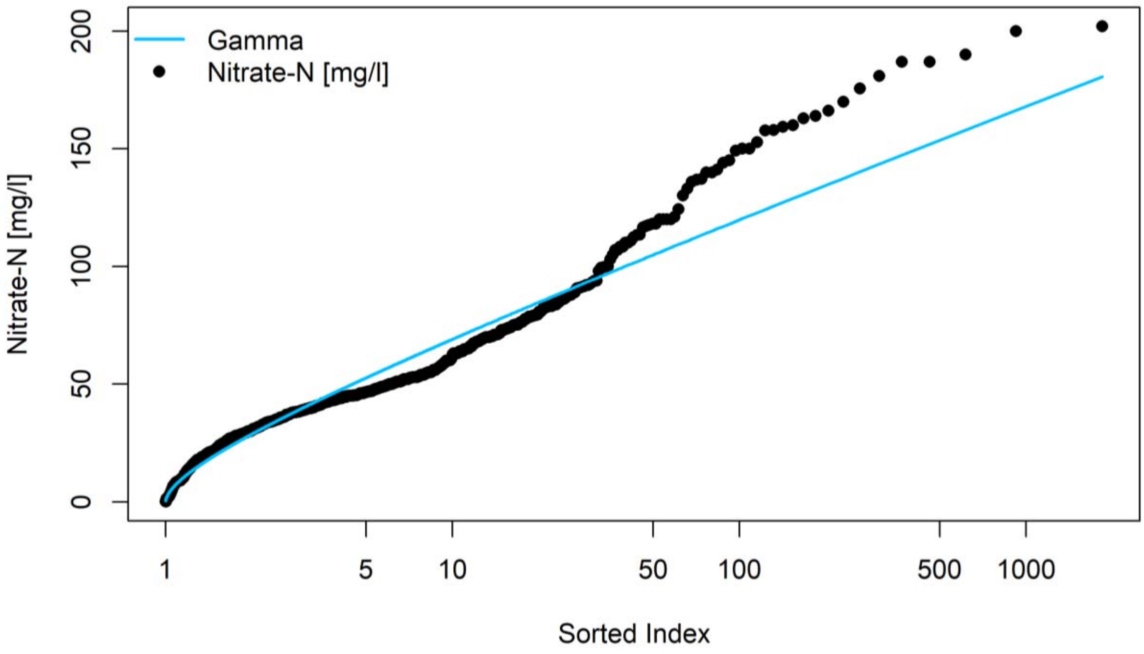

Figure 13: Distribution of groundwater data fitted to a gamma distribution.

The data was log-transformed and fitted to a Weibull distribution. The Weibull distribution is an exponential distribution, which is generalized and used for survival functions, among others (Harrell 2001). Even higher nitrate values are represented well by the Weibull distribution and lie within the confidence interval (Figure 14). The KS-Test of the log-transformed data showed a low D-Value of 0.0668. The D-Value represents the largest differences between data and distribution. It can be concluded that the Weibull distribution fits the data well.

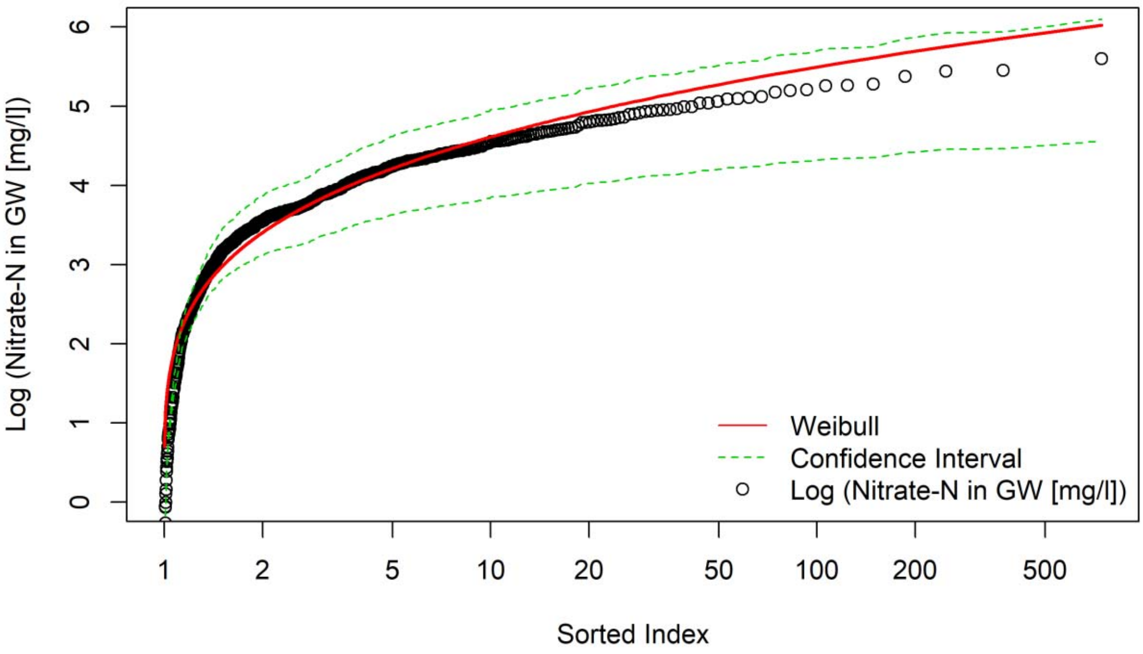

Figure 14: Groundwater data, log-transformed, fitted to a Weibull distribution.

Since the data are not normal distributed only non-parametric tests can be applied.

5.1.3. Trends in nitrate concentrations

The data set was tested for seasonal trends but none could be confirmed, i.e. variations between the seasons are not significant. All four seasons show a similar distribution and even the amount of outliers is similar (Figure 15). A Kruskal-Wallis Test confirmed the assumption that there is no significant difference between the mean values of each season. Harter et al. 2002 showed no large seasonal influences for nitrate concentrations in groundwater and so it can be assumed a yearly value gives a reliable average.

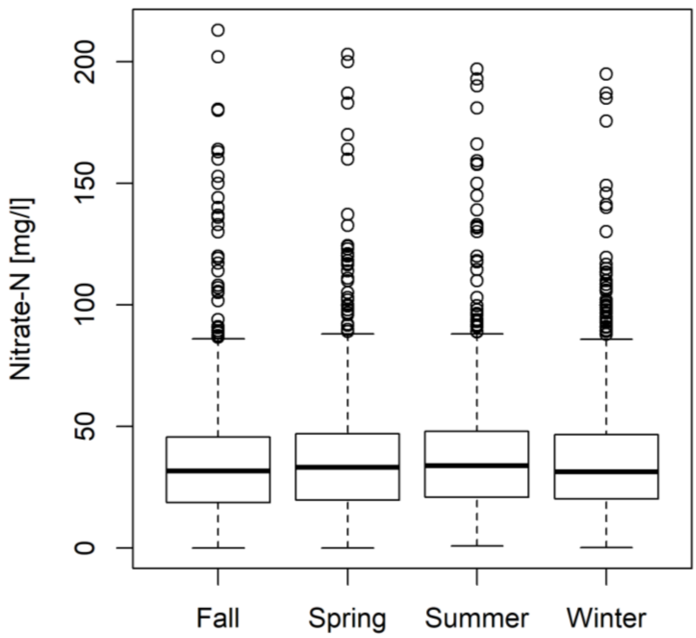

Figure 15: NO_3-N for all field monitoring wells per season.

Long-term trends in nitrate concentrations differ for each dairy farm. At some dairy farms nitrate concentrations vary within a certain range over consecutive years (farm CLA, DUR and FIS). Farms GEN and ZZI show a more or less constant trend with little variation at the beginning respectively the end of the observed time period. Farms DLF and LON show a small upward trend in the recent years. Farm SIE is the only dairy farm where there is a strong downward trend in observed nitrate concentrations (Figure 16).

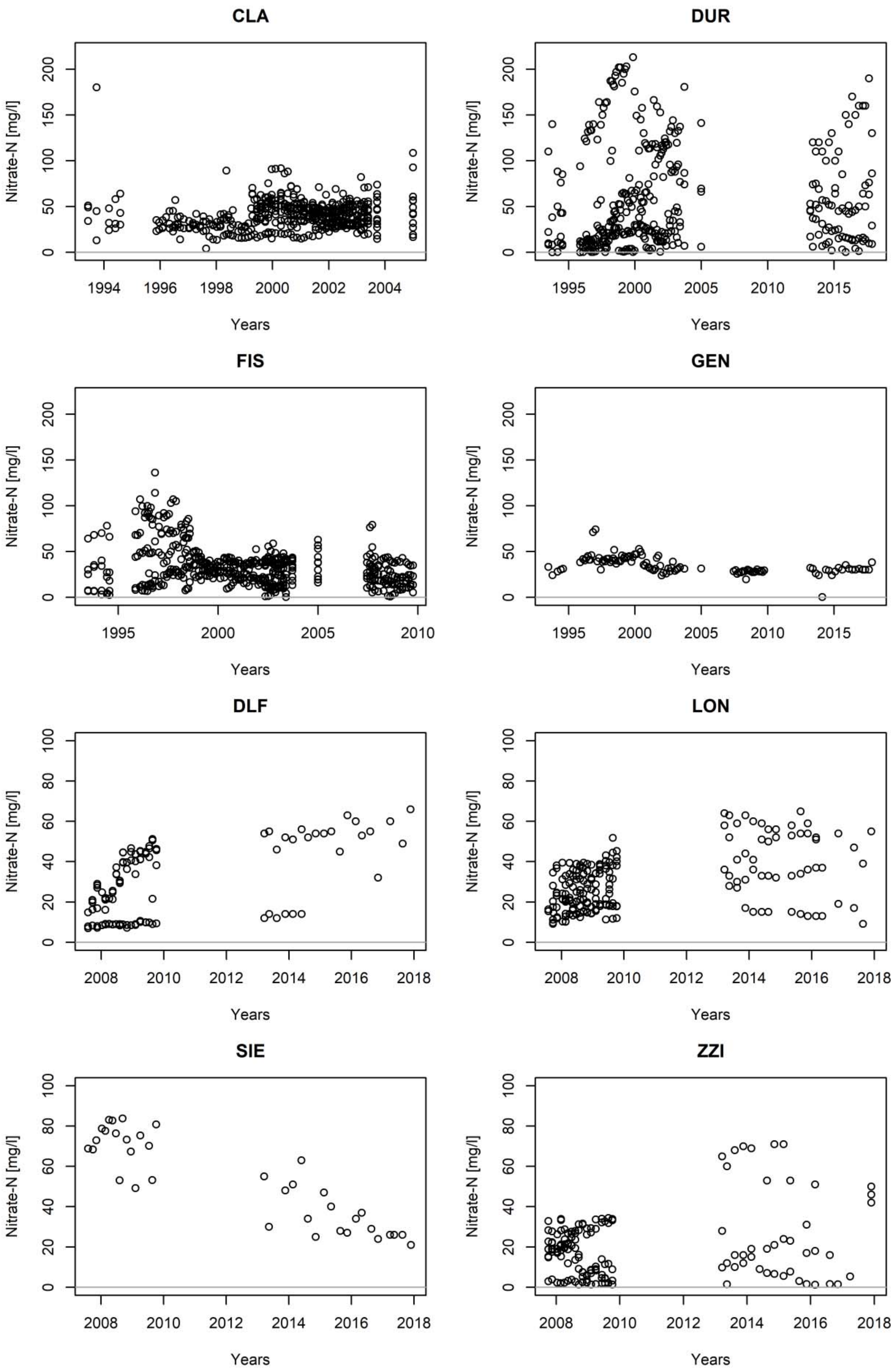

Figure 16: Changes in the NO_3-N concentration over time.

Mann-Kendall Tests were calculated to test the trends for significance. Kendall's Tau indicates the strength of the correlation. A p-value below 0.05 is seen as significant. There are significant downward trends for farm CLA, farm GEN, farm FIS, farm SIE and significant upward trends for farm DLF and farm LON. For both farm DUR and farm ZZI the values are highly variable from different wells from the same year. Overall the trend shows downwards representing each unique measurements of all wells on all dairy farms (Table 4).

Table 4: Results of Mann-Kendall test for NO_3-N values of field wells by dairy farm.

Dairy farm	**Tau**	**p-value**
DUR	0.128	0.128
GEN	-0.379	2.81e-10
FIS	-0.224	=<2e-16
CLA	0.101	0.000944
DLF	0.417	=<2e-16
ZZI	-0.032	0.425
FARM SIE	-0.553	2.48e-09
LON	0.227	=<2e-16
All Dairies	**-0.127**	**=<2e-16**

For the monitoring wells there are 11 wells with a positive trend, 13 with a negative trend and 14 which did not show a significant trend (see Table A 3). These data can be compared to the more extensive monitoring done by LSCE (2018) since 2012. The groundwater quality trend analysis for 62 dairy farms were investigated and showed that for about 25% of the monitoring wells there was an increase, for 25% decrease and for 50% stable nitrate values (LSCE 2018). For the subset of the field wells of eight dairy farms there is about a third of the wells in each group. Possible reasons can be longer time periods were chosen and different subset of management units. Also, the eight dairy farms are not located in all different parts of the CV like the dairy farms investigated by LSCE 2018. This means that different subsets of all dairy farms are compared and it is likely that they both represent a different basic population of dairy farms.

The mean groundwater values stay in the same range throughout the time series. For comparison with the estimated nitrate leakage from the N mass balance a linear regression was used to calculate the mean values for the missing years (Figure 17). Observed values are filled points, estimated values are non-filled points. For some dairy farms calculated nitrate concentrations in previous years show a large deviation from the groundwater data which is either lower (farms DLF, LON and ZZI) or higher than the observed range (farm SIE). These are the dairies where observed data is only available for last years. For dairy farms with a longer observed time period the predicted nitrate concentrations are within an expected range (farms GEN, DUR). Although for some dairy farms (farms CLA and FIS) the trend in previous years might be too steep in recent years. Generally, it seems the range of data is captured by the linear regression and the predicted values can be used for comparing them to the mass balance data.

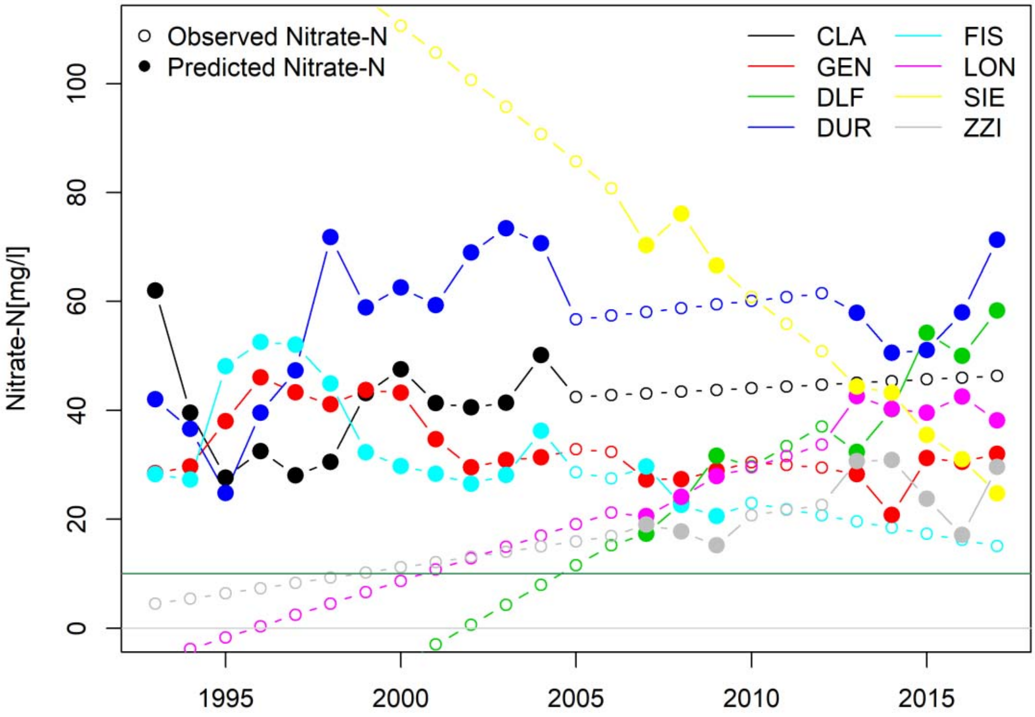

Figure 17: Observed and predicted nitrate-N concentrations in monitoring wells using linear regression.

