IDENTIFYING THE SOURCES OF NITRATE IN SURFACE AND GROUND WATERS USING STABLE ISOTOPES: A GLOBAL OVERVIEW

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Abstract

Nitrate pollution of freshwater systems is a pressing issue that affects nearly every region of the globe. Excessive levels of nitrate in surface and groundwater environments can cause severe impacts to human and ecosystem health. To effectively mitigate the adverse effects of nitrate pollution, the sources of nitrate to systems must be identified. For identification of nitrate sources, the dual isotope technique ($\delta^{15}N_{-NO3}$ and $\delta^{18}O_{-NO3}$) has been widely used in current research. This thesis aimed to provide a global synthesis of nitrate pollution in surface and groundwater to understand better how nitrate pollution varies spatially around the world with different climates, and land uses. It also assessed the current state of practice of water quality management of nitrate, its relation to nitrate sources in surface and groundwater and the economic complexity of nations. A global database of nitrate in surface and groundwater was produced collating data from available literature, statistical analysis was then performed to assess changes of nitrate concentrations and isotopic compositions with various variables. Next, a stable isotope mixing model was used to determine the sources of nitrate in surface and groundwaters around the world. Finally, the state of practice of water quality management of nitrate and its relation to identified nitrate sources and economic complexity was assessed. The analysis found that nitrate concentrations and isotopic compositions vary significantly between several groups of climate and land use. The modelling results showed that manure + sewage was the most commonly identified source of nitrate around the world in both surface and groundwater across land use and climate types. The importance of selecting site-specific data in stable isotope mixing models was also highlighted. A relationship was found between economic complexity and levels of wastewater treatment, with low development corelating with low levels of wastewater treatment. It also found that pollution of groundwaters by manure + sewage is prevalent regardless of the economic power of a nation. This research highlights that much more still needs to be done to mitigate nitrate pollution of freshwater around the world, not only in developing nations but also in developed nations that depend on groundwater for drinking water supply.

Key Words: Nitrate Pollution, Dual Isotopes, Surface and Groundwater, Development, Water Quality

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Contents

1. Introduction

With the global population proliferating, the demand for more food and sanitation is increasing. This increase in demand, in turn, leads to more fertiliser being applied in agriculture and more septic waste being released into the environment (Erisman et al., 2013). Since 1908, when the Haber-Bosh process for synthesising nitrogen-based fertiliser was created, nitrate-based fertilisers have become essential in supporting the global food chain. Around half of all food grown across the globe is produced with the use of N fertilisers (Erisman., et al 2008). This increase in population and amplified demand for more food and energy has augmented nitrogen pollution in freshwater environments. This increased input of reactive N into ecosystems can have devastating impacts on human and ecosystem health (Erisman et al., 2013).

The World Health Organisation has set a guideline of 50mg/l NO_3^- for the maximum concentration of nitrate in public drinking water (Ward et al., 2018). Despite this, the threshold has often been exceeded in surface and groundwaters around the globe (USGS, 2018). Consuming excessive levels of nitrate can produce adverse health effects in humans, with infants being especially vulnerable. The most common health impact of overconsumption of nitrate is methemoglobinemia, and this almost always occurs in infants under six months (Ward et al., 2018). Methemoglobinemia is a blood disorder which occurs when nitrate is ingested by infants and is reduced into nitrite in the infant's stomach, which is much less acidic than an adult. This nitrite binds to haemoglobin to form methaemoglobin which interferes with the oxygen carrying capacity of the blood and this can be life-threatening (Greer et al., 2005). Nitrate pollution has also had strong links to colorectal cancer, neural tube defects and thyroid disease (Ward et al.,2018).

As well as the negative impacts on human health, high nitrate levels in terrestrial water bodies can have adverse impacts upon ecosystems (Ormerod & Durance, 2009). When freshwater aquatic ecosystems have low acid neutralising capacity, they can become acidified through nitrate deposition. This can lead to shifting species composition at the base of the food chain and impact the early development of fish and other aquatic species (Ormerod & Durance, 2009). Another consequence of nitrate pollution in aquatic ecosystems is eutrophication. When nitrate levels increase, phytoplankton species are favoured as they can efficiently assimilate nitrate over other species. As a result, algal or cyanobacterial blooms can occur starving aquatic ecosystems of oxygen and, in some cases, release toxic compounds. This in turn drastically affects the ecosystem and can lead to invertebrates dying out (Camargo & Alonso, 2006).

Many steps have been taken by governments to mitigate the negative impacts of nitrate pollution to the environment and humans. An example of this is the European Union's Nitrate Directive (ND), which each member state of the European Union must adhere to. The ND states that each country must outline and define vulnerable zones to nitrate pollution and ensure that agricultural practices use fertilisers in a satisfactory manner to reduce the amount entering surface and groundwater (CEC, 2000). Furthermore, the European Union's Water Framework Directive ensures consistent measurement of nitrate concentrations in surface and groundwater to ensure this does not exceed 50 NO_3^- mg/l (CEC, 2000). Although this technique allows for an evaluation of water quality and can provide early warnings for high levels of contamination, it does not allow for the cause of the problem to be tackled, which could prevent pollution from reoccurring again in the future (Zhang et al., 2019). To effectively deal with nitrate pollution in surface and groundwater systems, it is, first and foremost, crucial to identify the different possible sources of nitrate to these systems. Potential sources of nitrate in freshwater include atmospheric N deposition, native soil organic matter, animal manure, sewage, industrial wastewater and agricultural fertilisers (Kendall,1998). Identifying sources of nitrate in the landscape can then be used by water quality managers to formulate source-specific management interventions and policy directives. In order to trace sources of nitrate, stable isotopes of nitrate ($\delta^{15}N_{-NO3}$ and $\delta^{18}O_{-NO3}$) can be used (Xue et al., 2009). This dual isotope technique is an effective method for gaining insights into nitrate sources because of their distinct N and O isotopic values (Zhang et al., 2019). The first uses of $\delta^{15}N$ as a tracer for nitrate in surface waters appeared in the 1970s (Khol et al., 1971). Although values of $\delta^{15}N$ can offer some robust insights into source identification alone, several of these sources isotopic signatures can overlap, causing difficulty identification. The dual isotope technique using $\delta^{15}N$ and $\delta^{18}O$ has been adopted by researchers to combat the overlapping of isotopic signatures as the addition of $\delta^{18}O$ values can further distinguish sources (Kendall, 1998). Stable NO_3^- isotope data has been used in a wide variety of studies around the world; Figure 1a shows the geographic range of these studies.

The methodology used to trace nitrate pollution with this $\delta^{15}N$ and $\delta^{18}O$ data has developed throughout the years and includes methods such as physical transport modelling approaches, statistically based approaches and chemical fingerprinting (Zendehbad et al., 2019). Researchers have also applied mass balance mixing models (MBMMs) to determine nitrate sources in surface waters, where the MBMM makes use of source isotopic compositions and the isotopic composition of the water sample to calculate the mixing fraction of each source to the water sample (Deutsch et al., 2006). MBMMs can provide unique solutions when three sources are considered, however, when the number of sources considered goes beyond the number of isotopic tracers plus one, MBMM are unable to be solved explicitly (Davis et al., 2006). This is particularly problematic when identifying nitrate sources as there are often five or six nitrate sources that contribute to surface and groundwaters in an area (Kendall, 1998). To combat this Bayesian stable isotope mixing models have been used by researchers (Xue et al., 2012). These models allow for more than three sources to be considered and can incorporate uncertainty into source isotopic compositions (Davis et al., 2016). The most common mixing model used was Stable Isotope Analysis in R (SIAR) (Zhang et al. 2018; Zendehbad et al. 2019; Xue et al. 2012), however, the upgrade to the SIAR package, Stable Isotope Mixing Models in R (SIMMR) was released in 2019 with a richer mixing model and improved plotting (Parnell and Inger, 2019).

1.1 Knowledge Gap

The current literature has extensively investigated the origins of NO_3^- in surface and groundwater in various regions around the world using a variety of methods. This research aims to build upon the current state of knowledge at the global scale. There is currently a lack of a global database of nitrate isotopes in surface and groundwater that allows for a quick analysis of nitrate pollution around the world (Zhang et al., 2019). Although there have been scattered studies where nitrate sources have been identified, the spatial variability of nitrate pollution in surface and groundwater across the globe has not yet been assessed. Although researchers have used stable isotope mixing models for nitrate source identification in the past, the levels of uncertainty associated with different assumptions made by the user and how they may impact upon source identification in real-world scenarios have not been explored in as much detail. The relationship between water quality management of nitrate pollution in surface and groundwater and economic complexity of nations and how this relates to the type of nitrate source identified through dual stable isotope techniques is also an area which has not received as much attention.

1.2 Research Aim and Questions

The aim of this thesis was to create a global analysis of nitrate pollution in surface and groundwaters. This allows for a deeper understanding of how nitrate pollution in surface and groundwater varies around the world with local conditions. This allows for the identification of certain climates or land uses which may be more frequently associated with high concentrations of nitrate in surface and groundwaters. Furthermore, the production of a database aims to provide a platform where stable nitrate isotope data and any other relevant variables, in a wide range of climates and countries, can easily be accessed for future research. Figure 1a shows the geographic spread of the data in the database, while Figure 1b-e shows the spread of data across groups of land use and climate. Performing nitrate source identification upon this global database permits for easy identification of which nitrate sources are common around the world and which will occur in a specific region or country. This thesis also aims to understand better the how incorporating site-specific information into a stable isotope mixing model for nitrate source identification can increase precision and thus reduce uncertainty. Finally, this thesis aims to gain a better understanding of water quality management of nitrate pollution in surface and groundwater around the world and how this may relate to nitrate pollution sources and countries economic complexitiy.

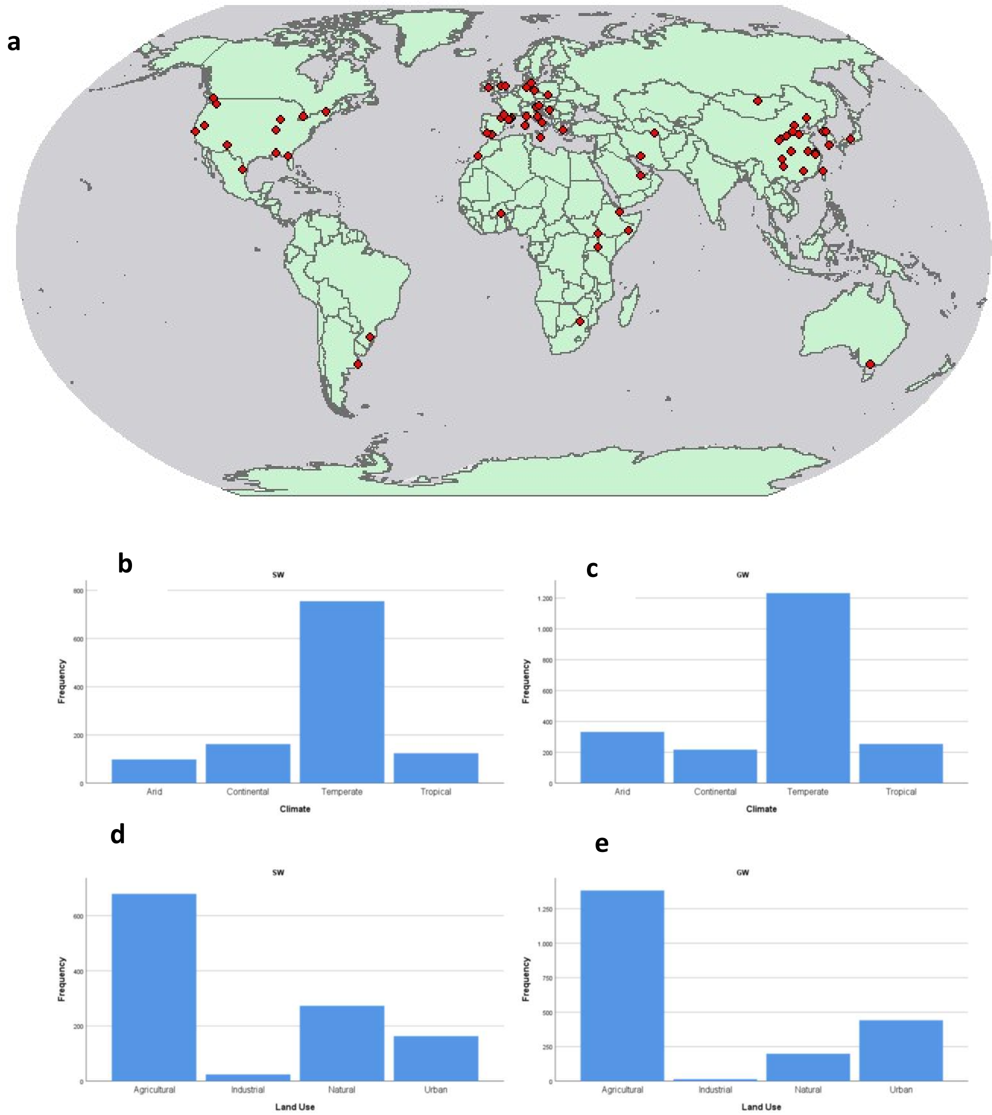

Figure 1: The spread of data across the database. a) geographic spread of study locations across the globe b) spread of surface water samples across groups of climate c) spread of groundwater samples across groups of climate d) spread of surface water samples across groups of land use e) spread of groundwater samples across groups of land use.

This research aim has led to the development of three central research questions with one sub-question:

1. How do nitrate concentrations and isotopic values in surface and groundwater change around the globe with different climates, land uses and moisture regimes?
2. What are the likely sources of nitrate in surface water and groundwater around the world?
   SQ 2.1: How do model runs with differing levels of uncertainty impact nitrate source identification in surface and groundwater?
3. What is the state-of-practice in water quality management concerning surface water and groundwater nitrate pollution, and how does this relate to the likely sources of nitrate pollution?

The approaches to answer these research questions, along with any hypothesis, are summarised in Table 1.

1.3 Societal Relevance

Nitrate pollution is a pressing contemporary issue. In October 2019, the United Nations (UN) announced the 'Colombo Declaration on Sustainable Nitrogen Management' (UNEP, 2019). The declaration has been endorsed by more than 30 countries and is the first-time global governments have cooperated to reduce nitrogen pollution, with the goal of the deceleration to cut nitrogen waste in half by 2030 (UNenvrionment, 2019). Researchers at the UN have developed the acronym 'WAGES' for the threats of nitrogen pollution, and this stands for water, air, greenhouse gases, ecosystems, and soils/stratospheric ozone depletion (Stedman, 2020). It is therefore clear that nitrogen pollution is a pressing societal issue, and this thesis will aim to contribute to solving the issue of nitrate pollution through a better understating of the water aspect of the WAGES acronym. Furthermore, management of nitrogen is critical to many of the UN's Sustainable Development Goals (SDGs). SDGs 6 (clean water and sanitation) and 14 (life below water) are of relevance to this thesis (UN, 2015).

Table 1
relevant approaches and hypothesis for each research question. H_0 represents the null hypothesis and H_1 as an alternative hypothesis.