5.2. Comparison of nitrate in mass balances and groundwater

The NO_3-N concentrations of the identified field wells were compared with the calculated N leakage concentrations from the mass balances. For the mass balances only data from 2012 to 2017 are available. This is the time period where there is observed data for the majority of the dairy farms available. For the groundwater data the available data on all field wells was used for all years.

5.2.1. Distribution of data

Both groundwater data and MB A and MB B results. The amount of available data for the mass balances is much lower than for the groundwater data. Groundwater data has only positive values of nitrate concentrations whereas both mass balances also estimated negative values for the potential nitrate leakage. MB B has the widest variability of the three data sets, while MB A has a very small variability and the smallest standard deviation. The mass balance data is close to a normal distribution. A Shapiro-Test confirmed this suggestion for both mass balances. A Wilcoxon-Rank Test showed no significant difference between the values of the two mass balances when testing whether they are from different populations having the same distribution. However, there are only 45 values for each and the differences in standard deviation are large. For MB A it is 14, for MB B it is 53.

Data of groundwater nitrate concentrations and estimated leakage of the mass balances as well as their respective frequency and Q-Q-Plots are shown in Figure 18.

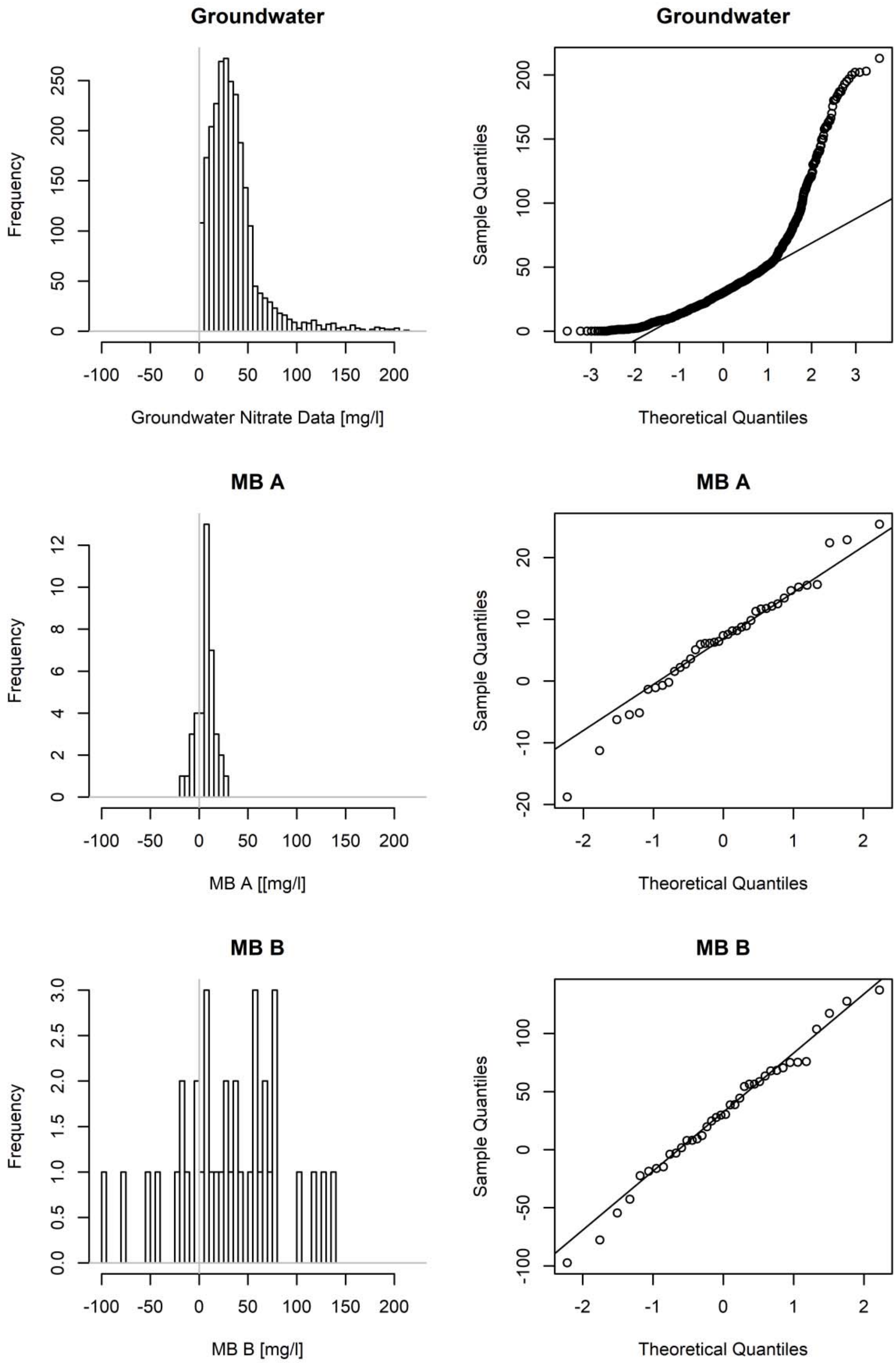

Figure 18: Description of total groundwater and mass balance data.

The variability of mass balance data is also reflected on individual farm level. Groundwater data and the MB B data varies more between the farms than the data of MB A. MB A is based on N applied and N harvested and the ratio between them is required to be below 1.4 by the Dairy Farm Order. The majority of the dairy farmers meet this standard (Miller et al. 2017). MB B based on the excreted manure show larger differences between the farms (Figure 19). Groundwater data was already shown and described in Figure 12 but is plotted again for comparison purposes with the mass balance data.

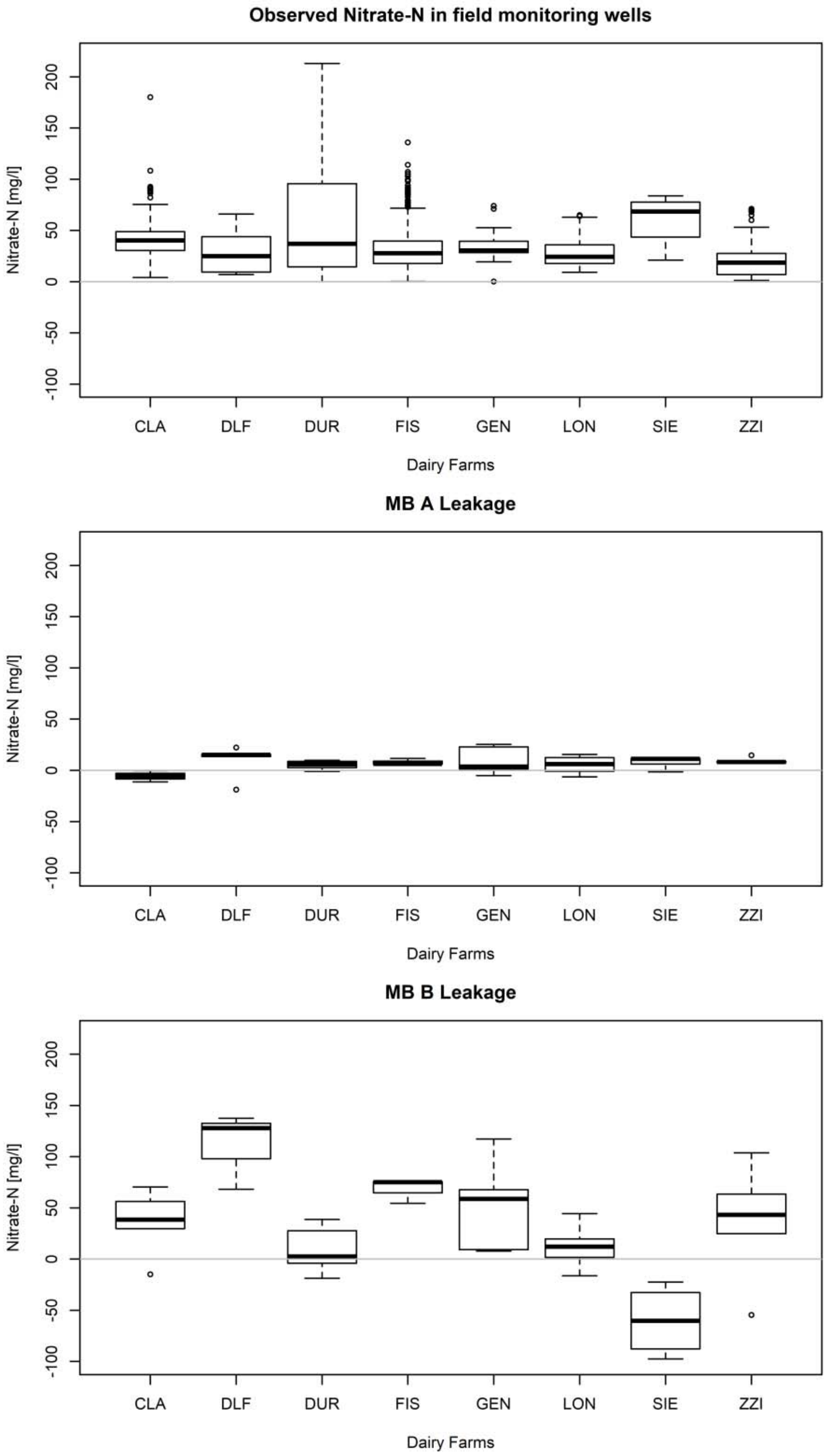

Figure 19: NO_3-N in groundwater and estimated from mass balances per dairy farm.

5.2.2. Graphical comparison per year with extended data

In the first step groundwater data and the mass balance data are compared using the data of all years. Due to losses to the atmosphere and processes in the soil like denitrification higher nitrate concentrations from the mass balances than in the groundwater should be expected. However, a systematic underestimation of the potential leakage for MB A is shown, which indicates a major systematic error (Figure 20).

The comparison with MB B shows the data scattered around the 1:1-line including negative values (Figure 20). In spite of the scattering MB B seems to provide more realistic results.

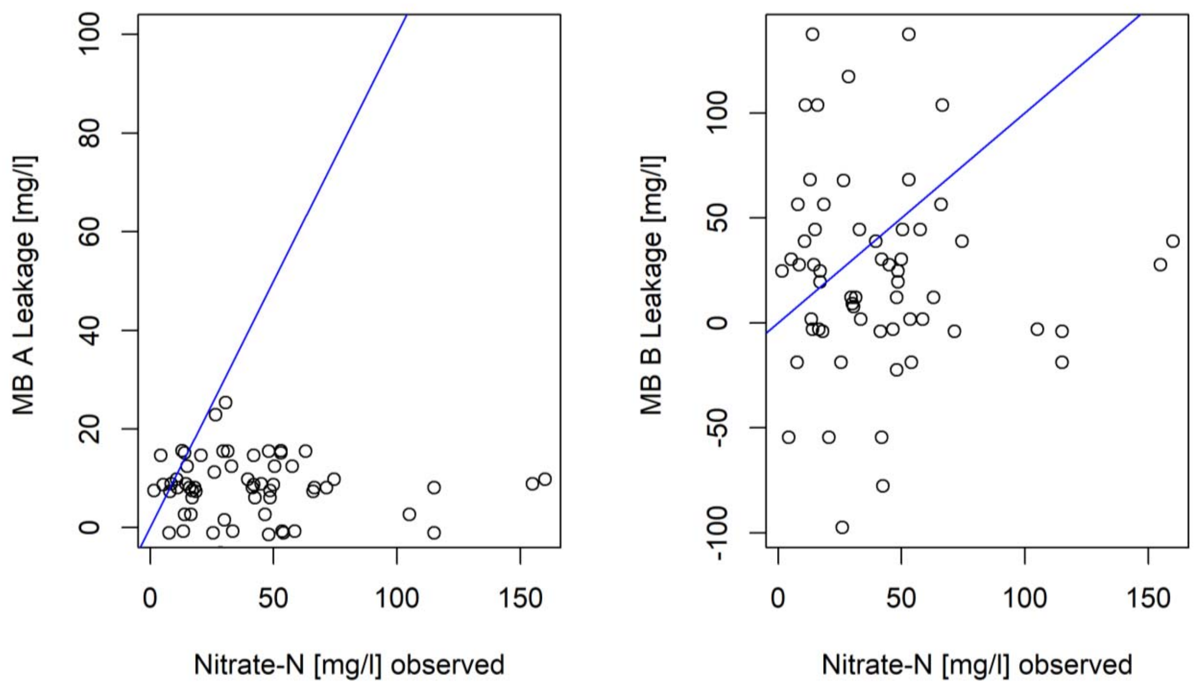

Figure 20: Scatterplots of NO_3-N in groundwater and estimated from two mass balances.

The potential leakages from mass balances were compared to the observed groundwater values per year and each dairy farm for the years 2012 to 2017 (Figure 21). Some groundwater values were calculated using a linear regression of the original data set. Both MB A and MB B have some missing values. For MB B there is more missing data than for MB A. The mass balance data was not extended as the variability of the data is much larger than in the groundwater data (5.2.1).

The NO_3-N leaching data from MB A tend to be lower than the observed ground nitrate content in most cases. While the data for some farms (FIS, GEN, SIE, ZZI) are close, the difference of the others farms are significantly larger. Higher changes in year-to-year variations for the mass balance might be due to different crops planted (farms GEN, DLF and ZZI). For the farms DUR, GEN, DLF, LON, SIE and ZZI only the fields assumed to have an impact on the monitoring wells were taken into account. However there is no difference when looking at the discrepancies to the mass balance data.