Research Question	Method/Approach	Hypothesis
1- How do nitrate concentrations and isotopic values in surface and groundwater change around the globe with different climates, land uses and moisture regimes?	Creation of a global database of nitrate in surface and groundwater. Perform non-parametric statistical tests to understand how nitrate concentrations and isotopic values change with factors such as climate, land use and moisture regime.	H_0: There are no significant differences in nitrate concentration and isotopic values between different land use, climates and moisture regime. H_1: There are significant differences in nitrate concentrations and isotopic values across at least one of the following variables; land use, climate and moisture regime.
2-What are the likely sources of nitrate in surface water and groundwater around the world?	Using the global database identify likely sources of nitrate pollution using Stable Isotope Mixing Model in R (SIMMR) in various locations around the world. Statistical analysis to understand how sources change with different climates and land use.	H_0: There is no significant relationship between most likely nitrate source identified and land use/climate H_1: There is a significant relationship between most likely nitrate source and groups of climates and land use.
SQ 2.1- How do model runs with differing levels of uncertainty impact nitrate source identification in surface and groundwater?	Nitrate source identification. Firstly, where the main nitrate sources and their values from the literature were used in the model, secondly, each study was individually considered for possible sources and source values.	The change in the modelling approach will alter at least one of sources identified as the most likely nitrate source in both surface and groundwater.

3- What is the state-of-practice in water quality management concerning surface water and groundwater nitrate pollution, and how does this relate to the likely sources of nitrate pollution?	Quantification of water quality management using the Untreated Connected Wastewater scores from Aqueduct Atlas 3.0 and comparison with the development of countries, then relating this to the sources of nitrate found during the modelling.	H_0: There is no significant relationship between UCW score and economic development H_1: There is a significant relationship between UCW score and economic development.

2. Theory

In this section, relevant concepts relating to nitrate pollution in surface and groundwater will be explored for a better understating of how nitrates occur in surface and groundwater environments as well as the water quality management processes associated with nitrate pollution.

2.1 The Nitrogen Cycle

To understand the occurrence of nitrogen in surface and groundwaters a brief explanation of the nitrogen cycle is required. Nitrogen is a primary nutrient essential for living organisms, and, although nitrogen is very abundant in the atmosphere in the form of nitrogen gas (N_2), it is mainly inoperative in this form for most organisms (Bernhard, 2010). The nitrogen cycle is the movement of nitrogen between the atmosphere, terrestrial and marine ecosystems through various biogeochemical processes (Lehnert et al., 2010). In freshwater systems, nitrogen cycling is an extremely complex process which involves many forms of N and associated oxidation states (Durand et al., 2011).

Initially, nitrogen is taken from the atmosphere and converted into reactive forms of nitrogen by biological reduction of N_2 into ammonium compounds in a process called fixation (Fowler et al., 2013). The fixed nitrogen is later transformed into various nitrogen species through several transformation processes. These reactive forms of nitrogen can then be used throughout terrestrial and marine environments. How nitrogen is cycled through the environment into surface and groundwater can be seen below in Figure 2. After its use, nitrogen can return to the atmosphere in a process called denitrification, which occurs in soils, freshwater, marine waters and sediments. If denitrification occurs in groundwater environments however, gas may be unable to be returned to the atmosphere and may remain as dissolved N_2. Denitrification can be summarised as nitrate being converted to molecular nitrogen (Lehnert et al., 2010). More details of the various biogeochemical cycling processes and how they impact nitrate source identification are discussed in section 2.6

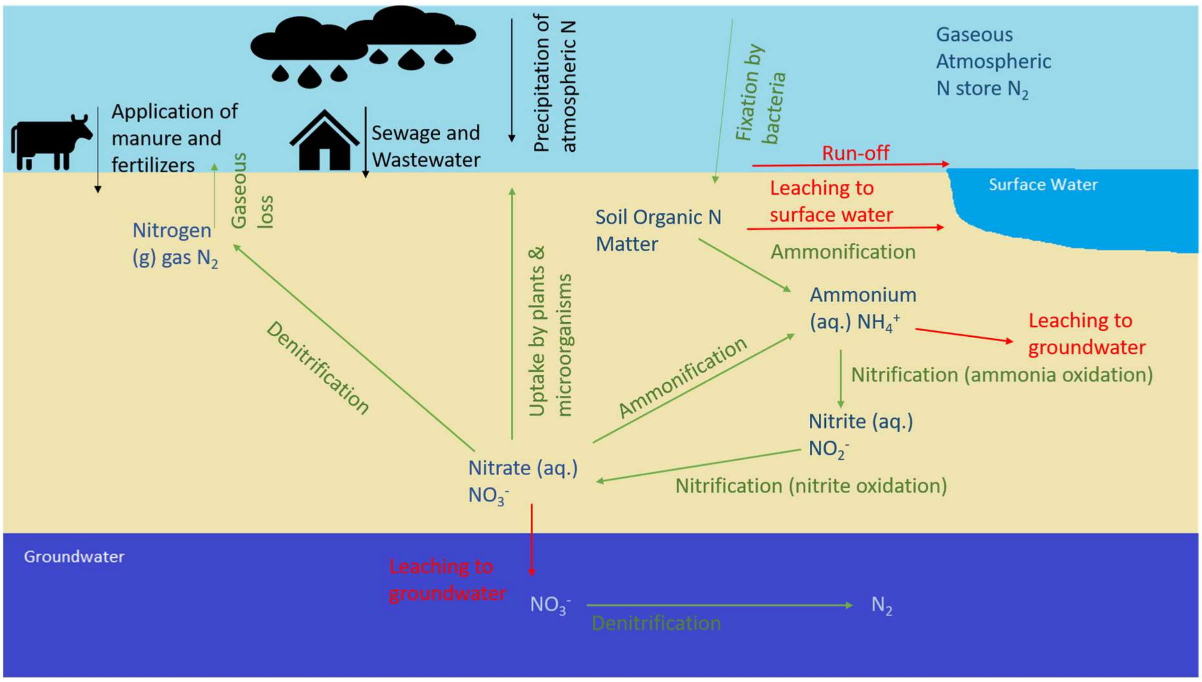

Figure 2: an overview of the nitrogen cycle. Black text and arrows represent inputs of nitrogen to the environment, the blue text represents stores of nitrogen throughout the system, green text and arrows represents movements and biogeochemical processes, red arrows and text represent the movement of nitrate to surface and groundwater

2.2 Stable Nitrate Isotope Concepts

An isotope is defined as an atom of a specific element that has a different mass due to the number of neutrons in the nucleus. In the case of nitrate (NO_3^-) this would be nitrogen and oxygen (Kendall, 1998). A stable isotope does not undergo radioactive decay; however, it may be radiogenic meaning it was produced by radioactive decay (Kendall, 1998). Nitrogen has two natural stable isotopes, $^{15}N/^{14}N$, while oxygen has three stable isotopes, ^{16}O, ^{17}O and ^{18}O. The lighter isotopes ^{14}N and ^{16}O are much more naturally abundant than their heavier counterparts (Xue et al., 2009). Stable isotopes are normally expressed as a ratio of the heavier isotope to that of its lighter isotope counterpart. These ratios are then expressed in delta (δ) per mil (‰) relative to the international standard. Isotope mass spectrometry is used to determine the ratio of stable isotopes (Xue et al., 2009). The equation for this is shown below:

$$\delta\ (‰) = [(R_{sample} - R_{standard} / R_{standard})] \quad \textit{Equation 1}$$

R_{sample} indicates the ratio of heavy to light isotope in the measured sample, and $R_{standard}$ is the ratio in the standard (Kendall, 1998). When δ is a negative value, this corresponds to a lower isotopic ratio in the sample than the standard; therefore, it is depleted in the heavy isotope in comparison to the standard. Alternatively, if the δ value is positive, the sample is enriched in the heavy isotope in comparison to the standard (Xue et al., 2009).