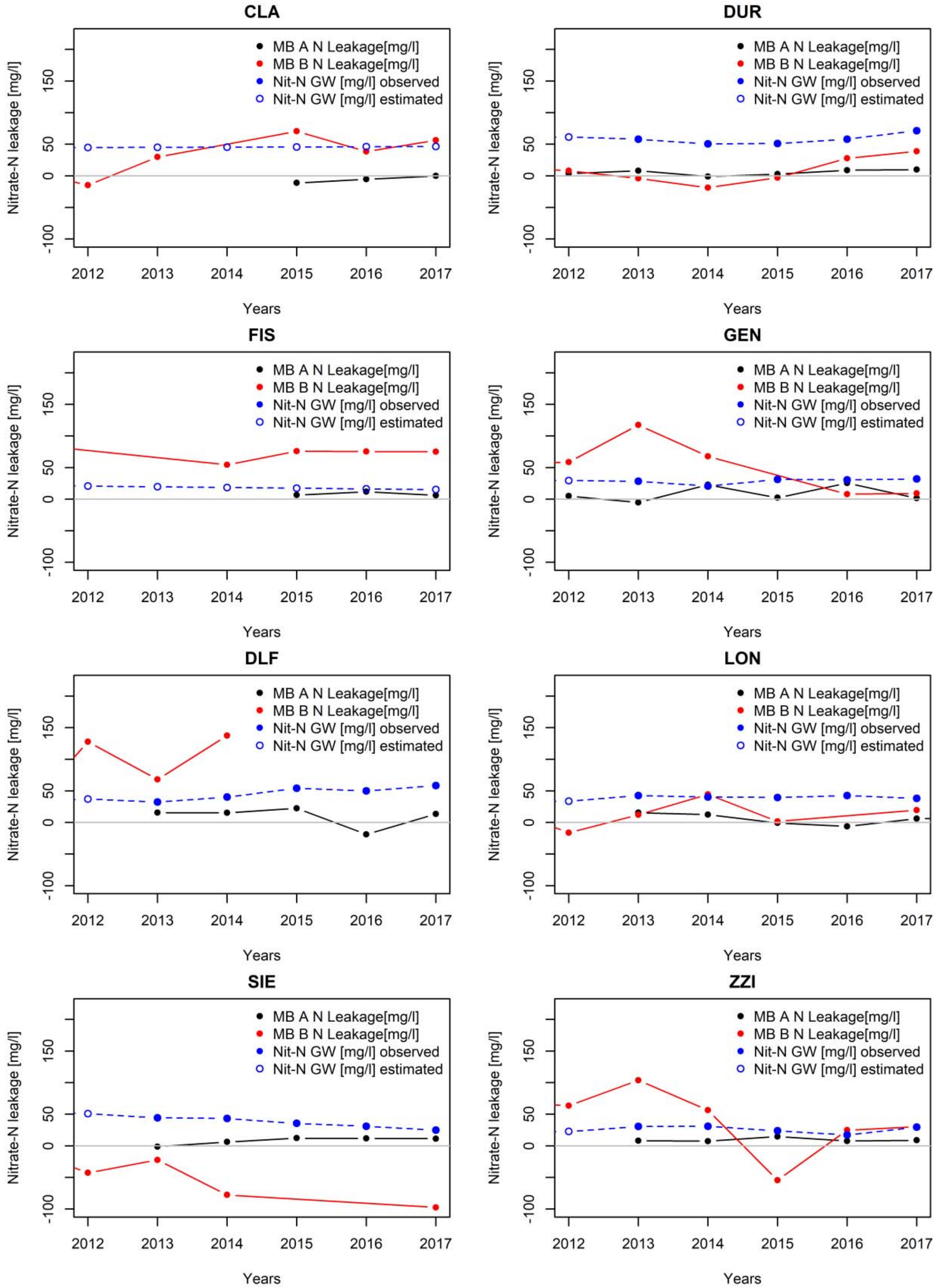

Figure 21: Observed or predicted NO_3-N in groundwater and estimated mass balance leakages.

For MB B the annual variations are significantly higher than for MB A. Some farms show negative leakage in some years (farms DUR, LON and ZZI). Farm SIE shows only negative values. According to the reports farm SIE significantly exported manure off the farm while the harvested N remained the same. A reason for this might be reduced lagoon capacity. The decrease of nitrate concentration in the groundwater of farm SIE is based on one monitoring well only. This well might be influenced by local factors and is not necessarily representative for the entire farm. For farms CLA, DLF and ZZI there is a high variation for each year. Reasons for this could be changes in herd size, planted area or imports of forage. All in all, there are no apparent trends for all farms visible. This suggest that important farm specific factors, e.g. local hydrological conditions or individual farm management practices, are not considered in the mass balance.

Other possible reasons for discrepancies are discussed in 5.6.

5.2.3. Ratio of estimated leakage to observed values

As shown above the values of the dairy farms vary significantly. For better comparison of the individual dairy farms a ratio was calculated. The ratio is the potential leakage of each mass balance divided by the observed or estimated groundwater nitrate concentration. The ratio is calculated per year. These ratios show the results from all dairy farms at the same scale (Figure 22).

A ratio of 1 (green line) means that both compared data sets show equal values. This is rarely the case (e.g. farm LON for MB B in 2014). A ratio above 1 means that the mass balance shows higher values than the groundwater data which would be expected for all values. This is only the case for farm FIS. All other dairies are partly below this line except farm DUR where all estimated values are lower than the expected groundwater data.

The ratios for nearly all dairy farms show high variations for the plotted time period. The variability between the dairy farms is similarly high as in Figure 21. The results show no clear trends. More farm specific data and further analysis are required for better understanding.

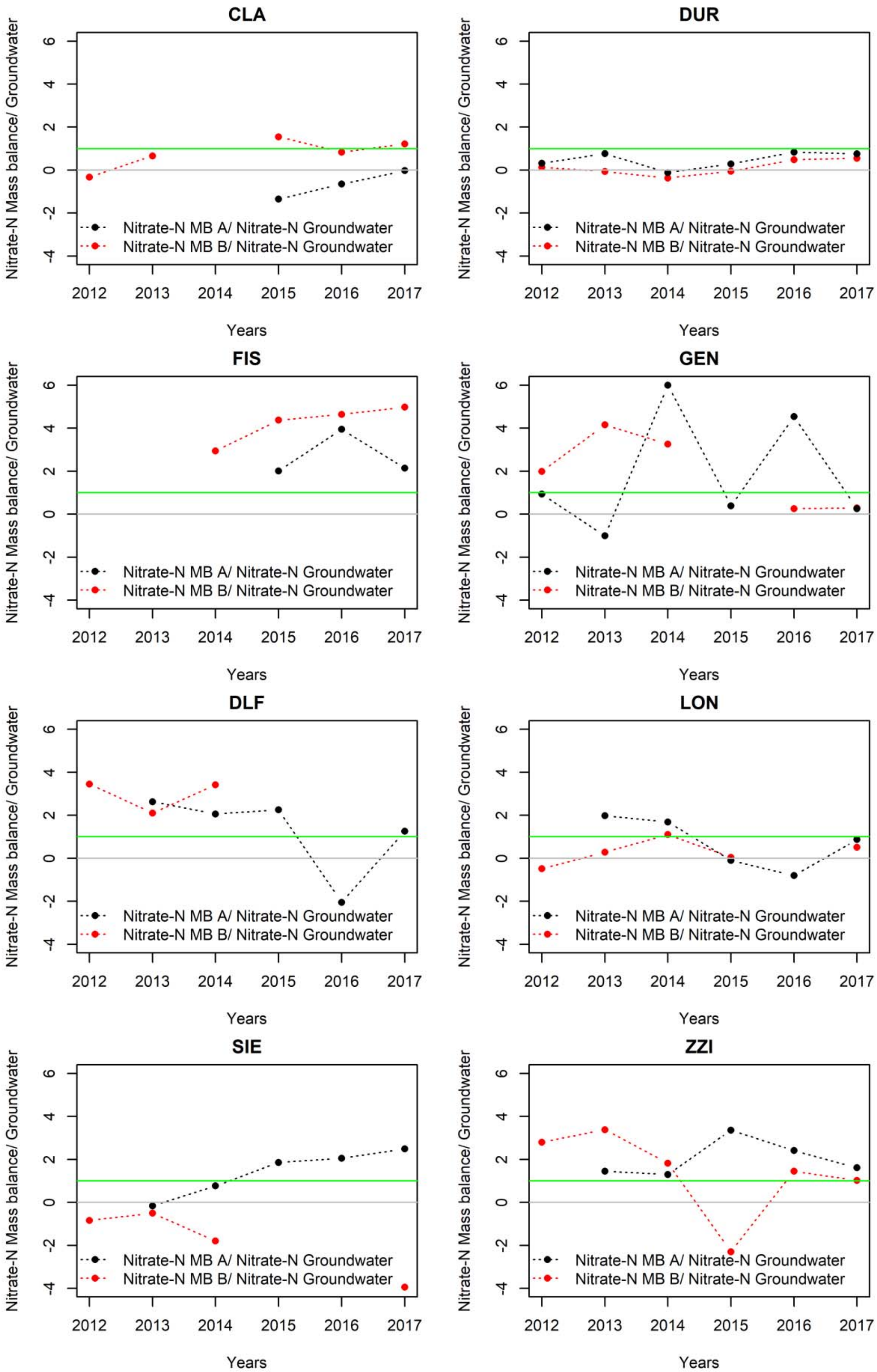

Figure 22: Ratio of mass balance A and mass balance B for each year.

The variations of the individual dairy farms might be explained by additional factors. Two additional factors are investigated here, dairy farm age and DTW. These were chosen as data was available for most of the dairies and years. For DTW two dairy farms (CLA, FIS) did not have any measurements after 2012. For these dairy farms the six most recent available years were chosen which are 1998 to 2003. It is assumed that the variations for these different decades are within the same range.

The dairy farm age does not show any apparent trend for MB A. The dairy farms can be clustered in two general categories according to the DTW which are due to the different general depth in groundwater in different regions (Figure 23).

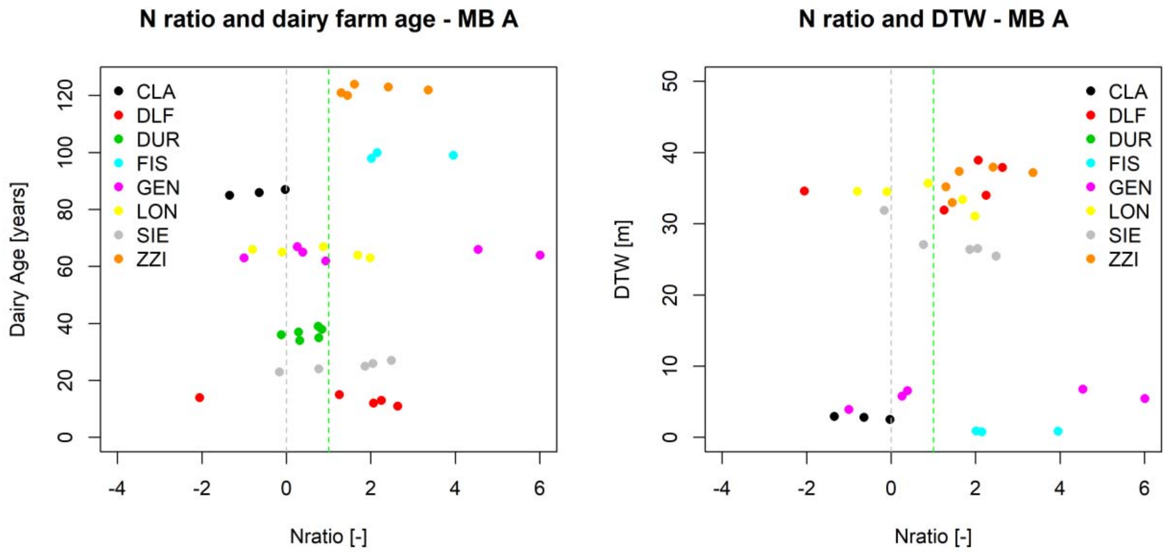

Figure 23: Ratio of mass balance A plotted against dairy farm age and DTW.

Similar to MB A no apparent trend is visible between MB B and dairy farm age. For DTW the expected two clusters are shown (Figure 24). As described above the variations of the dairy farms seem to be too high so that no trends between the two data sets can be observed. Other additional variables to assess the discrepancies between the two data sets are discussed in the following chapter.

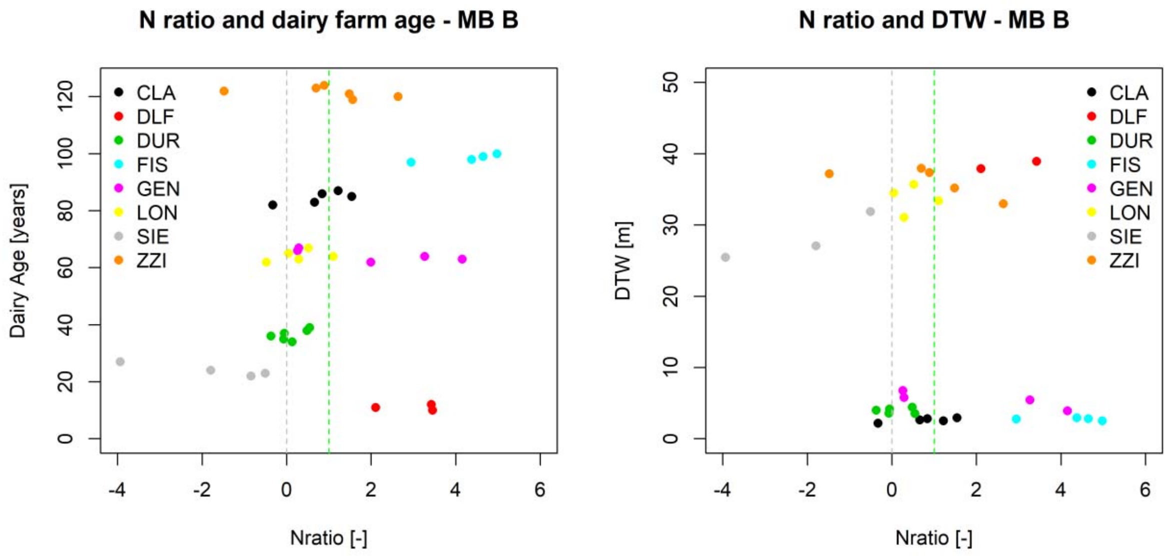

Figure 24: Ratio of mass balance B plotted against dairy farm age and DTW.

5.3. Possible variables influencing NO_3-N in groundwater

In the previous part (0) significant discrepancies were found between the sampled groundwater data and the estimated values from the mass balances. Observed groundwater values are available for many years and at significant sample size, while only a low number of mass balance data exist. That is why, it was chosen to analyze the data from groundwater samples regarding impacting parameters.

To assess the impact of the various parameters on the NO_3-N values, the data was divided into categories and the mean values of the categories were compared using either a Wilcoxon-Rank-Sum Test or a Kruskal-Wallis test. Both were used successfully in other studies comparing groundwater and mass balances (Lockhart et al. 2013; Mu et al. 2016). This chapter starts with an overview of the results of the tests and then describes the influence of each parameter separately.

For both tests all groundwater data of an individual monitoring well was aggregated. Parameters with less than 10 values per category were not considered. Most of the parameters show no significant difference. Only the nitrate concentrations in different parts of the CV show a significant difference (Table 5 and Table 6). All variables are discussed below in further detail.

Table 5: Parameters tested with Wilcoxon-Rank-Sum-Test.

Parameter	p-Value (in bold significant p <0.05)	
	Aggregated by median	**Aggregated by mean**
DTW (>/<12m)	0.08	0.019
DO/Mn categories	Not enough values	Not enough values
Texture in drill logs of MW (sand and clay)	0.086	0.06
Different parts of the CV (Fresno vs. Sacramento office)	**0.024**	**0.0045**
Dairy farm age (>/<40years)	0.9	0.78
Season	0.29	0.29

Table 6: Parameters tested with Kruskal-Wallis-Test.

Parameter	p-Value (in bold significant p <0.05)	
	Aggregated by median	**Aggregated by median**
Housing (Free stall vs. Open lot vs. Combination)	Not enough values	Not enough values
Well Source Areas (see 5.1.1)	**$< 2 \times 10^{-16}$**	**$< 2 \times 10^{-16}$**

5.3.1. Depth to water table

Due to decreasing Oxygen content NO_3-N levels are expected to decrease with deeper water levels. This means in shallow groundwater higher NO_3-N levels are measured. One study in the CV found that lower DTW (< 21 m) is related to higher nitrate levels, deeper DTW to lower nitrate levels (Lockhart et al. 2013).

Several monitoring wells show a decrease of DTW over the last few years and then a sudden increase in 2017 (Figure 25). For farm SIE this cannot be shown because there is only few observations available. The decrease is probably the impact of the Californian drought where more groundwater pumping led to decreasing water levels (Thomas et al. 2017). However, most of the fields are irrigated so the reason for the decline is not the missing precipitation in itself which implies less recharge but the overall decreasing groundwater level. Note the different scale for the upper four dairy farms plotted. The dairy farms on bottom generally have sandy-loamy soils and a higher DTW.