2.3 Isotope Fractionation

As thermodynamic properties of an atom depend on mass, identical chemical compounds that contain different isotopes, e.g. $^{15}N/^{14}N$, have different thresholds for characteristics such as melting and boiling point (Kendall et al., 2007). These slight differences in mass allow for physical, chemical and biological processes to alter the ratios of isotopes of the same element; this is known as fractionation (Garrard, 2019). Heavy Isotopes form bonds with lower vibrational frequencies than lighter isotopes, and this creates lower zero-point energy in heavier isotopes. As the heavier isotopes have lower zero-point energy, they can form stronger chemical bonds (Kendall, 1998). These stronger bonds lead to enrichment of ^{15}N and ^{18}O in remaining nitrate after specific biogeochemical processes such as denitrification, as less energy is required to break the bonds of the lighter ^{14}N and ^{16}O, so they are preferentially broken down, leaving more of the heavy isotopes behind (Zhang et al., 2014). It is a consequence of this fractionation why solutes can have individual isotopic compositions, which then, in turn, can be used to trace the source. The two key isotopic fractionation processes are kinetic and equilibrium (Garrard, 2019).

Equilibrium fractionation reactions redistribute isotopes between products and reactants or between phases when forward and backward reaction rates of any particular isotope are the same (Kendall and McDonnell, 1998) This usually occurs in closed systems which are well mixed, so back reactions can transpire. During equilibrium reactions, the heavier isotope usually accumulates in the product rather than the original reactant (Kendall and McDonnell, 1998). Kinetic fractionation occurs in unidirectional, incomplete and irreversible reactions. When a system is out of equilibrium reaction rates moving forward, and backward are not the same and can become unidirectional when a physical separation of products and reactants is present (Kendall and McDonnell, 1998). An example of this is evaporation, where water vapour is transported away from the source of liquid water or a solute diffusing into a surrounding matrix such as nitrate diffusing from stream water into benthic sediment (Hoefs, 2009). The extent of kinetic fractionation is dependent on the reaction rate, relative bond energies and reaction pathways involved in the reaction (Kendall and McDonnell, 1998).

2.4 Nitrate Sources

The primary sources of nitrate in surface and groundwater are atmospheric nitrate, ammonium fertiliser/rain, nitrate fertiliser, microbially-produced soil NO_3^-, manure, sewage, industrial and domestic wastewater (Zhang et al., 2014). NO_3^- sources show characteristic $\delta^{15}N$ values with lighter

$\delta^{15}N$ in precipitation (−10‰ to 8‰) and chemical fertiliser (−6‰ to +6‰) (Xue et al., 2009). After the process of nitrification by microorganisms, the δ15N value of soil nitrogen is around −3‰ to 5‰ (Zhang et al., 2019). Manure and sewage have heavier δ15N values (7‰ to 20‰) (Zhang et al., 2019). Although $\delta^{15}N$-$_{NO3}$ can be useful to identify specific sources, some sources are produced through the same processes, which leads to similar and overlapping ranges of isotopic values. This is where $\delta^{18}O$-$_{NO3}$ and the dual isotope technique becomes useful. $\delta^{18}O$-$_{NO3}$ allows for identification of sources that $\delta^{15}N$-$_{NO3}$ would not capture individually. The $\delta^{18}O$ in microbially-produced soil NO_3^-, precipitation and nitrate fertiliser are regulated by different processes giving them considerably different $\delta^{18}O$ values, allowing for these sources to be separated (Xue et al., 2009). Precipitation usually has $\delta^{18}O$ values in the range of +20‰ and +70‰. $\delta^{18}O$ values in nitrate fertilizer have a specific range usually around +17‰ to +25‰. In-situ microbially-produced NO_3^- is usually between −5‰ and 5‰ (Xue et al., 2009). The ranges of nitrate sources are shown below in Figure 3. The values have been taken from a variety of sources and to provide a robust overview for source signatures from both agricultural and urban environments.

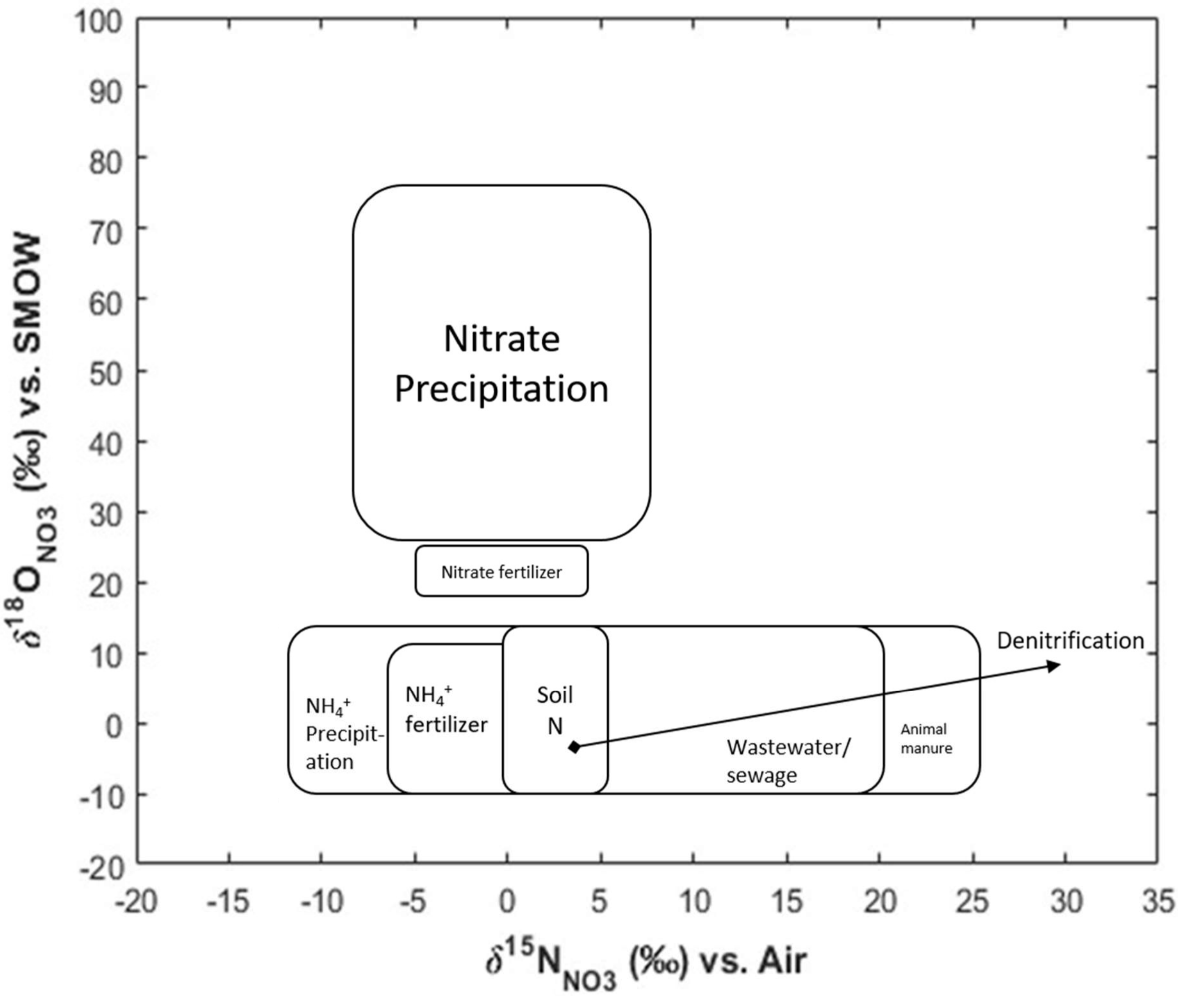

Figure 3: Ranges of $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ from the main sources of nitrate. Source ranges extracted from: Kendall et al.(2007); Choi et al. (2007); Piatek et al. (2005); Xue et al. (2009). Arrow represents the typical slope (0.5-0.8) for data when denitrification is present.

The use of NO_3^- concentrations can be used in combination with isotopic values to further aid source identification. When manure was the primary source in groundwater NO_3^- concentrations correlate with more positive $\delta^{15}N$-$_{NO3}$ values, this being due to manure raising the isotopic values above the background levels of degradation of soil organic matter (Choi et al., 2007). Alternatively, when fertilisers were the predominate source of nitrate in groundwater a correlation between increasing NO_3^- concentrations and a more negative $\delta^{15}N_{-NO3}$ value has been observed (Kendall et al., 2007), again due to the change from the background of soil-derived NO_3^- in groundwater. These correlations may only be useful when there is only a single pollution source, and fractionation processes are minimal (Xue et al., 2009).

2.5 Nitrate Sinks

The sources mentioned in the previous section can end up in two main sinks of terrestrial water, surface water and groundwater. Nitrogen is transferred into groundwaters through either leaching of soils, river seepage through the hyporheic zone and point- sources discharge especially through septic tank systems (Durand et al., 2011). While certain discharges, such as those from point sources, arrive in the form of ammonium, in the unsaturated zone nitrification into nitrate usually occurs. This movement through the unsaturated zone happens at a prolonged rate, and it can often take years for nitrate fronts to reach deep groundwater. Once past the water table, groundwater flow allows the nitrate to spread throughout the aquifer and eventually into surface waters (Durand et al., 2011). At a global scale, storage of nitrate in groundwater is comparatively small, at a catchment scale, it can contain a large portion of the catchment nitrogen budget (Durand et al., 2011). Due to the long-term nature of nitrate arriving in groundwaters, the original application of nitrogen on the surface could take several decades to reach aquifers and in turn surface waters. As many aquifers provide drinking water sources or replenishment of reservoirs, it could take a long time before any water quality improvements to reduce nitrates are implemented and observed. (Durand et al., 2011).

Nitrate can end up in surface waters such as rivers and lakes. Nitrogen can reach theses environments through several pathways such as deposition from the atmosphere directly on the catchment or water body, transfer from groundwater and through leaching from diffuse and point sources (Durand et al., 2011). Lakes can receive N from direct atmospheric inputs as both wet and dry deposition. The fixation of N_2 cyanobacteria in lakes is much more significant than in rivers due to the higher surface area allowing for a larger area for the exchange to occur (Durand et al., 2011).

2.6 Nitrogen Biogeochemical Processes

The contribution of the many nitrate sources to surface and groundwater coupled with the multiple N-cycling processes and the complex fractionations that result from them can alter the original $\delta^{18}O_{NO3}$ and $\delta^{15}N_{NO3}$ values (Kendall et al., 2007). This section describes such biogeochemical processes and their associated fractionation potential to understand how isotopic signatures may be altered before they enter surface and groundwater.

Fixation: The process of atmospheric N_2 being converted to biologically available forms of nitrogen. Fractionation associated with fixation usually Is around -3 to +1‰ (Hobbie and Ouimette, 2009). Fixation usually can be indicated by low $\delta^{15}N$ values in organic material; however, as the production of ammonium (NH_4^+) fertilisers involves fixation, this leads to similar values of $\delta^{15}N$ in sources of NH_4^+ (Kendall et al., 2007) which can be seen in Figure 3.

Assimilation: The uptake of reactive forms of nitrogen such as NO_3^-, NO_2^- and NH_4^+ by biota and plants. The lighter ^{14}N is preferentially taken up, which leads to slight fractionation of the remaining material. The amount of fractionation that occurs depends on the environment, with higher fractionation occurring in aquatic environments (-27 - 0 ‰) than in other environments however the impact upon nitrate signatures in surface and groundwater is negligible. (Kendall and McDonnell, 1998).

Mineralisation: This is the production of organic nitrogen into inorganic forms from soil organic matter, which has a small amount of fractionation, around 1‰, and has a minimal impact upon source identification in surface and groundwater (Kendall & Mcdonnell, 1998).

Nitrification: This is the oxidation of ammonium to nitrate, which is carried out by a range of archaea and autotrophic bacteria. This results in nitrate depleted in ^{15}N relative to the initial ammonium, while the remaining ammonium is enriched. The amount of fractionation depends on the amount of substrate available. When systems are N limited fractionation is minimal; however, application of NH_4^+ fertilisers can simulate nitrification. Initially, the produced nitrate from oxidation has low $\delta^{15}N$ values and oxidation of NH_4^+ is the rate-determining step; however, $\delta^{15}N$ values increase as ammonium is diminished, and oxidation of NH_4^+ is no longer rate determining. This means that the $\delta^{15}N$ that is leaked to surface and groundwater is very difficult to measure and the effect of nitrification fractionation is hard to assess. Measurements would need to be taken from beneath the field where fertiliser was applied after enough time has elapsed, so fractionation effects do not skew measurements (Kendall et al., 2007).

The oxidation of NH_4^+ to NO_3^- requires three O atoms, and these are incorporated with one coming from atmospheric O_2 and the other two coming from H_2O. The following equation can summarise this:

$$\delta^{18}O - NO_3 = \frac{2}{3}\left(\delta^{18}O_{H_2O}\right) + \frac{1}{3}\left(\delta^{18}O_{O_2}\right) \qquad \textit{Equation 2}$$

When the H_2O is in the normal range of -25 to +4 ‰ and the O_2 is in the range of atmospheric O_2 (ca. +23.5‰) the δ18O-NO_3 produced in soil through nitrification is usually in the range of -10 to +10‰ (Kendall et al., 2007).

Volatilisation: The process of ammonia gas from the soil returning to the atmosphere as NH_3 gas. It has been shown that volatilisation causes a 2-3‰ increase in $\delta^{15}N$ values in groundwater relative to the initially applied fertiliser (Kendall et al., 2007).

Denitrification: The reduction of nitrate which results in nitrogen gas (N_2) once the process is complete or N_2O or NO intermediary gaseous N products. Denitrification only occurs under anaerobic conditions or low concentrations of dissolved oxygen (<2 mg/l), meaning that it only usually occurs in groundwater environments and not surface water (Kendall et al., 2007). In groundwater, the products of denitrification usually remain as dissolved N_2 gas (Lapworth et al., 2008). Denitrification causes a substantial increase in ^{15}N in the residual nitrate. For example, denitrification of ammonium fertiliser with a $\delta^{15}N$ of 0‰ produces a residual nitrate value of +15 to +30‰ (Kendall et al., 2007). Denitrification also has a similar effect on $\delta^{18}O$ values, meaning impacts of denitrification on nitrate are coupled (Kendall et al., 2007). In freshwater systems, it is accepted that when the plot of $\delta^{15}N_{NO3}$: $\delta^{18}O_{NO3}$ has a trajectory between 0.5 and 0.8, the pattern can be explained by the presence of denitrification (Granger & Wankel, 2016).

From these processes', denitrification can cause the most difficulty in source identification because of extensive fractionation and its ubiquity in many environments. It is therefore critical to identify denitrification and determine the initial isotopic nitrate values to account for denitrification (Kendall et al., 2007)

2.7 Water Quality Management of Nitrate Pollution Concepts

As this thesis is interested in pollution of surface and groundwaters by nitrate, the relevant aspect of water management is the treatment of wastewater and sewage to remove nitrate and regulation of fertiliser and manure use in agriculture. Treatment of wastewater consists of three stages. First is primary treatment; this is where objects are removed from sewage. Large objects are removed, followed by grit, then suspended solids through a sedimentation tank (Gerba and Pepper, 2019). Secondary treatment removes organic matter through the use of aerobic biological processes, making use of the bacteria in the wastewater (Gerba and Pepper, 2019). Finally, tertiary treatment aims to raise the water quality of wastewater released to the environment to that of domestic or industrial standards. Wastewater treatment plants require specialised technologies for the tertiary stage (Gerba and Pepper, 2019). It is at the tertiary stage where nitrate removal is expected to take place. Physio-chemical denitrification, biological and chemical reductions are some of the most widely used methods for nitrate removal (Yun et al., 2018). Due to the costs involved in water treatments, it is often absent in developing countries. Compounding this problem is the issue that across several developing nations population growth has exceeded improvements in sanitation and wastewater infrastructure (Qadir, 2010). Thus, much wastewater in developing countries is not treated and is often used by farmers for irrigation, adding contaminants back to the environment (Sato et al., 2013). Alternatively, in developed countries, stringent effluent discharge regulations mean tertiary treatment is nearly always in place. In arid climates, the competition over freshwater resources in developed nations leads to more motivation for wastewater to be treated to domestic standards so it can be reused (Sato et al., 2013). Other methods of water quality management of nitrate include ensuring that agricultural does not use excessive levels of fertilisers. It has been shown that the negative consequences associated with fertiliser use can be mitigated by proper agricultural management (Peña-Haro et al., 2010).