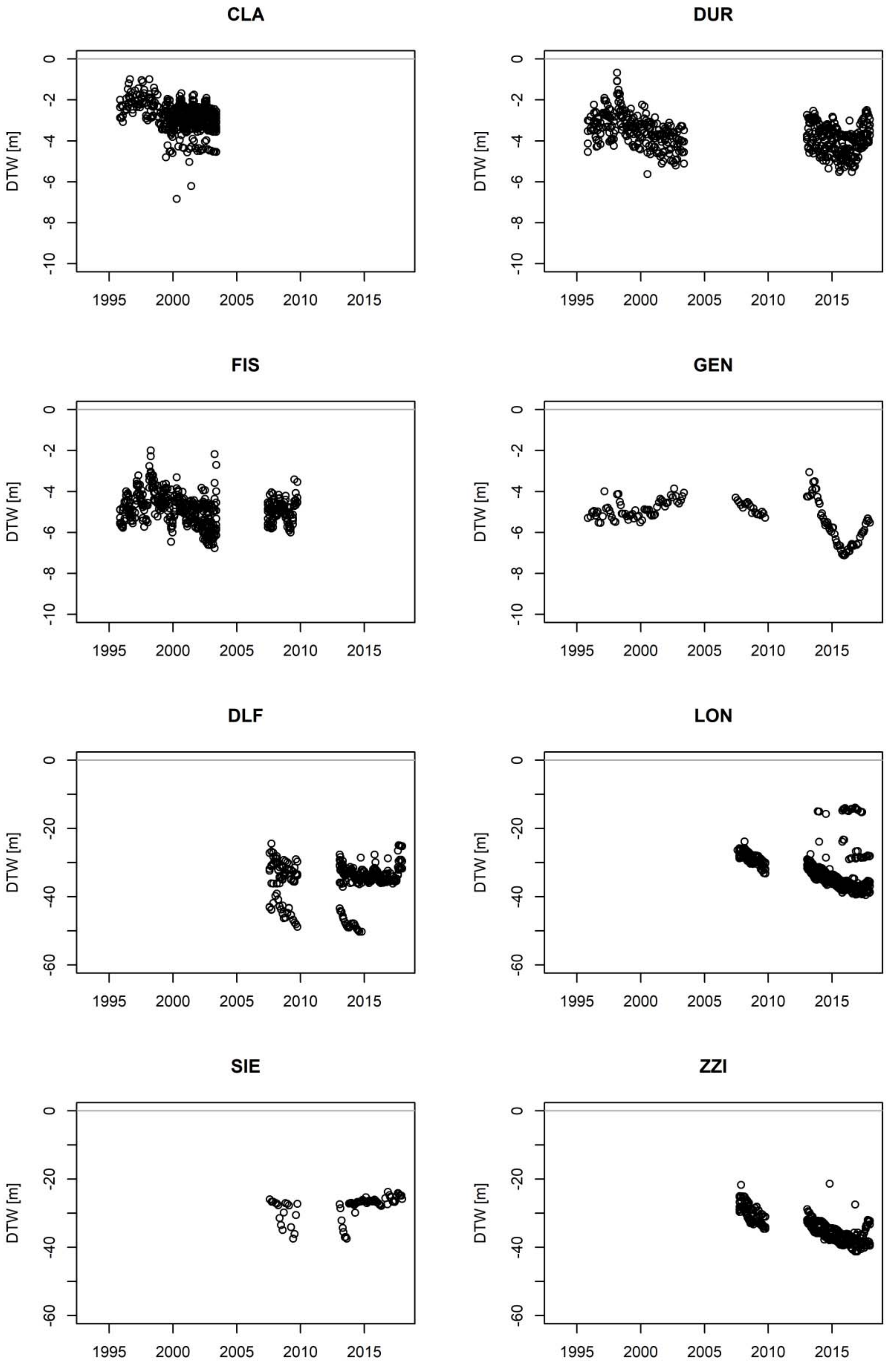

Figure 25: Changes in DTW in field monitoring well per dairy farm over years.

Increasing DTW and decreasing nitrate concentrations would be expected when comparing the two parameters. However, the data by dairy farm do not show any trend (Figure 26).

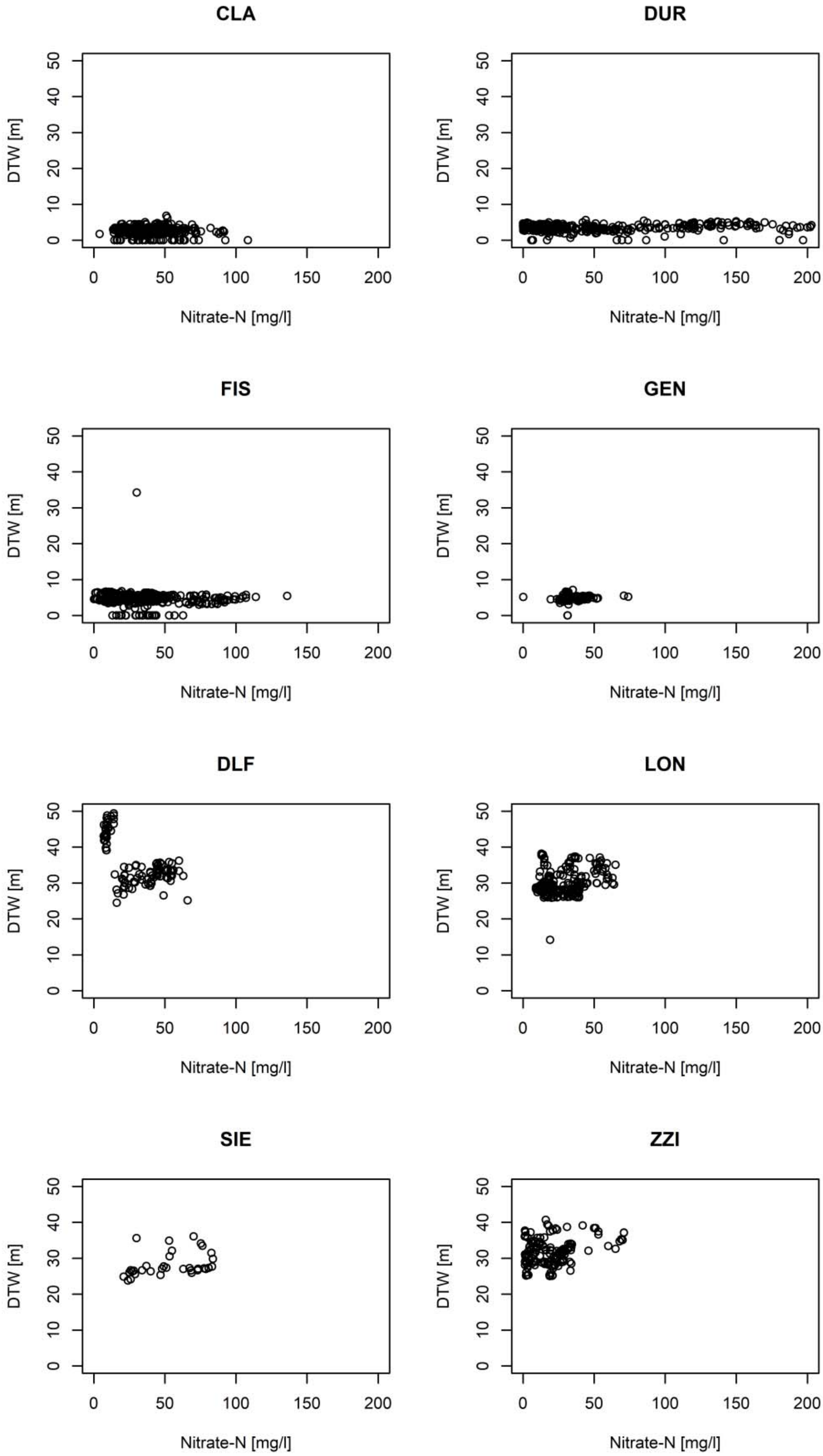

Figure 26: DTW and NO_3-N per dairy farm.

Data from all field monitoring wells shows the expected trend of nitrate concentrations relative to DTW. The larger the DTW the smaller the nitrate concentrations in the groundwater (Figure 27). Still, there is a lot of variation in the data.

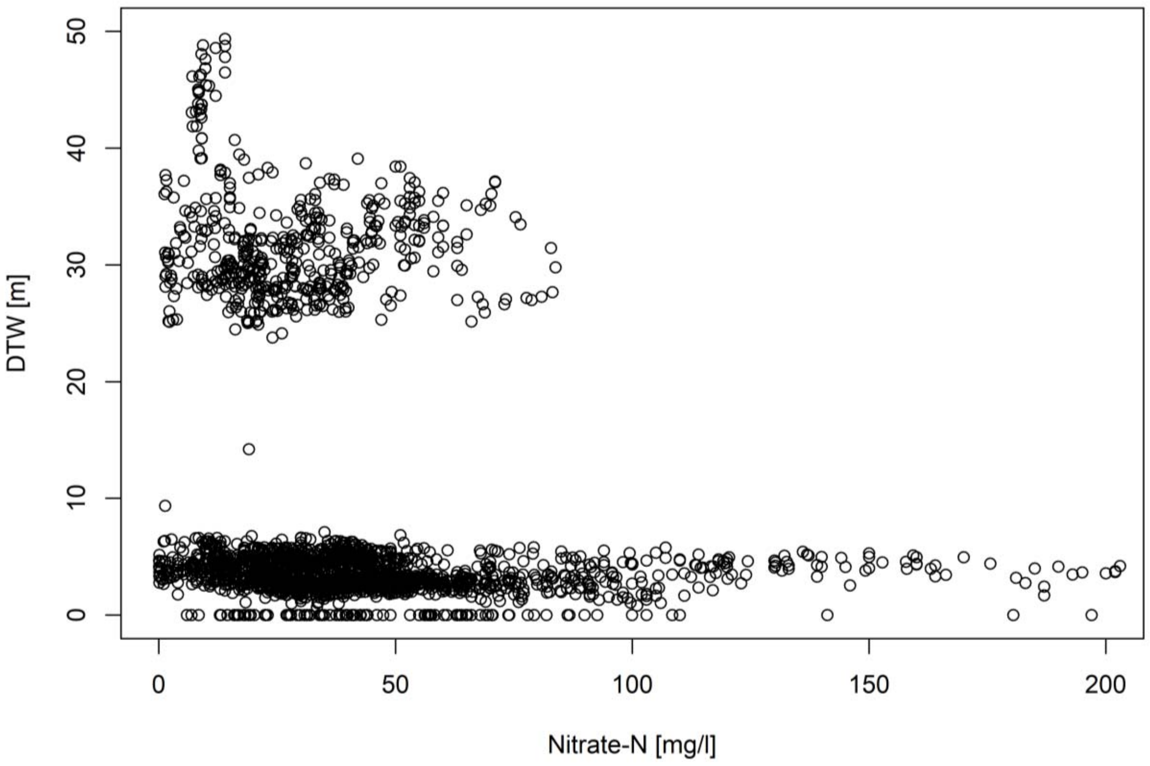

Figure 27: DTW and NO_3-N for all field monitoring wells.

5.3.2. Mn and DO concentrations

Several studies show that areas with low DO and high Mn show low NO_3-N (Collins et al. 2017; Ransom et al. 2018). For the data set of the eight dairy farms it was investigated whether a similar result can be found.

For the eight dairy farms only few DO and Mn measurements were available. 970 samples showed non-detects while about 250 samples from 2001-2008 provides usable data. The wells were clustered into low DO (< 0.5 mg/l) and high Mn (> 50 mg/l). The thresholds were chosen according to the sampling procedure of the USGS (Rosecrans et al. 2017). However, only two wells had a total of four samples where DO was < 0.5 mg/l and Mn > 50 mg/l. Note that high values of Mn are required for this analysis. The groundwater quality data was aggregated by year and monitoring well using arithmetic mean.

The nitrate concentrations in groundwater for measurements with low DO and high Mn seem to be higher than the others (Figure 28). None of the wells fall in the category of expected low NO_3-N conditions for the total period, which is shown in the aggregated data. Hence the expected trend cannot be shown by the data available. However, all wells in this study have high NO_3-N values, i.e. no wells are expected to show low DO and high Mn (Collins et al. 2017; Ransom et al. 2018).

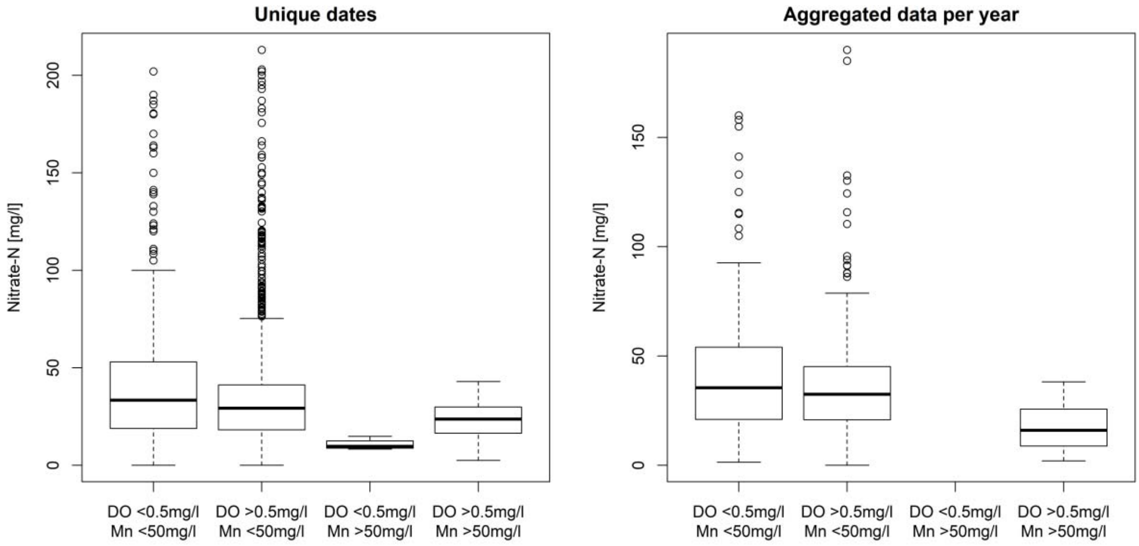

Figure 28: Boxplots for field wells data by unique date and by median per year.

5.3.3. Texture

Texture is an important factor as it influences the recharge and the denitrification. The monitoring well drill logs describe the geology as texture classes along the drill hole. The wells were divided according to the drill logs into either mainly sandy or clay. The texture was calculated by taking the highest percentage of either sand or clay per well drill log. Most of the wells were assigned the texture sand.

The class clay has lower nitrate concentrations than the monitoring wells with texture sand (Figure 29). This meets the expectations that on sandy soils faster recharge and therefore less denitrification takes place.

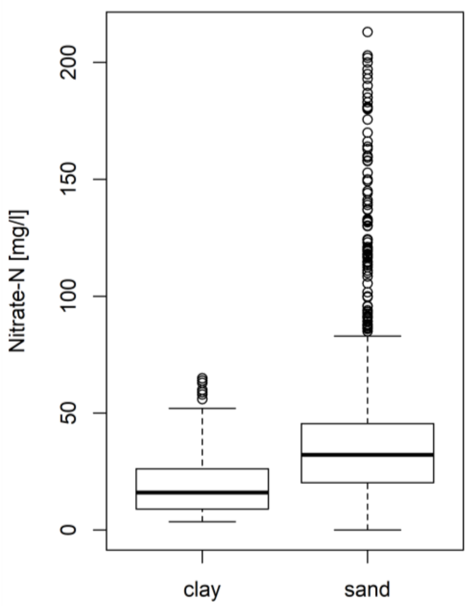

Figure 29: NO_3-N according to main texture of monitoring wells.