3. Methodology

3.1 Creation of a Global Database

To understand the spatial variability of nitrate pollution in surface and groundwater around the world a global database of stable isotopes of O and N in nitrate in surface and groundwater was produced. This allows for an understanding of how nitrate concentrations and isotopic values vary around the world spatially with different climates and with different land use types. The creation of such a database will also allow for easy access to all relevant nitrate data for further research.

Relevant literature was found using the search engines Google Scholar and Scopus with the terms "(NO3- OR nitrate) AND (dual isotope* OR (15 N AND 18O) OR (N-15 AND O-18))". When a paper was found any N(NO_3-(mg/L)), N(δ^{15}N-$_{NO3}$(‰)) and N(δ^{18}O-$_{NO3}$(‰)) data was extracted either from reported tables or using the data extraction tool *grab it* in the software MATLAB. Any relevant non-nitrate data that could aid in future research were also extracted, this included sodium concentrations (Na^+ mg/l) and the stable isotope of boron (δ11B [‰]) as they can be used as an addition tracer (Xue et al., 2009). Following this, coordinates from the sample location were taken. If no coordinate information was available from the source paper, then the locations were extracted manually through Google Maps or georeferencing in ArcMap. Next, the sample was noted if it was taken from surface water or groundwater. Next, the climate class of each study location was determined using the Köppen-Geiger climate classification (Kottek et al., 2006). Only the five main climates, A (tropical), B (arid), C (temperate), D (continental), and E (polar) were considered to allow for useful data analysis. Following this, the moisture regime when the sample was taken in the field was determined, this was done to assess if levels of precipitation has any significant effect on the occurrence of nitrate in surface and groundwater. This was assessed by comparing the precipitation levels of the month when the sample was taken in the field to the yearly average of the location where the study was conducted. If the month has lower than average precipitation amounts, then it is considered a dry moisture period. Alternatively, if it had higher precipitation than average, it was considered a wet moisture period. Finally, the land use of the sample location was taken from the source paper and recorded. To then produce practical analysis, the land uses were placed into four common groups: Agricultural, Urban, Industrial and Natural.

Statistical tests were then completed to understand how nitrate concentrations and isotopic values in surface and groundwaters vary spatially with climate, land use and moisture regime. The software SPSS 25 was used for all statistical analysis. Tests for normality were run to understand which statistical tests to use on the data. The NO_3^- mg/l, δ^{15}N-$_{NO3}$ and δ^{18}O-$_{NO3}$ data all showed non-normally distributed data with a significance of .000. This result led to non-parametric tests being used for statistical analysis. Wilcoxon ($p<0.05$) and Steel-Dwass ($p<0.05$) nonparametric pairwise comparison tests were used to assess the differences between categories of land use, climate and moisture regime.

3.2 Nitrate Source Identification

To then identify nitrate pollution sources in surface and groundwater around the world, source identification was completed using a stable isotope mixing model. This aimed to provide a good understanding of how nitrate sources change in different regions of the globe and with different climate types and land use classes. This source identification was ran using different levels of uncertainty for comparison and an understanding of how source selection and source end-member values in the model can affect source identification and model performance.

The Bayesian mixing model Stable Isotope Mixing Model in R (SIMMR) was used to determine which N sources are contributing to pollution of surface and groundwaters around the world, (Parnell & Inger, 2019). The model calculates the contribution of each source to the sink; in this case, this was either surface or groundwater. The model then produces a value of each source's contribution, from most likely to least likely as a ratio out of one. Sets of mixture measurements (N) are defined on isotopes (j) with source contributors (k) the model can be expressed as:

$$X_{ij} = \sum_{k=1}^{k} P_k \left(S_{jk} + C_{jk}\right) + \varepsilon_{ij},$$
$$S_{jk} - N\left(\mu_{jk,}\omega_{jk}^2\right),$$
$$C_{jk} - N\left(\lambda_{jk},\tau_{jk}^2\right),$$
$$\varepsilon_{ij} - N\left(0,\sigma_j^2\right),$$

Equation 3

Where X_{ij} indicates the observed isotope value of the mixture, *j* is the isotope value, and *i* is the mixture. S_{jk} is the source value *k* for the isotope *j* which follows a normal distribution with mean μ_{jk} and standard deviation ω_{jk}. P_k is the proportional contribution of source (*k*) which is estimated by the model. C_{jk} is the fractionation factor for isotope *j* on source *k*, and again this follows a normal distribution with mean λ_{jk} and variance is τ. The residual error ε_{ij}, represents the additional unquantified variation between the individual mixtures. The mean a and standard deviation are 0 here (Xue et al., 2012). In SIMMR prior distributions of source contributions can be chosen as vague or informative based, which is based on available information (Parnell & Inger, 2019). The full script used for source identification is included in appendix A.

3.2.1 Shotgun Approach

Although mixing models can be a powerful tool when identifying sources, there are some limitations that if gone unaddressed can lead to high levels of uncertainty. For example, given the wide ranges of sources, it is necessary to mention the assumptions when assigning values to source values and ranges. In this thesis, two approaches were used when assigning sources and their corresponding values with each approach carrying a different level of uncertainty.

To better assess the uncertainties of SIMMR in nitrate source identification, a 'shotgun approach' was used first. This approach was deemed the 'shotgun' approach as it involves a low level of precision when inputting source information. One issue that can lead to higher uncertainty in a mixing model is the overlapping of source ranges. As the number of sources considered by the model increases the diagnostic power of SIMMR decreases and uncertainty rises (Davis et al., 2016). Another problem which can cause higher uncertainty is that source values and ranges are not homogenous in every region of the world. For example, $\delta^{15}N$ values for synthetic fertiliser change depending on the type of crop or agriculture in a region (Bateman and Kelly, 2007). For the first model run, values for the five potential nitrate sources were defined based on the available literature, and these are ammonium fertiliser/precipitation, nitrate fertiliser, nitrate precipitation, microbially-produced soil NO_3^- and manure + sewage. SIMMR requires mean and standard deviation as source inputs. $\delta^{15}N$ source values were calculated based on the boxplots in Xue et al. (2009). The tool *grab it* was used to extract the typical minimum and maximum source values. The 50th percentile value was taken, then assumed as the mean in SIMMR. $\delta^{18}O$ values were taken from the Kendall et al. (2007), with the means taken as the middle of the source ranges on the typical ranges plot. Standard deviations were then estimated based off the respective plot's minimum and maximum source ranges, with larger standard deviations for sources with larger source ranges. These two sources were chosen for source end-member values as Xue et al. (2009) collated sources values from a wide array of papers to obtain an extensive review of $\delta^{15}N$ values, while Kendall et al. (2007) provides information on $\delta^{18}O$ that is not covered by the former.

All nitrate sources $\delta^{18}O$ values were taken from Kendall et al. (2007) for consistency. Dual isotope data from each study was then inputted into the model and ran individually. Once the model run was completed the most likely source contributing to the study was taken along with the mean contribution value. If a study took samples from both surface and groundwater, then these were run separately.