5.3.4. Geographical region

Four dairy farms are located in the central part of the CV, the SJV (farms CLA, DUR, FIS and GEN). The other four farms are located in the southern part of the CV (farms DLF, LON, SIE and ZZI). There is a significant difference in NO_3-N values between the two geographical regions (Figure 30). The regional differences are associated with integrated factors such as DTW or texture. It shows an integrated influence of various factors such as geology and hydrology.

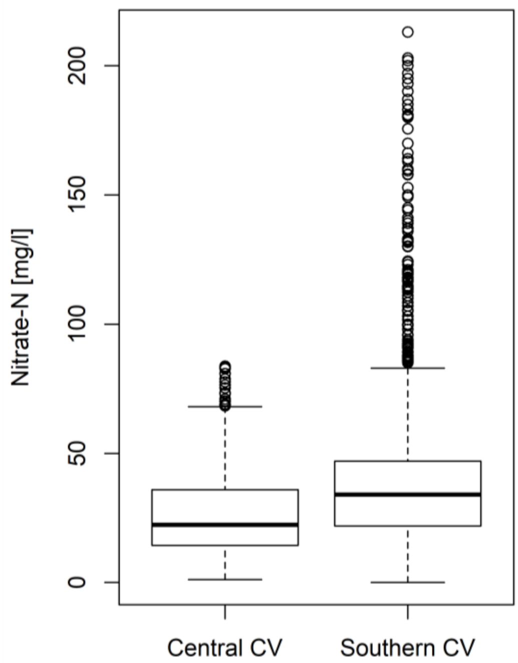

Figure 30: NO_3-N observations in different areas in the CV (north and south).

5.3.5. Age of dairy farms

It is assumed that the age of dairy farms influences the NO_3-N values in the groundwater. Newly built dairy farms should have less impact on the groundwater if there was no dairy farm at the same location before. Additionally, it may take several years before an impact can be measured in the groundwater.

The farms were divided into two categories of age of dairy farms. No significant difference between the two groups in nitrate concentrations in the groundwater has been identified.

5.3.6. Summary of parameters

The selection of parameters was done by looking at significant factors in other studies and by choosing available data for the eight dairy farms. There are a couple of variables which are depended on each other, e.g. the texture class depends on the region. This must not be neglected when further interpreting the data.

The selected parameters were explained above. Other parameters which were not analyzed here shall be mentioned.

Soil type is an important factor as it influence the recharge and denitrification (Boumans et al. 2005).

Changes of management practices e.g. timing and rate of N application and frequent manure removal from corrals can have an impact on nitrate levels, but cannot be directly linked because even similar management practices are highly variable (LSCE 2018). Therefore it was decided not to investigate the management practices of the eight dairy farms. However, a study states that factors like DTW or recharge might have a higher influence on nitrate in groundwater than management practices (Boumans et al. 2001).

Certain geological structures might also influence the nitrate concentrations. An increasing trend of nitrate contamination was found in the eastern part of the fans of the CV (Burow et al. 2013).

Lastly, non-agricultural factors in the well source area should not be ignored as a possibility to influence nitrate level (Gutiérrez et al. 2018).

5.4. Linear Mixed Model

Different LMMs were calculated using the parameters described in 4.3.2. Originally it was intended to include all possible variables in one model. However, there was not enough data available so an analysis was done for each individual parameter separately. Groundwater data was aggregated on a yearly base as this is the scale of the mass balance data. In total six dairy farms (farms DLF, DUR, GEN, LON, SIE and ZZI) and 15 monitoring wells were taken into account. The data was taken from the years 2013 to 2017. There were only about 60 observations for each value when using the aggregated data by year and monitoring well. Model inputs and results are shown in Table A 4. It is assumed that a small p-Value (<0.05) indicate a significant influence of the investigated variable. None of the calculated LMMs showed a significant influence. For Mn and DO data a cluster approach could not be used since there was not enough data.

When applying a LMM usually all fixed variables show the same direction in trend. However, as shown in 5.1.2 there is a high variability. Using dairy farms as a fixed variable assumes that they all differ from each other. However, some are located quite close to each other and might have some properties in common.

Verloop et al. 2006 used a LMM with the REML algorithm (residual maximum likelihood) to compare observed nitrate concentrations in groundwater to cropping history. The random effect was the sampling location for each dairy farm. All fixed parameters were included except grazing and N surplus which were added to the model separately to study the effect of management variables. Verloop et al. 2006 compared different crops and their rotation and had a larger data set. This suggests a larger data set is necessary to analyze variables using a LMM.

5.5. Central Valley data

For 729 dairy farms in the CV the potential leakage of the mass balance B was calculated. Variables like region, DTW as well as probability of Mn and DO were considered. The mean for the groundwater data is 44.05mg/l, for the MB B it is 92.63 mg/l.

For the NO_3-N data the values were within the expected limit and might be higher as wells with various source areas were included. Overall, the scale is within the same as for the subset of eight dairy farms (Table 7). However, there are various outliers in both data sets.

Table 7: NO3-N values in groundwater in the Central Valley, divided by region.

Region	**Mean NO_3-N**	**Min. NO_3-N**	**Max. NO_3-N**	**Standard Dev. NO_3-N**	**Median NO_3-N**
Fresno	38.95	0.04	215.82	31.71	31.58
Redding	23.69	3.1	74.62	18.79	16.76
Sacramento	62.03	0.77	270.65	50.85	44.93

The distribution of the mass balance data varies highly compared to the observed NO_3-N concentrations in groundwater. Still, the majority of each data set is within the same range of 0 to 250 mg/l (Figure 31). The Shapiro-Test showed that the data is not normally distributed.

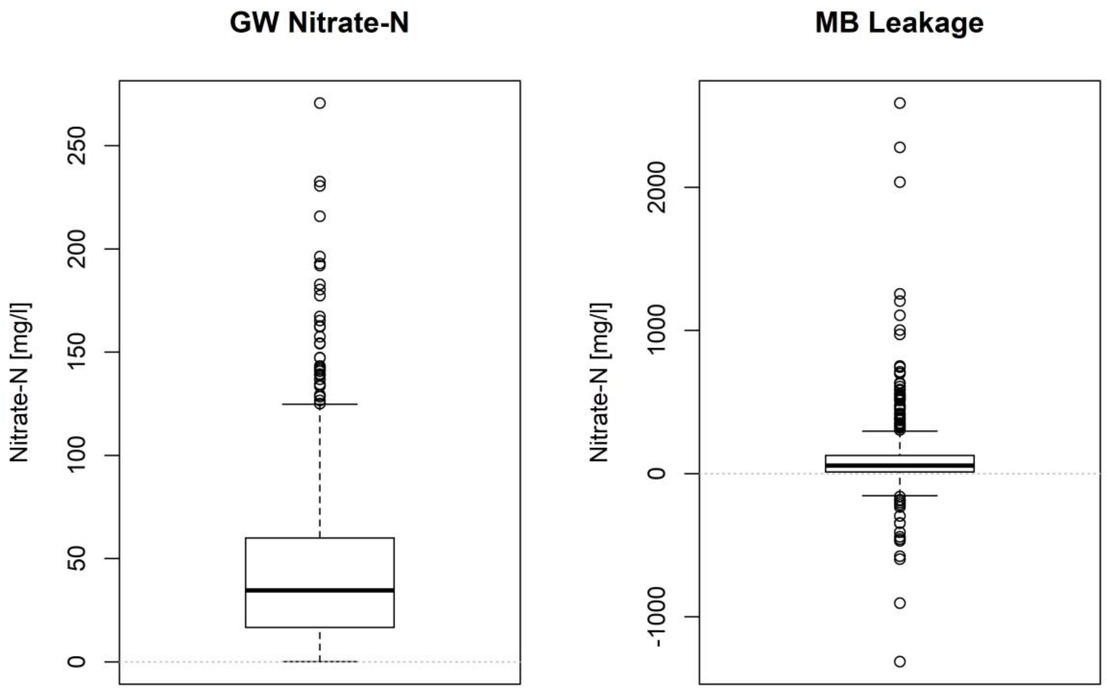

Figure 31: Boxplots for all NO_3-N and MB B data. One value is equal to one dairy farm.

A direct comparison of the nitrate concentrations in groundwater and the potential leakage of the mass balance shows significant variability (Figure 32). One value represents one dairy farm. The Kendall-Tau test for non-parametric data showed that there is a correlation (p-Value = 0.014). To assess the discrepancies between the two data sets different variables were identified.

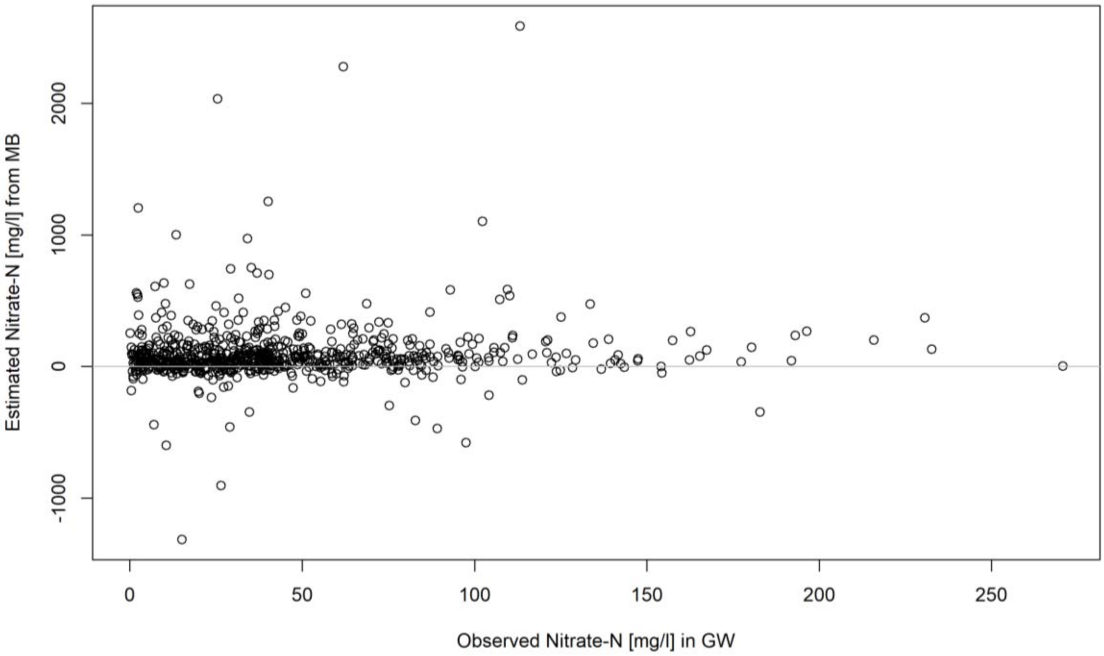

Figure 32: Aggregated data for CV. One value represents one dairy farm.

For further comparison three additional variables, the probability of Mn/DO, DTW and region of the dairy farm, were used to assess the relationship between observed NO_3-N in ground water and estimated nitrate from the mass balance. A Wilcoxon Rank sum test showed that the data differs significantly (p-value = 0.0017). This means that probability for high Mn and low DO has an important impact on the NO_3-N values. For the DTW data was clustered into above and below 12m. The p-Value was very low (<0.0001) so here is also a significant difference. For the three regions a Kruskal-Wallis-Test found a significant difference between the NO_3-N values in groundwater for each region (Table 8).

Additionally, all three tests were calculated for the MB B. No differences were identified between the three sub regions. For the DTW and the Mn/ DO data significant differences for the entire CV were identified (p-Values = 0.04 and 0.03) (Table 8).

Table 8: Parameters tested for significance in the Central Valley.

Type of data	Parameter	Test	p-Value (significant in bold)
Nitrate sampled in groundwater	Counties	Kruskal-Wallis-Test	**<0.0001**
	DTW	Wilcoxon Rank-Sum-Test	**<0.0001**
	Mn/DO	Wilcoxon Rank-Sum-Test	**0.0017**
Nitrate leakage estimated	Counties	Kruskal-Wallis-Test	0.17
	DTW	Wilcoxon Rank-Sum-Test	**0.04**
	Mn/DO	Wilcoxon Rank-Sum-Test	**0.03**

It was shown that there is a significant difference between the nitrate concentrations and therefore an influence of the three variables. The significant influence shown for the CV data set was not identified for the eight dairy farms investigated. This is probably due to the larger sample size of the CV data set and its higher variability. Additionally, the time period for the groundwater data differed between the data sets. However, detailed data on well source area is not available for the CV data set. Therefore the data is not comparable to the results found in the first part for the subset of eight dairy farms. For further research a longer time series of mass balance data and groundwater data would be needed.

5.6. Possible reasons for discrepancies between estimated and observed nitrate

In the last subchapters analyses showed that there are significant discrepancies between the estimated and the observed nitrate. Additionally, the discrepancies vary between the selected dairy farms. This chapter discusses possible reasons for this. The observed trends in groundwater are not discussed again.

5.6.1. Measurement uncertainties

The data sets include measurement uncertainties which are systematic and/or random. Reasons for this are the measurement method and its execution and the heterogeneity of the measured object.

For the groundwater NO_3-N data uncertainty is reported to be small (Ransom et al. 2018). Still, there might exist a bias because of different data sources and different sampling methods for certain groundwater quality parameters (Burow et al. 2013).

For the mass balance there exist uncertainties for all measured parts which are N applied and N harvested as well as manure imports and exports. N applied to field includes N in the manure, fertilizer and the irrigation water. The amount of N in manure and irrigation water can be very heterogeneous (Chen et al. 2013). Only a few reference samples per dairy farm are required for manure, process wastewater and harvest by the General Dairy Order, e.g. four samples of N in manure per year. This limits sample size and data quality for the mass balances. Larger sample sizes would lead to significant additional cost.

5.6.2. Estimation uncertainties

Several factors of the mass balance are estimated.

The atmospheric deposition is generally estimated to be low (Chang et al. 2005).

The atmospheric volatilization of NH_3 depends on pH, temperature and moisture (Viers et al. 2012). Farm management factors such as manure collection, manure storage duration and field application influence the NH_3 losses. Viers et al. (2012) estimate the volatilization prior to land application to be about 38%. Other studies include denitrification and estimate about 20 to 40% loss (Chang et al. 2005). For the required Annual Reports a factor of 30% loss of excreted N was chosen which is lower than stated in the studies above. Additionally, some farmers use dry manure for bedding which is not considered in the mass balances. In this study an additional factor of 10% has been applied in MB B to consider ammonia emissions, transportation losses and other losses.

The recharge was estimated using other studies and considered as constant (Harter 2012a). The recharge is influenced by soil type and crop but irrigation practice leads to low variations in recharge.

In spite of these uncertainties according to Viers et al. (2012) estimations lead to better result than ignoring important factors.

5.6.3. Unconsidered parameters

Denitrification is not considered in the mass balance. Denitrification depends mainly on groundwater age and DO availability (Green et al. 2008). The general data from CV show variations in DO which indicate a variability in denitrification.

N runoff from fields is not considered in the mass balances because of high infiltration rates of sandy soils and the flat topography in the CV.

Other possible inputs of N from sources outside of agriculture such as septic tanks or landfill leakages were not considered (Gutiérrez et al. 2018).