Table 2: Source values used across each study in the shotgun approach

Nitrate Source	N($\delta^{15}N_{-NO3}$(‰)) (Mean ± SD‰)	N($\delta^{18}O_{-NO3}$(‰)) (Mean ± SD‰)
Ammonium Fertiliser/Rain[1]	-0.89 ± 2.66	0.8 ± 2.3
Nitrate fertiliser[1]	1.079 ± 2.5	20.1 ± 1.1
Nitrate precipitation[1]	-1.16 ± 3.75	50 ± 12.5
Soil N[1]	4.19 ± 1.1	0.1 ± 1.3
Manure + Sewage[1]	10.53 ± 4.8	-2 ± 8

[1] $\delta^{15}N$ values taken from Xue et al (2009), $\delta^{18}O$ values taken from Kendall et al (2007).

3.2.2 Intelligent Approach

The next model run was completed to reduce the uncertainty that was created through the shotgun approach. It also allowed for an assessment of the differences in results between the two different approaches. The approach was termed 'intelligent' as each paper was individually considered for the sources in order to increase precision and thus reduce uncertainty. The consideration if a source is present or not can significantly impact findings. When all sources are considered, it is assumed that all sources contribute to the solution. This assumption forces all sources to acquire importance, which could be a dubious interpretation as it is based on a broader set of assumptions rather than what might have been applicable at a specific site (Fry, 2013). As mentioned previously, the means and standard deviation of each source may not be the same in each geographic location, which could skew source identification. To address this uncertainty, each paper was analysed to identify which sources were present in each study location and which were absent. This was first based on any information within the paper and then based on analysis of the area itself. For example, if an area had no agricultural land use, then fertiliser would not be considered. Furthermore, if any site-specific measurements of end-member values were present, then these were used as source values in the model as an alternative to the end member values taken from the literature. Again, each study was run individually and the rank-order of likely sources from most likely to least likely were reported. This approach allowed for a comparison of how the model performs when site-specific information is taken into account. The two approaches were compared by plotting the most likely sources for each water type against each other. The other most likely sources were then investigated through graphical analysis.

3.2.3 Nitrate Pollution Sources Around the World

Following the completion of the model runs, maps were created and graphical analysis was carried out to understand if there were any visual differences in nitrate sources between variables around the world. The results from the intelligent run were used for this because it was deemed as the modelling scenario that closely reflects site-specific conditions. Subsequently, statistical tests were used to understand if there was any significant relationship between variables such as climate, land use and the sources of nitrate in surface or groundwater. As both the predictor and outcome variables are categorical a Fisher Exact test ($p<0.005$) was used to understand if there are any significant relationships between the variables. A Fishers Exact test was used as an alternative to a Chi-Squared test as when 20% of cells have expected frequencies < 5 the approximation method is inadequate, and Fisher's exact test must be used as an alternative (Kim, 2017). Due to a large number of variables in this study, there were more than 20% of cells with an expected count below five which led to Fisher's exact test being used. A Phi and Cramer's V test was also used to understand the effect size of any relationship. SPSS 25 was used for statistical analysis.

3.3 Water Quality Management Concerning Nitrate Pollution of Surface and Groundwater

A second database was produced showing the current state-of-practice in water quality management concerning surface water and groundwater nitrate pollution and its relation to the development of countries. This was done to give an overview of how management practices for nitrate pollution in surface and groundwater differ globally and understand the relation to countries development. This was done using the Aqueduct Water Risk Atlas 3.0 created by the World Resources Institute. Aqueduct uses data from hydrological modelling, remotely sensed data and published data into an online platform. Aqueduct has 13 indicators in across three groups, physical risk quantity, physical risk quality and regulatory and reputational risk (Hofste et al., 2019). As this thesis is interested in nitrate pollution, and one of the key sources of nitrate to surface and groundwater is wastewater or sewage, the relevant indicator in Aqueduct is Untreated Connected Wastewater (UCW).UCW; 'measures the percentage of domestic wastewater that is connected through a sewerage system and not treated to at least a primary treatment level (Hofste et al., 2019)'. UCW has a spatial resolution on a country level (Hofste et al., 2019).

As mentioned previously in section 2.7 of this thesis, nitrate is only removed at tertiary stage of wastewater treatment. Therefore, as UCW only accounts for up to primary treatment and does not distinguish between primary secondary and tertiary treatment, the limitation of using UCW score as an indicator for nitrate pollution must be acknowledged (Hofste et al., 2019). Despite this limitation, this indicator allows for two critical aspects of wastewater management to be combined, connection to sewerage systems and level of wastewater treatment. The non-existence of primary treatment reflects the capacity of a country's ability to treat wastewater, while connection rate reflects household access to public sewerage systems (Hofste et al., 2019). Together these two aspects indicate how well a country manages wastewater, and, in turn gives a valid representation of a countries technological and institutional abilities to prevent nitrate pollution by sewage and wastewater. Countries performing well on UCW are much more likely to have higher standards of wastewater treatment. The UCW raw value is calculated by the following equation:

$$UCW = \begin{cases} -1, c \geq 1\% \\ 100\% - \left((100\% - u) \cdot c\right), otherwise \end{cases}$$

$$Where: \; UCW = Unimproved/connected\ wastewater\ raw\ value\ in [\%]$$

$$u = Percent\ untreated\ wastewater\ in\ [\%]$$

$$c = Percent\ connected\ wastewater\ in\ [\%]$$

Equation 4

Raw values are given a score for example, a <30% would indicate a low score and a low risk category for UCW. As raw values increase so does score, which ranges between 0-5. Scores between 0-1 are low risk, 1-2 low to medium risk, 2-3 medium-high risk, 3-4 high risk, 4-5 extremely high risk, 5 is no (100%) connected wastewater.

Aqueduct allows importation of latitude and longitude data as a .csv file to create a table of UCW scores. The sites gathered in creating the global database was used for this, giving a table of UCW scores for each location, which indicates the level of water quality management concerning nitrate pollution in surface and groundwaters. As UCW scores are at a country scale and the isotope database is at a finer resolution, nitrate sources per water type had to be narrowed down to the country level. This was done by selecting the most commonly observed nitrate source in each country for each water type. If there was a tie for the most commonly observed nitrate source in a country, the source with the highest magnitude was selected as that country's nitrate source. To assess the relationship between water quality management of nitrate and economic development the indicator Economic Complexity Index (ECI) was used (Hausman et al., 2014). The ECI is a measure of a country's economic capacity. This is calculated based on the complexities of a countries economy, with better performing countries having more complex economic activities i.e. products, industries, technologies used (Hausman et al., 2014). ECI is a good indicator to test for relationships with UCW and nitrate pollution as highly economically complex nations with high technical capacities usually always have tertiary treatment in place, due to stringent regulatory standards for water contamination (Sato et al., 2013). ECI was plotted against UCW scores with most likely nitrate sources to assess any potential relationships. ECI was used as the preferred indicator over other indicators such as the Human Development Index (HDI) (UN, 2019). This was because indicators such as the HDI measure factors important to development overall, such as education and life expectancy, but these are irrelevant factors for management of nitrate pollution. ECI on the other hand is a good measure as it reflects a nations economic and technological capacity to manage pollution of nitrate.

4. Results

The results from this research are presented in the following order: Firstly, a general overview of the statistical analysis of how nitrate concentrations and isotopic compositions change with different land use, climates and moisture regimes is presented. Following this, the results from the modelling runs are described, and the differences between the two runs are compared. The sources of nitrate in surface water and groundwater around the world are then presented. Finally, the current state of water quality management in relation to nitrate pollution is analysed.