5.6.4. Inconsistencies in reported data

The reported data used for the mass balance showed extremely low nutrient recovery rates. Possible explanations are differences in storage duration. Miller et al. 2017 concluded that the amount of nutrients are not reliably documented in the Annual Reports. Inconsistencies include an unexpected range of N volatilization and a reported N-Ratio (N Applied/ N harvested) of often less than 1.4 which is the target of the General Dairy Order (Miller et al. 2017).

5.6.5. General assumptions for mass balance

A mass balance is a simplification of processes with several assumptions (Ruijter et al. 2007). The impacts of these assumptions are presented here.

To create a mass balance, the long-term storage of N in the soil is assumed to be constant (Viers et al. 2012). Uniform boundary conditions for the fields or the well source areas are assumed (Baram et al. 2016).

Alfalfa fields are excluded from analysis but it is not investigated what happens to fields which are changed from or to growing alfalfa. However, there were 15 fields on five dairy farms which changed from or to alfalfa within the observed period and only one field on one dairy farm which was an alfalfa field for the entire observed period.

Mix in groundwater age might be a reason that mass balances are less directly comparable with the actual observed samples. Especially in the data for the entire CV this might be an issue as the well source area and the direction of groundwater flow are not known (Ransom et al. 2018).

For the direct comparison it is also assumed that there is no time lag between the years. However, it is known that reduced N inputs do not lead to lower the NO_3-N levels immediately. The travel time in the unsaturated zone depends on the depth to groundwater and the recharge rate (Boyle et al. 2013). (Burow et al. 2008) showed that the age of groundwater and travel time to deeper zones of public supply wells represent the nitrate leakage of 40 to 50 years ago.

5.6.6. Area vs. point scale

In this study the representativeness of unique locations or fields sampled for the entire dairy farm was not investigated. However, the mass balance takes into account the entire dairy farm and not individual fields. This may cause some discrepancies between the two data sets.

In general the mass balance is a good approach to estimate the N ratio. It focuses on the dairy farm level which represents an area. Therefore it is not directly comparable to the groundwater measurements which are point measurements. There probably exist some local impacts on the monitoring wells which are not part of the mass balances.

5.6.7. Influence of drought

Recent years showed a decline in groundwater levels throughout the CV. 2017 was a wet year which can also be seen in the monitoring wells. Drought can have impact on NO_3-N observed in groundwater such as denitrification or groundwater flow. However, there is no direct connection to precipitation because of the high amount of irrigation in the investigated dairy farms. The drought led to an increase in groundwater pumping which has effect on groundwater levels.

6. Conclusion and outlook

6.1. Summary of key findings

The objective was to analyze the relationship between the two data sets of estimated nitrate leakage to groundwater and the observed nitrate concentrations from eight dairy farms.

Overall, the comparison between the estimated NO_3-N leakage and the observed values showed a high variability. It cannot predict a value for a specific year or location. Therefore the approach of using a mass balance needs to be improved.

To understand the relationship better possible reasons for the discrepancies were analyzed. An important reason is the scale differences of location and time. The monitoring well represents a point measurement at a specific date whereas the estimated leakage is based on an area and estimated for one year. This makes it difficult to make a direct comparison.

Other reasons are the uncertainties in the input data, the small sample size and multiple assumptions made for the mass balance. Generally, there was a higher variability of the estimated leakage from the mass balances than for the observed groundwater values. This suggests that more efforts are needed to improve the mass balances.

For the eight dairy farms different parameters were tested to explain variations in observed NO_3-N in shallow groundwater and estimated leakages from two mass balances. For the farms significant correlations were not identified. An aggregation of the data led to further information loss. Only aggregated data on region level showed a significant correlation with the NO_3-N data.

Applying the analysis to data of the entire CV showed different results. Three parameters showed an influence on nitrate-concentration. This suggests that a bigger sample is needed to identify correlations between estimated and observed values.

6.2. Recommendations for further research

Mass balances are a powerful tool to analyze systems. However, improvements are required. To improve mass balances more representative data from farm reports are needed. For this the whole farming system, i.e. the corral, lagoon and field, must be considered. Additionally, the estimated parts (assumptions) of the mass balances need further research to reduce uncertainty. Time series covering several decades should be sought to be able to assess long-term changes and time lags of the systems studies (Rankinen et al. 2007; Viers et al. 2012). Buczko et al. 2010 showed that N mass balances work well when used on a farm scale and for multiple years of data e.g. a minimum of 10 years. Furthermore, the relation between point data from monitoring wells and spatial data of mass balances need further investigation.

Potential impacting factors such as DTW, Mn/DO concentrations or texture should be analyzed further. Farm management practices, such as corral cleaning or manure application, farm infrastructure, such as type of corral floors or lagoon coverage and cropping practice and related soil organic matter changes should be considered. Finally, the system needs to be analyzed regarding other critical impacting factors.

A development of comprehensive system models including additional impacting factors would allow to apply advanced methods to deal with uncertain data such as Monte-Carlo.

While the mass balance approach is widely used other concepts for quantifying nitrate leaching to groundwater such as index systems should not be neglected.

7. Bibliography

Aguerre, M. J.; Wattiaux, M. A.; Hunt, T.; Lobos, N. E. (2012): Effect of nitrogen content and additional straw on changes in chemical composition, volatile losses, and ammonia emissions from dairy manure during long-term storage. In *Journal of Dairy Science* 95 (6), pp. 3454–3466. DOI: 10.3168/jds.2011-4839.

Almasri, Mohammad N.; Kaluarachchi, Jagath J. (2004): Assessment and management of long-term nitrate pollution of ground water in agriculture-dominated watersheds. In *Journal of Hydrology* 295 (1-4), pp. 225–245. DOI: 10.1016/j.jhydrol.2004.03.013.

Baram, S.; Couvreur, V.; Harter, T.; Read, M.; Brown, P. H.; Kandelous, M. et al. (2016): Estimating Nitrate Leaching to Groundwater from Orchards: Comparing Crop Nitrogen Excess, Deep Vadose Zone Data-Driven Estimates, and HYDRUS Modeling. In *Vadose Zone Journal* 15 (11), p. 0. DOI: 10.2136/vzj2016.07.0061.

Bertoldi, Gilbert L.; Johnston, Richard. H.; Evenson, K. D. (1991): Groundwater in the Central Valley, California - a summary report. Regional Aquifer-System Analysis - Central Valley, California. U.S. Geological Survey. Washington (Professional Paper, 1401-A).

Blume, Hans-Peter; Brümmer, Gerhard W.; Horn, Rainer; Kandeler, Ellen; Kögel-Knabner, Ingrid; Kretzschmar, Ruben et al. (2010): Scheffer/Schachtschabel: Lehrbuch der Bodenkunde: Springer-Verlag.

Bockstaller, Christian; Guichard, Laurence; Makowski, David; Aveline, Anne; Girardin, Philippe; Plantureux, Sylvain (2008): Agri-environmental indicators to assess cropping and farming systems. A review. In *Agron. Sustain. Dev.* 28 (1), pp. 139–149. DOI: 10.1051/agro:2007052.

Botros, Farag E.; Onsoy, Yuksel S.; Ginn, Timothy R.; Harter, Thomas (2012): Richards Equation–Based Modeling to Estimate Flow and Nitrate Transport in a Deep Alluvial Vadose Zone. In *Vadose Zone Journal* 11 (4), p. 0. DOI: 10.2136/vzj2011.0145.

Boumans, L.J.M.; Fraters, B.; van Drecht, G. (2001): Nitrate in the upper groundwater of 'De Marke' and other farms. In *Netherlands Journal ofAgricultural Science* 49, pp. 163–177.

Boumans, Leo J. M.; Fraters, Dico; van Drecht, Gerard (2005): Nitrate leaching in agriculture to upper groundwater in the sandy regions of the Netherlands during the 1992–1995 period. In *Environ Monit Assess* 102 (1-3), pp. 225–241. DOI: 10.1007/s10661-005-6023-5.

Boyle, D.; King, A. M.; Kourakos, George; Lockhart, K. M.; Mayzelle, M.; Fogg, G. E.; Harter, T. (2013): Task Report 7: Long-term Effects of Dairies On Groundwater Nitrate. Project: "Long Term Risk of Groundwater and Drinking Water Degradation from Dairies and Other Nonpoint Sources in the San Joaquin Valley". Proposition 50 Nonpoint Source -- CALFED Drinking Water Quality. State Water Resources Control Board. Available online at http://groundwater.ucdavis.edu.

Buczko, Uwe; Kuchenbuch, R. O.; Lennartz, B. (2010): Assessment of the predictive quality of simple indicator approaches for nitrate leaching from agricultural fields. In *Journal of environmental management* 91 (6), pp. 1305–1315. DOI: 10.1016/j.jenvman.2010.02.007.

Burchill, W.; Lanigan, G. J.; Li, D.; Williams, M.; Humphreys, J. (2016): A system N balance for a pasture-based system of dairy production under moist maritime climatic conditions. In *Agriculture, Ecosystems & Environment* 220, pp. 202–210. DOI: 10.1016/j.agee.2015.12.022.

Burger, M.; Lazcano, C.; Horwarth, W. (2013): Assessment of nitrous oxide emissions in California's dairy systems. Final Report. Edited by W. Horwarth, M. Burger, Stuart Pettygrove.

Burkart, M. R.; Stoner, J. D. (2002): Nitrate in aquifers beneath agricultural systems. In *Water Science and Technology* 45 (9), pp. 19–29. DOI: 10.2166/wst.2002.0195.

Burow, Karen R.; Jurgens, Bryant C.; Belitz, Kenneth; Dubrovsky, Neil M. (2013): Assessment of regional change in nitrate concentrations in groundwater in the Central Valley, California, USA, 1950s–2000s. In *Environ Earth Sci* 69 (8), pp. 2609–2621. DOI: 10.1007/s12665-012-2082-4.

Burow, Karen R.; Shelton, Jennifer L.; Dubrovsky, Neil M. (2008): Regional nitrate and pesticide trends in ground water in the eastern San Joaquin Valley, California. In *Journal of environmental quality* 37 (5 Suppl), S249-63. DOI: 10.2134/jeq2007.0061.

Burow, Karen R.; Shelton, Jennifer L.; Hevesi, Joseph A.; Weissmann, Gary S. (2004): Hydrogeologic Characterization of the Modesto Area, San Joaquin Valley, California. U.S. Geological Survey Scientific Investigations Report (2004-5232).

Burow, Karen R.; Stork, Sylvia S.; Dubrovsky, Neil M. (1998): Nitrate and Pesticides in GroundWater in the Eastern San Joaquin Valley, California: Occurrence and Trends. National Water-Quality Assessment Program. USGS (Water Resources Investigations Report, 98-4040).

California Department of Water Resources (2018): Groundwater Information Center Interactive Map Application. Available online at https://gis.water.ca.gov/app/gicima/, checked on 11/1/2018.

Cannavo, P.; Recous, S.; Parnaudeau, V.; Reau, R. (2008): Modeling N Dynamics to Assess Environmental Impacts of Cropped Soils. In : Advances in Agronomy Volume 97, vol. 97: Elsevier (Advances in Agronomy), pp. 131–174.

Carey, Barbara M.; Pitz, Charles F.; Harrison, Joseph H. (2017): Field nitrogen budgets and post-harvest soil nitrate as indicators of N leaching to groundwater in a Pacific Northwest dairy grass field. In *Nutr Cycl Agroecosyst* 107 (1), pp. 107–123. DOI: 10.1007/s10705-016-9819-5.

CDFA, USDA (2017): California Dairy Statistics Annual. 2017 Data. Sacramento, CA. Available online at https://www.cdfa.ca.gov/dairy/pdf/Annual/2017/2017_Statistics_Annual.pdf.

Chang, Andrew; Harter, Thomas; Letey, John; Meyer, Deanne; Meyer, Roland D.; Mathews, Marsha C. et al. (2005): Managing Dairy Manure in the Central Valley of California. University of California Division of Agriculture and Natural Resources Committee of Experts on Dairy Manure Management.

Chen, Longjian; Xing, Li; Han, Lujia (2013): Review of the application of near-infrared spectroscopy technology to determine the chemical composition of animal manure. In *Journal of environmental quality* 42 (4), pp. 1015–1028. DOI: 10.2134/jeq2013.01.0014.

Cherry, K. A.; Shepherd, M.; Withers, P.J.A.; Mooney, S. J. (2008): Assessing the effectiveness of actions to mitigate nutrient loss from agriculture: A review of methods. In *Science of The Total Environment* 406 (1-2), pp. 1–23. DOI: 10.1016/j.scitotenv.2008.07.015.

Collins, S.; Singh, R.; Rivas, A.; Palmer, A.; Horne, D.; Manderson, A. et al. (2017): Transport and potential attenuation of nitrogen in shallow groundwaters in the lower Rangitikei catchment, New Zealand. In *Journal of Contaminant Hydrology* 206, pp. 55–66. DOI: 10.1016/j.jconhyd.2017.10.002.

Comly, Hunter H. (1945): Cyanosis in infants caused by nitrates in well water. In *Jama* 129 (2), pp. 112–116.

Croft, M. G. (1972): Subsurface Geology of the Late Tertiary and Quarternary Water-Bearing Deposits of the Southern Part of the San Joaquin Valley, California. Contributiongs to the Hydrology of the United States. With assistance of California Department of Water Resources. Washington (DC) (Geological Survey Water-Supply Paper, H).

CRWQCB (2007): GENERAL ORDER FOR EXISTING MILK COW DAIRIES. R5-2007-0035.

CRWQCB (2013): Reissued Waste Discharge Requirements General Order For Existing Milk Cow Dairies. R5-2013-0122. In *Cartographic Perspectives* (74), p. 1.

Delgado, J. A.; Shaffer, M.; Hu, C.; Lavado, R.; Cueto-Wong, J.; Joosse, P. et al. (2008): An index approach to assess nitrogen losses to the environment. In *Ecological Engineering* 32 (2), pp. 108–120. DOI: 10.1016/j.ecoleng.2007.10.006.

Di, Hong Jie; Cameron, Keith C. (2016): Inhibition of nitrification to mitigate nitrate leaching and nitrous oxide emissions in grazed grassland: a review. In *J Soils Sediments* 16 (5), pp. 1401–1420. DOI: 10.1007/s11368-016-1403-8.

Einarsson, Rasmus; Cederberg, Christel; Kallus, Jonatan (2018): Nitrogen flows on organic and conventional dairy farms: a comparison of three indicators. In *Nutr Cycl Agroecosyst* 110 (1), pp. 25–38. DOI: 10.1007/s10705-017-9861-y.

EPA (2018): 2018 Edition of the Drinking Water Standards and Health Advisories Tables (EPA 822-F-18-001). With assistance of U.S. Environmental Protection Agency, Office of Water.

Galloway, James N. (2003): The Global Nitrogen Cycle.

Galloway, James N.; Cowling, Ellis B. (2002): Reactive Nitrogen and The World. 200 Years of Change. In *AMBIO: A Journal of the Human Environment* 31 (2), pp. 64–71. DOI: 10.1579/0044-7447-31.2.64.

Galloway, James N.; Townsend, Alan R.; Erisman, Jan Willem; Bekunda, Mateete; Cai, Zucong; Freney, John R. et al. (2008): Transformation of the nitrogen cycle. Recent trends, questions, and potential solutions. In *Science (New York, N.Y.)* 320 (5878), pp. 889–892. DOI: 10.1126/science.1136674.

Gorelick, Steven M.; Zheng, Chunmiao (2015): Global change and the groundwater management challenge. In *Water Resour. Res.* 51 (5), pp. 3031–3051. DOI: 10.1002/2014WR016825.

Green, Christopher T.; Puckett, Larry J.; Böhlke, John Karl; Bekins, Barbara A.; Phillips, Steven P.; Kauffman, Leon J. et al. (2008): Limited occurrence of denitrification in four shallow aquifers in agricultural areas of the United States. In *Journal of environmental quality* 37 (3), pp. 994–1009. DOI: 10.2134/jeq2006.0419.

Gurdak, Jason J.; Qi, Sharon L. (2012): Vulnerability of recently recharged groundwater in principal corrected aquifers of the United States to nitrate contamination. In *Environmental science & technology* 46 (11), pp. 6004–6012. DOI: 10.1021/es300688b.

Gutiérrez, Mélida; Biagioni, Richard N.; Alarcón-Herrera, Maria Teresa; Rivas-Lucero, Bertha A. (2018): An overview of nitrate sources and operating processes in arid and semiarid aquifer systems. In *The Science of the total environment* 624, pp. 1513–1522. DOI: 10.1016/j.scitotenv.2017.12.252.

Harrell, Frank.E.Jr. (2001): Regression Modeling Strategies. With Applications to Linear Models, Logistic Regression, and Survival Analysis: Springer.

Harter, T.; Meyer, Roland D.; M. C. Mathews (2001): Nonpoint Source Pollution from Animal Farming in Semi-Arid Regions: Spatio-Temporal Variability and Groundwater Monitoring Strategies.

Harter, T.; Viers, J. H.; Liptzin, D.; Rosenstock, T. S.; Jensen, V.; Hollander et al. (2013): Task Report 6: Dairies and other Sources of Nitrate Loading to Groundwater. Project: “Long Term Risk of Groundwater and Drinking Water Degradation from Dairies and Other Nonpoint Sources in the San Joaquin Valley”. Proposition 50 Nonpoint Source -- CALFED Drinking Water Quality. State Water Resources Control Board. Available online at http://groundwater.ucdavis.edu.

Harter, Thomas (2012a): Hydrology, Hydrogeology, and Groundwater Quality, Dairyland Farms, Tipton, California. Technical Report. Submitted to Dairyland Farms. UC Davis.

Harter, Thomas (2012b): Hydrology, Hydrogeology, and Groundwater Quality, Elkhorn Dairy, Visalia, California. Technical Report. Submitted to Elkhorn Dairy. UC Davis.

Harter, Thomas (2012c): Hydrology, Hydrogeology, and Groundwater Quality, Genasci Ranch, Modesto, California. Technical Report. Submitted to Genasci Ranch. UC Davis.

Harter, Thomas (2012d): Hydrology, Hydrogeology, and Groundwater Quality, Giacomazzi Dairy, Hanford, California. Technical Report. Submitted to Giacomazzi Dairy. UC Davis.

Harter, Thomas (2012e): Hydrology, Hydrogeology, and Groundwater Quality, Longfellow Dairy, Hanford, California. Technical Report. Submitted to Longfellow Dairy. UC Davis.

Harter, Thomas (2012f): Hydrology, Hydrogeology, and Groundwater Quality, Sierra View Dairy, Tulare, California. Technical Report. Submitted to Sierra View Dairy. UC Davis.

Harter, Thomas; Davis, Harley; Mathews, Marsha C.; Meyer, Roland D. (2002): Shallow groundwater quality on dairy farms with irrigated forage crops. In *Journal of Contaminant Hydrology* 55 (3-4), pp. 287–315. DOI: 10.1016/S0169-7722(01)00189-9.

Helsel, Dennis R. (2005): Nondetects and data analysis: Statistics for censored environmental data: John Wiley & Sons. Available online at http://pubs.er.usgs.gov/publication/70180734.

Herridge, David F.; Peoples, Mark B.; Boddey, Robert M. (2008): Global inputs of biological nitrogen fixation in agricultural systems. In *Plant Soil* 311 (1-2), pp. 1–18. DOI: 10.1007/s11104-008-9668-3.

Horn, Judith E.; Harter, Thomas (2009): Domestic well capture zone and influence of the gravel pack length. In *Ground water* 47 (2), pp. 277–286. DOI: 10.1111/j.1745-6584.2008.00521.x.

Hristov, A. N.; Hanigan, M.; Cole, A.; Todd, R.; McAllister, T. A.; Ndegwa, P. M.; Rotz, A. (2011): Review: Ammonia emissions from dairy farms and beef feedlots. In *Can. J. Anim. Sci.* 91 (1), pp. 1–35. DOI: 10.4141/CJAS10034.

Kanakidou, M.; Myriokefalitakis, S.; Daskalakis, N.; Fanourgakis, G.; Nenes, A.; Baker, A. R. et al. (2016): Past, Present, and Future Atmospheric Nitrogen Deposition. In *J. Atmos. Sci.* 73 (5), pp. 2039–2047. DOI: 10.1175/JAS-D-15-0278.1.

Kohn, R.A (2015): Nitrogen EMissions from Animal Agricultural Systems and Strategies to Protect the Environment. In Pradeep Malik, Raghavendra Bhatta, Junichi Takahashi, Richard A. Kohn, Cadaba S. Prasad (Eds.): Livestock production and climate change. Wallingford: CABI (CABI climate change series, v.6), pp. 61–73.

Korevaar, H. (1992): The nitrogen balance on intensive Dutch dairy farms: a review. In *Livestock Production Science* 31 (1-2), pp. 17–27. DOI: 10.1016/0301-6226(92)90049-A.

Körschens, Martin; Weigel, Annett; Schulz, Elke (1998): Turnover of soil organic matter (SOM) and long-term balances - tools for evaluating sustainable productivity of soils.

In *Z. Pflanzenernaehr. Bodenk.* 161 (4), pp. 409–424. DOI: 10.1002/jpln.1998.3581610409.

Ledgard, S. F.; Steele, K. W. (1992): Biological nitrogen fixation in mixed legume/grass pastures. In J. K. Ladha, T. George, B. B. Bohlool (Eds.): Biological Nitrogen Fixation for Sustainable Agriculture. Dordrecht: Springer Netherlands, pp. 137–153.

Liptzin, D.; Dahlgren, R. A.; Harter, T. (2016): A California Nitrogen Mass Balance for 2005. In T. P. Tomich, S. B. Brodt, R. A. Dahlgren, K. M. Scow (Eds.): The California nitrogen assessment. Challenges and solutions for people, agriculture, and the environment. Oakland, California: University of California Press.

Lockhart, K. M.; King, A. M.; Harter, T. (2013): Identifying sources of groundwater nitrate contamination in a large alluvial groundwater basin with highly diversified intensive agricultural production. In *Journal of Contaminant Hydrology* 151, pp. 140–154. DOI: 10.1016/j.jconhyd.2013.05.008.

Lord, E. I.; Anthony, S. G.; Goodlass, G. (2002): Agricultural nitrogen balance and water quality in the UK. In *Soil Use and Management* 18 (4), pp. 363–369. DOI: 10.1079/SUM2002145.

LP DAAC (2018): Shuttle Radar Topography Mission (SRTM GL3) Global 90m(SRTM_GL3). With assistance of NASA EOSDIS Land Processes Distributed Active Archive Center. USGS/Earth Resources Observation and Science (EROS) Center. Sioux Falls, South Dakota. Available online at http://opentopo.sdsc.edu, checked on 12/18/2018.

LSCE (2018): Central Valley Dairy Representative Monitoring Program. Year 6 Annual Report (2017). Part I of VI. Luhdorff & Scalmanini Consulting Engineers.

Mann, Henry B. (1945): Nonparametric Tests Against Trend. In *Econometrica* 13 (3), pp. 245–259. DOI: 10.2307/1907187.

Massey, Frank J. (1951): The Kolmogorov-Smirnov Test for Goodness of Fit. In *Journal of the American Statistical Association* 46 (253), pp. 68–78. DOI: 10.1080/01621459.1951.10500769.

McLeod, A. Ian (2005): Kendall rank correlation and Mann-Kendall trend test. In *R Package Kendall*.

Meyer, D. (2008): Process Wastewater (Liquid Manure) Sampling Protocol. CDQAP - WDR General Order Reference Binder TAB 5.3. Version 2-29-08. UC Davis.

Meyer, D.; Mullinax, Denise (2008): Solid Manure Sampling Protocol. CDQAP - WDR General Order Reference Binder TAB 5.2. Version 2-29-08. UC Davis.

Miller, Christine M. F.; Price, Patricia L.; Meyer, Deanne (2017): Mass balance analyses of nutrients on California dairies to evaluate data quality for regulatory review. In *The Science of the total environment* 579, pp. 37–46. DOI: 10.1016/j.scitotenv.2016.10.092.

Mu, W.; van Middelaar, C. E.; Bloemhof, J. M.; Oenema, J.; Boer, I.J.M. de (2016): Nutrient balance at chain level: a valuable approach to benchmark nutrient losses of milk production systems. In *Journal of Cleaner Production* 112, pp. 2419–2428. DOI: 10.1016/j.jclepro.2015.09.116.

Nennich, T. D.; Harrison, J. H.; VanWieringen, L. M.; Meyer, D.; Heinrichs, A. J.; Weiss, W. P. et al. (2005): Prediction of Manure and Nutrient Excretion from Dairy Cattle. In *Journal of Dairy Science* 88 (10), pp. 3721–3733. DOI: 10.3168/jds.S0022-0302(05)73058-7.

Oenema, Oene; Kros, Hans; Vries, Wim de (2003): Approaches and uncertainties in nutrient budgets: implications for nutrient management and environmental policies. In *European Journal of Agronomy* 20 (1-2), pp. 3–16. DOI: 10.1016/S1161-0301(03)00067-4.

Page, R. W. (1986): Geology of the Fresh Ground-water Basin of the Central Valley, California, with texture maps and sectins. Regional Aquifer-System Analysis. Washington: U.S. Geological Survey Professional Paper (1401-C).

Peoples, M. B.; Herridge, D. F.; Ladha, J. K. (1995): Biological nitrogen fixation: An efficient source of nitrogen for sustainable agricultural production? In J. K. Ladha, M. B. Peoples (Eds.): Management of Biological Nitrogen Fixation for the Development of More Productive and Sustainable Agricultural Systems. Dordrecht: Springer Netherlands, pp. 3–28.

Pinheiro, José C.; Bates, Douglas M. (2009): Mixed-effects models in S and S-PLUS. reprinted paperback ed. of the 2000 ed. New York: Springer (Statistics and computing).

Powell, J. M.; Gourley, C.J.P.; Rotz, C. A.; Weaver, D. M. (2010): Nitrogen use efficiency: A potential performance indicator and policy tool for dairy farms. In *Environmental Science & Policy* 13 (3), pp. 217–228. DOI: 10.1016/j.envsci.2010.03.007.

Powell, J. M.; Rotz, C. A. (2015): Measures of nitrogen use efficiency and nitrogen loss from dairy production systems. In *Journal of environmental quality* 44 (2), pp. 336–344. DOI: 10.2134/jeq2014.07.0299.

QGIS Development Team (2018): QGIS Geographic Information System. Version 2.18.24: Open Source Geospatial Foundation Project. Available online at http://qgis.osgeo.org.

R Core Team (2018): R: A language and environment for statistical computing. Version 3.5.1. Vienna, Austria: R Foundation for Statistical Computing. Available online at https://www.R-project.org/.

Rankinen, Katri; Salo, Tapio; Granlund, Kirsti; Rita, Hannu (2007): Simulated nitrogen leaching, nitrogen mass field balances and their correlation on four farms in south-western Finland during the period 2000-2005. In *Agricultural and Food Science* 16, pp. 387–406.

Ransom, Katherine M.; Bell, Andrew M.; Barber, Quinn E.; Kourakos, George; Harter, Thomas (2018): A Bayesian approach to infer nitrogen loading rates from crop and land-use types surrounding private wells in the Central Valley, California. In *Hydrol. Earth Syst. Sci.* 22 (5), pp. 2739–2758. DOI: 10.5194/hess-22-2739-2018.

Ransom, Katherine M.; Nolan, Bernard T.; A Traum, Jonathan; Faunt, Claudia C.; Bell, Andrew M.; Gronberg, Jo Ann M. et al. (2017): A hybrid machine learning model to predict and visualize nitrate concentration throughout the Central Valley aquifer, California, USA. In *The Science of the total environment* 601-602, pp. 1160–1172. DOI: 10.1016/j.scitotenv.2017.05.192.

Rivett, Michael O.; Buss, Stephen R.; Morgan, Philip; Smith, Jonathan W. N.; Bemment, Chrystina D. (2008): Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. In *Water research* 42 (16), pp. 4215–4232. DOI: 10.1016/j.watres.2008.07.020.

Rodriguez-Galiano, V. F.; Luque-Espinar, J. A.; Chica-Olmo, M.; Mendes, M. P. (2018): Feature selection approaches for predictive modelling of groundwater nitrate pollution: An evaluation of filters, embedded and wrapper methods. In *Science of The Total Environment* 624, pp. 661–672. DOI: 10.1016/j.scitotenv.2017.12.152.

Rosecrans, Celia Z.; Nolan, Bernard T.; Gronberg, JoAnn M. (2017): Prediction and visualization of redox conditions in the groundwater of Central Valley, California. In *Journal of Hydrology* 546, pp. 341–356. DOI: 10.1016/j.jhydrol.2017.01.014.

Rosenstock, Todd S.; Liptzin, Daniel; Dzurella, Kristin; Fryjoff-Hung, Anna; Hollander, Allan; Jensen, Vivian et al. (2014): Agriculture's Contribution to Nitrate Contamination of Californian Groundwater (1945-2005). In *Journal of environmental quality* 43 (3), pp. 895–907. DOI: 10.2134/jeq2013.10.0411.

Rotz, C. A. (2004): Management to reduce nitrogen losses in animal production. In *J. Anim. Sci.* 82 (E.Suppl.) (E119-E137).

RStudio Team (2016): RStudio: Integrated Development for R. Version 1.1.463. Boston, MA: RStudio, Inc. Available online at http://www.rstudio.com/.

Rudolph, D. L.; Barry, D.A.J.; Goss, M. J. (1998): Contamination in Ontario farmstead domestic wells and its association with agriculture: 2. Results from multilevel monitoring well installations. In *Journal of Contaminant Hydrology* 32, pp. 295–311.

Ruijter, F. J. de; Boumans, L. J. M.; Smit, A. L.; van den Berg, M. (2007): Nitrate in upper groundwater on farms under tillage as affected by fertilizer use, soil type and groundwater table. In *Nutr Cycl Agroecosyst* 77 (2), pp. 155–167. DOI: 10.1007/s10705-006-9051-9.

Sainju, Upendra M. (2017): Determination of nitrogen balance in agroecosystems. In *MethodsX* 4, pp. 199–208. DOI: 10.1016/j.mex.2017.06.001.

Sakamoto, Yosiyuki; Ishiguro, Makio; Kitagawa, Genshiro (1986): Akaike information criterion statistics (81).

Schröder, J. J.; Aarts, H.F.M.; van Middelkoop, J. C.; Schils, R.L.M.; Velthof, G. L.; Fraters, B.; Willems, W. J. (2007): Permissible manure and fertilizer use in dairy farming systems on sandy soils in The Netherlands to comply with the Nitrates Directive target. In *European Journal of Agronomy* 27 (1), pp. 102–114. DOI: 10.1016/j.eja.2007.02.008.

Shapiro, Samuel Sanford; Wilk, Martin B. (1965): An analysis of variance test for normality (complete samples). In *Biometrika* 52 (3/4), pp. 591–611.

Siebert, Stefan (2005): Global-Scale Modeling of Nitrogen Balances at the Soil Surface.

Sieling, K.; Kage, H. (2006): N balance as an indicator of N leaching in an oilseed rape – winter wheat – winter barley rotation. In *Agriculture, Ecosystems & Environment* 115 (1-4), pp. 261–269. DOI: 10.1016/j.agee.2006.01.011.

Singleton, M. J.; Esser, B. K.; Moran, J. E.; Hudson, G. B.; McNab, W. W.; Harter, T. (2007): Saturated Zone Denitrification: Potential for Natural Attenuation of Nitrate Contamination in Shallow Groundwater Under Dairy Operations. In *Environ. Sci. Technol.* 41 (3), pp. 759–765. DOI: 10.1021/es061253g.

Soils Resource Lab (2018): California Soil Resource Lab. SoilWeb Online Soil Survey Browser. Available online at https://casoilresource.lawr.ucdavis.edu/gmap/, checked on 10/4/2018.

Spears, R. A.; Kohn, R.A; Young, A. J. (2003): Whole-Farm Nitrogen Balance on Western Dairy Farms. In *Journal of Dairy Science* 86 (12), pp. 4178–4186. DOI: 10.3168/jds.S0022-0302(03)74033-8.

State Water Resources Control Board (1988): Nitrate in Drinking Water. Report to the Legislature.

Stenberg, Maria; Aronsson, Helena; Lindén, Börje; Rydberg, Tomas; Gustafson, Arne (1999): Soil mineral nitrogen and nitrate leaching losses in soil tillage systems combined with a catch crop. In *Soil and Tillage Research* 50 (2), pp. 115–125. DOI: 10.1016/S0167-1987(98)00197-4.

Thomas, Brian F.; Famiglietti, James S.; Landerer, Felix W.; Wiese, David N.; Molotch, Noah P.; Argus, Donald F. (2017): GRACE Groundwater Drought Index: Evaluation of California Central Valley groundwater drought. In *Remote Sensing of Environment* 198, pp. 384–392. DOI: 10.1016/j.rse.2017.06.026.

Tomich, T. P.; Brodt, S. B.; Dahlgren, R. A.; Scow, K. M. (Eds.) (2015): THE CALIFORNIA NITROGEN ASSESSMENT. Challenges and Solutions for People, Agriculture, and the Environment. Executive Summary. UC Davis.

UC Davis (1994): Description of Dairy Groundwater Monitoring Project. Report about Early Dairy Monitoring Study.

US Census Bureau (2016): CA State Boundary. 2016 MAF/TIGER database. California Open Data Portal. Available online at https://data.ca.gov/dataset/ca-geographic-boundaries, updated on 1/31/2018, checked on 11/4/2018.

van Beek, C. L.; Brouwer, L.; Oenema, O. (2003): The use of farmgate balances and soil surface balances as estimator for nitrogen leaching to surface water. In *Nutrient Cycling in Agroecosystems* 67 (3), pp. 233–244. DOI: 10.1023/B:FRES.0000003619.50198.55.

van der Schans, Martin L.; Harter, Thomas; Leijnse, Anton; Mathews, Marsha C.; Meyer, Roland D. (2009): Characterizing sources of nitrate leaching from an irrigated dairy farm in Merced County, California. In *Journal of Contaminant Hydrology* 110 (1-2), pp. 9–21. DOI: 10.1016/j.jconhyd.2009.06.002.

Verloop, J.; Boumans, L. J. M.; van Keulen, H.; Oenema, J.; Hilhorst, G. J.; Aarts, H. F. M.; Sebek, L. B. J. (2006): Reducing Nitrate Leaching to Groundwater in an Intensive Dairy Farming System. In *Nutr Cycl Agroecosyst* 74 (1), pp. 59–74. DOI: 10.1007/s10705-005-6241-9.

Viers, J. H.; Liptzin, D.; Rosenstock, T. S.; Jensen, V. B.; Hollander, A. D.; McNally, A. et al. (2012): Nitrogen Sources and Loading to Groundwater. Technical Report 2. In: Addressing Nitrate in California's Drinking Water with a Focus on Tulare Lake Basin and Salinas Valley Groundwater. Report for the State Water Resources Control Board Report to the Legislature. Center for Watershed Sciences, University of California, Davis.

Ward, Mary H.; DeKok, Theo M.; Levallois, Patrick; Brender, Jean; Gulis, Gabriel; Nolan, Bernard T.; VanDerslice, James (2005): Workgroup report: drinking-water nitrate and health—recent findings and research needs. In *Environmental health perspectives* 113 (11), pp. 1607–1614.

Watanabe, Naoko; Harter, Thomas H.; Bergamaschi, Brian A. (2008): Environmental occurrence and shallow ground water detection of the antibiotic monensin from dairy farms. In *Journal of environmental quality* 37 (5 Suppl), S78-85. DOI: 10.2134/jeq2007.0371.

WHO (2017): Guidelines for Drinking-water Quality. Fourth edition incorporating the first addendum. Geneva: World Health Organization.

Wick, Katharina; Heumesser, Christine; Schmid, Erwin (2012): Groundwater nitrate contamination: factors and indicators. In *Journal of environmental management* 111, pp. 178–186. DOI: 10.1016/j.jenvman.2012.06.030.

Wilcoxon, Frank; Katti, S. K.; Wilcox, Roberta A. (1970): Critical values and probability levels for the Wilcoxon rank sum test and the Wilcoxon signed rank test. In *Selected tables in mathematical statistics* 1, pp. 171–259.

Young, Megan; Kendall, Carol; Lockhart, K. M.; Esser, B. K.; Harter, T. (2013): Task Report 2: Using Nitrate and Water Isotopes to Evaluate Groundwater Quality Beneath Dairy Farms in California. Project: "Long Term Risk of Groundwater and Drinking Water Degradation from Dairies and Other Nonpoint Sources in the San Joaquin Valley". Proposition 50 Nonpoint Source -- CALFED Drinking Water Quality Grant. State Water Resources Control Board. Available online at http://groundwater.ucdavis.edu.

Yuan, H.; Qin, S.; Dong, W.; Hu, C.; Manevski, K.; Li, X. (2017): Denitrification Rates and Controlling Factors for Accumulated Nitrate in the 0-12 m Intensive Farmlands: a Case Study in the North China Plain. In *Pedosphere*. DOI: 10.1016/S1002-0160(17)60472-7.

8. Appendix

Table A 1: Data sources used.

Type of data	**Content**	**Years sampled**	**Source**	**File location and name**
GROUNDWATER DATA				
DTW	7 dairy farms CVDRMP	2013-2017	CVDRMP	GW/Export Data for T_WL_7 Dairies.xlsx
Management Units	Mgmt. units for wells not in CVDRMP	1995-2003	UC Davis	GW/SamplingData w MgmtUnit.xls
Management Units	7 dairy farms	2017	CVDRMP	GW/CVDRMP select wells and source areas 20180810.xlsx
Water Quality	7 dairy farms CVDRMP	2013-2017	CVDRMP	GW/Export Data for T_WQ_7 Dairies.xlsx
Water Quality	Phase 2 samples	1995-2009	UC Davis	GW/Database_as_Table.xlsx
Water Quality	Samples	2007-2009	UC Davis	GW/HarterDairy_COMBO_MasterFile-Version4 - 975 samples w attributes.xls
Water Quality	Phase 2 samples	1995-2009	UC Davis	GW/tbl Sampling Data.xlsx
Water Quality	Isotopes, incl. DO/Mn	2008-2009	UC Davis	GW/HarterDairy_ISOTOPE_MasterFile_22Dec11.xls
Water Quality	5 dairy farms	1993-1994	UC Davis	GW/dairy farms_93-94.xlsx
Well Information	7 dairy farms CVDRMP	2013	CVDRMP	GW/Export Data for T_Well_7 Dairies.xlsx
MASS BALANCE DATA				
MB	7 dairy farms, UCD	2012	UC Davis	MB/N_balance_dairy farm_reports.xlsx
MB	7 dairy farms, CVDRMP	2011-2016	Annual Reports	MB/Table 5-3 query export_7 select dairy farms.xlsx
MB	9 dairy farms	2007-2014	Annual Reports	MB/SummaryData(Felicia).xlsx
MB	Data per field	2007-2014	Annual Reports	MB/Field Data.xlsx

Table A 1 (continued):

Type of data	Content	Years sampled	Source	File location and name
MB	5 dairy farms	1993-1994	Pre-Reports	MB/dairy farms_93-94.xlsx
MB	8 dairy farms on dairy farm scale and field scale	2015-2107	Annual Reports	MB/dairy farm_reports2015-17.xlsx
WELL DRILL LOGS				
Well Drill Logs	DLF, farm LON, farm ZZI; official well drill logs		UC Davis	Official Well Drilling Logs.xls
Well Drill Logs	CLA, USS		UC Davis	V&W-monitoring wells core records.xls
OTHER DATA				
Housing, Irrigation and Lagoons	Infra-structure	2017	CVDRMP	R Code
Dairy farm age	Age of Dairies		UC Davis	R Code
GIS DATA				
GIS	Dairies	2018	UC Davis	GIS data base
GIS	Wells, WQ	2018	UC Davis	GIS data base
GIS	DEM (SRTM)	2018	LP DAAC 2018	GIS data base
GIS	CA State Boundary	2016	US Census Bureau 2016	GIS data base

Table A 2: Groundwater data from field dairy farm monitoring wells for eight dairy farms with mean, minimum, maximum, standard deviation and median of NO_3-N concentrations.

Well Name	Mean	Minimum	Maximum	Standard deviation	Median
CLA-MW11	55.48	35.10	82.20	13.01	52.10
CLA-MW13	39.66	25.60	64.00	9.34	38.00
CLA-MW14	49.34	38.15	70.30	6.82	47.95
CLA-MW19	52.04	26.40	92.61	20.94	45.40
CLA-MW20	35.80	14.90	51.70	8.19	33.90
CLA-MW21	40.97	14.49	69.10	12.70	43.20
CLA-MW22	44.11	31.90	63.10	8.28	43.60
CLA-MW23	49.10	44.00	56.82	4.03	48.10
CLA-MW25	49.20	39.90	65.10	6.30	48.70
CLA-MW4	36.33	4.00	89.10	12.78	34.20
CLA-MW5	45.04	22.50	180.00	22.35	38.00
CLA-MW6	22.86	13.00	34.60	5.69	22.70
DLF-MW5	9.23	6.92	14.00	1.51	8.98
DLF-MW6	36.72	14.78	66.00	12.30	39.66
DUR-MW6	55.86	ND	166.20	31.43	53.90
DUR-MW7	135.53	18.10	213.00	39.80	133.00
DUR-MW8	19.56	ND	111.00	22.83	11.30
DUR-MW9	23.40	5.20	95.70	17.10	19.40
FIS-MW11	50.62	29.80	136.00	22.62	40.07
FIS-MW12	21.79	2.50	58.60	11.86	21.45
FIS-MW13	16.44	9.70	42.36	11.08	12.20
FIS-MW14	24.09	5.11	53.05	17.70	13.00
FIS-MW15	15.62	4.50	56.75	14.22	10.50
FIS-MW16	30.59	1.00	79.17	30.88	15.95
FIS-MW17	33.13	19.31	41.60	8.03	37.10
FIS-MW18	38.57	23.41	54.60	8.50	38.80

Table A2 (continued):

Well Name	Mean	Minimum	Maximum	Standard deviation	Median
FIS-MW7	28.18	13.97	61.00	12.93	22.00
FIS-MW8	41.93	ND	114.00	21.93	35.00
FIS-MW9	17.56	0.76	44.20	10.82	14.15
GEN-MW7	33.76	ND	74.00	9.03	30.44
LON-MW4	35.85	15.35	58.00	8.55	35.80
LON-MW5	20.80	10.12	37.00	5.94	19.27
LON-MW6	15.58	9.07	36.00	4.97	14.52
LON-MW7	32.15	9.10	65.00	14.29	31.08
SIE-MW1	59.88	21.00	83.75	20.88	68.40
ZZI-MW5	31.07	11.87	71.00	13.71	29.17
ZZI-MW6	17.58	3.61	42.00	8.61	17.00
ZZI-MW9	8.44	1.20	46.00	8.43	4.28

Table A 3: Results of Mann-Kendall test for NO_3-N values of monitoring field wells.

Monitoring wells	tau	p-value
CLA-MW11	0.3000	0.080
CLA-MW13	0.0387	0.755
CLA-MW14	-0.1165	0.342
CLA-MW19	-0.1705	0.168
CLA-MW20	-0.1597	0.182
CLA-MW21	-0.6125	$3.96x10^{-7}$
CLA-MW22	-0.7109	$2.06\ x10^{-9}$
CLA-MW23	0.3636	0.033
CLA-MW25	-0.2273	0.057
CLA-MW4	-0.0925	0.268
CLA-MW5	0.3133	0.000
CLA-MW6	0.0181	0.832
DLF-MW5	0.4475	$1.19\ x10^{-7}$
DLF-MW6	0.7027	0.000
DUR-MW6	0.4246	0.000
DUR-MW7	-0.0245	0.744
DUR-MW8	0.1534	0.035
DUR-MW9	0.3068	$2.50\ x10^{-5}$
FIS-MW11	-0.3936	$1.75\ x10^{-9}$
FIS-MW12	0.0253	0.712
FIS-MW13	0.8112	$7.70\ x10^{-5}$
FIS-MW14	0.2751	0.137
FIS-MW15	0.0909	0.755
FIS-MW16	0.9724	$1.79\ x10^{-6}$
FIS-MW17	-0.7081	0.000
FIS-MW18	0.1630	0.386
FIS-MW7	-0.6713	0.000

Table A 3 (continued):

Monitoring wells	tau	p-value
FIS-MW8	-0.6229	2.55×10^{-21}
FIS-MW9	-0.1881	0.005
GEN-MW7	-0.3789	2.81×10^{-10}
LON-MW4	0.4654	0.000
LON-MW5	0.0251	0.729
LON-MW6	0.5622	0.000
LON-MW7	0.5191	0.000
SIE-MW1	-0.5531	$2.48 \times 10\text{-}^{9}$
ZZI-MW5	0.7301	0.000
ZZI-MW6	-0.4004	2.36×10^{-8}
ZZI-MW9	-0.2183	0.002

Table A 4: Results from LMM.

Fixed Parameters Model 1	**Fixed Parameters Model 0**	**Random parameter**	**p-value (ANOVA)**	**Number of observations**
Log(GW-Nitrate-N), MB A	Log(GW-Nitrate-N)	dairy farm	0.83	60
Log(GW-Nitrate-N), MB B	Log(GW-Nitrate-N)	dairy farm	0.77	60
Log(GW-Nitrate-N), MB A, texture	Log(GW-Nitrate-N), MB_A,	dairy farm	0.5	57
Log(GW-Nitrate-N), MB B texture	Log(GW-Nitrate-N) MB_B	dairy farm	0.42	57
Log(GW-Nitrate-N), MB A, DTW	Log(GW-Nitrate-N), MB_A,	dairy farm	0.24	60
Log(GW-Nitrate-N), MB B, DTW	Log(GW-Nitrate-N) MB_B	dairy farm	0.16	60
Log(GW-Nitrate-N), MB A, age of dairy farm	Log(GW-Nitrate-N), MB_A	dairy farm	0.063	60
Log(GW-Nitrate-N), MB B, age of dairy farm	Log(GW-Nitrate-N), MB_B	dairy farm	0.06	60
Log(GW-Nitrate-N), MB A, region	Log(GW-Nitrate-N), MB_A	dairy farm	0.36	60
Log(GW-Nitrate-N), MB B, region	Log(GW-Nitrate-N), MB_B	dairy farm	0.24	60

9. Statutory Declaration

I declare that I have authored this thesis independently and that I have not used other than the declared sources and resources.

Hiermit erkläre ich, dass die Arbeit selbständig und nur unter Verwendung der angegebenen Hilfsmittel angefertigt wurde.

Place and Date: ________________________ Signed: __________________

Felicia Linke