4.1 Spatial Variability of Nitrate in Surface and Groundwaters Across the Globe

The median values of nitrate concentrations across the various variables collected can be seen below in Table 3. Overall, nitrate concentrations were much higher in groundwater than in surface water across all variables. In groundwater arid climates tended to have much higher nitrate concentrations than any other climate class, with the median value over the recommended safe threshold of 30 mg/l (Ward et al., 2018). Despite the high concentration in arid groundwater environments, nitrate concentrations were the lowest in arid environments for surface water. High nitrate concentrations were observed in groundwater where the land use is dominated by industrial practices. However, the surface water concentrations were much lower in industrial areas. Although groundwater in urban areas have high nitrate concentrations on average, the concentrations in the surface water equivalent were the lowest out of all the land use types. Finally, median concentrations were higher in wet moisture periods compared to dry. To further investigate how nitrate concentrations and isotopic values of nitrate change with different climates, land uses and moisture regime, statistical tests were carried out.

Table 3
Median nitrate concentrations (NO_3^- mg/l) across variables within the global database. Interquartile ranges in brackets. If a significant difference exists between categories, this is represented with the same letter next to the median values of both categories. Statistical analysis was done with the Steel-Dwass method used for climate and land use, while the Wilcoxon method was used for moisture regime.

	Climate			
Water Type	**Tropical**	**Temperate**	**Arid**	**Continental**
Surface water	2.8 (8.8)[c]	4.39 (12.27)[a,d]	0.44 (0.79)[a,b,c]	3.2 (4.23)[b,d]
Groundwater	6.65 (13.71) [a,c,f]	16.65 (47.95)[e,f]	39.35 (78.75) [b,c,d,e]	14.7 (38.77) [a,b,d]
	Land use			
	Natural	**Agricultural**	**Urban**	**Industrial**
Surface water	4.39 (8.02)[a]	3.30 (12.18)[b]	1.58 (4.41)[a,b]	2.97 (3.49)
Groundwater	7.75 (24.61)[a,b]	16.98 (56.74)[b]	17.5 (37.84)[a]	78.05 (348.0)
	Moisture Regime			
	Wet	**Dry**		
Surface water	3.29 (8.79)	3.37(9.09)		
Groundwater	18.5 (44.92)[a]	13.04 (48.8)[a]		
	Overall			
Surface water	3.38 (9.68)			
Groundwater	19.4 (55.817)			

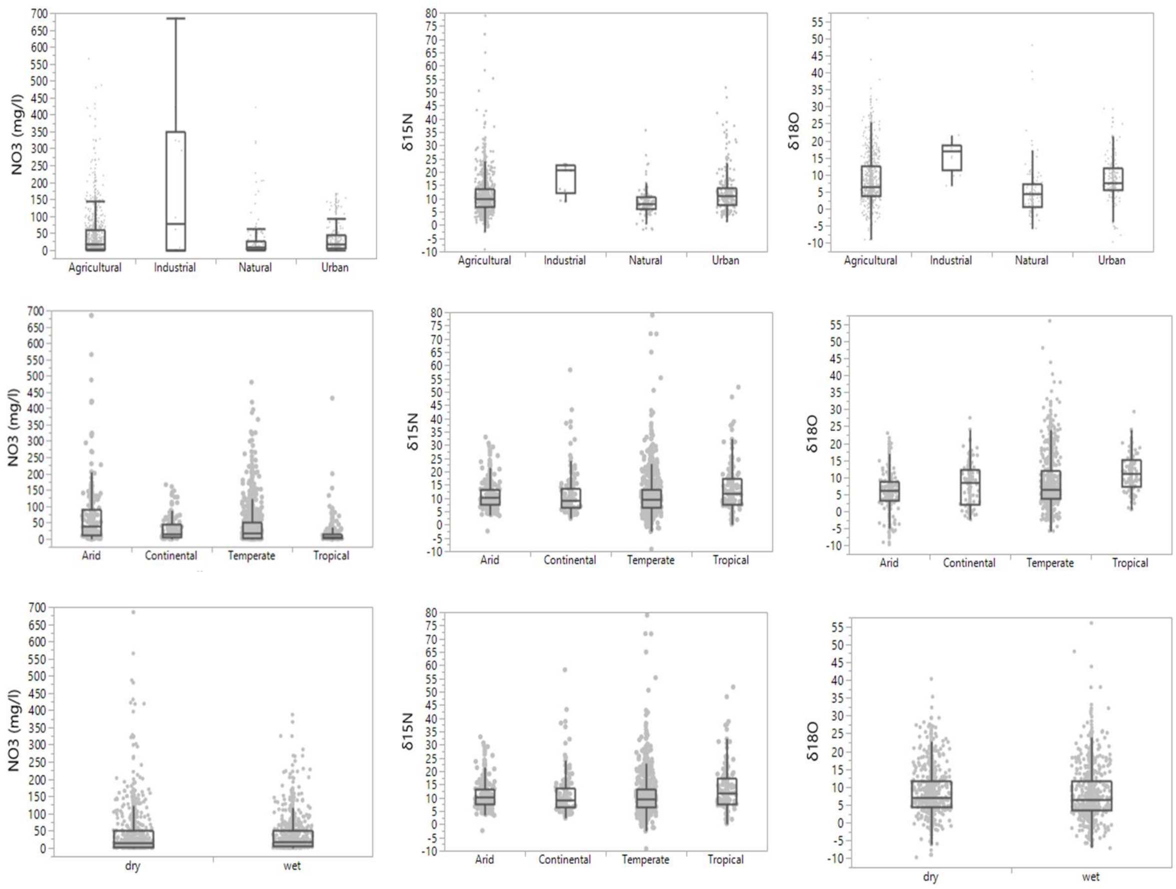

Figure 4: Boxplots across all variables in groundwater. From top row to bottom; land use, climate, moisture regime

Table 4

Median (N(δ[15]N-NO3(‰)) across variables within the global database. Interquartile ranges in brackets. If a significant difference exists between categories, this is represented with the same letter next to the median values of both categories. Statistical analysis was done with the Steel-Dwass method used for climate and land use, while the Wilcoxon method was used for moisture regime.

	Climate			
Water Type	**Tropical**	**Temperate**	**Arid**	**Continental**
Surface water	8.6 (8.5)	8.76 (5.27)[a]	8.95 (4.8)	7.95 (5.6)[a]
Groundwater	12.2 (9.81)[a,b]	9.82 (6.61)[a,c]	10.49 (5.66)[c]	9.39 (7.3)[b]
	Land use			
	Natural	**Agricultural**	**Urban**	**Industrial**
Surface water	6.06 (3.05)[a,c]	9.21 (4.45)[b,c]	9.4 (4.55)[a]	8.1 (4.2)[b]
Groundwater	9.9 (4.36)[b,c,e]	8.14 (7.0)[a,e]	11.4 (6.27)[b,d]	20.8 (10.67)[a,c,d]
	Moisture Regime			
	Wet	**Dry**		
Surface water	8.8 (5.44)	8.5 (4.41)		
Groundwater	9.86 (6.2)	10.36 (7.0)		
	Overall			
Surface water	8.6 (4.91)			
Groundwater	10 (6.57)			

Statistical analysis revealed there were significant differences between several groups of climate and land use across both nitrate concentrations and isotopic values in both water types. Significant differences between groups of climate, land use and moisture regime can be seen by the letters in Tables 3,4 and 5. Variables where there were many statistical differences between groups include; differences in nitrate concentrations between climate groups in groundwater environments, with arid environments having the highest concentrations. Concentrations in natural groundwater environments were also significantly different to areas dominated by agricultural and urban land use types. Other variables where there were many significant differences between groups include, $\delta^{15}N$ values between land use groups for both water types, and between $\delta^{18}O$ values between land use groups in groundwater environments, $\delta^{18}O$ values between climate groups in both water types. The only statistically significant difference between wet and dry moisture regimes was between nitrate concentrations in groundwater environments.

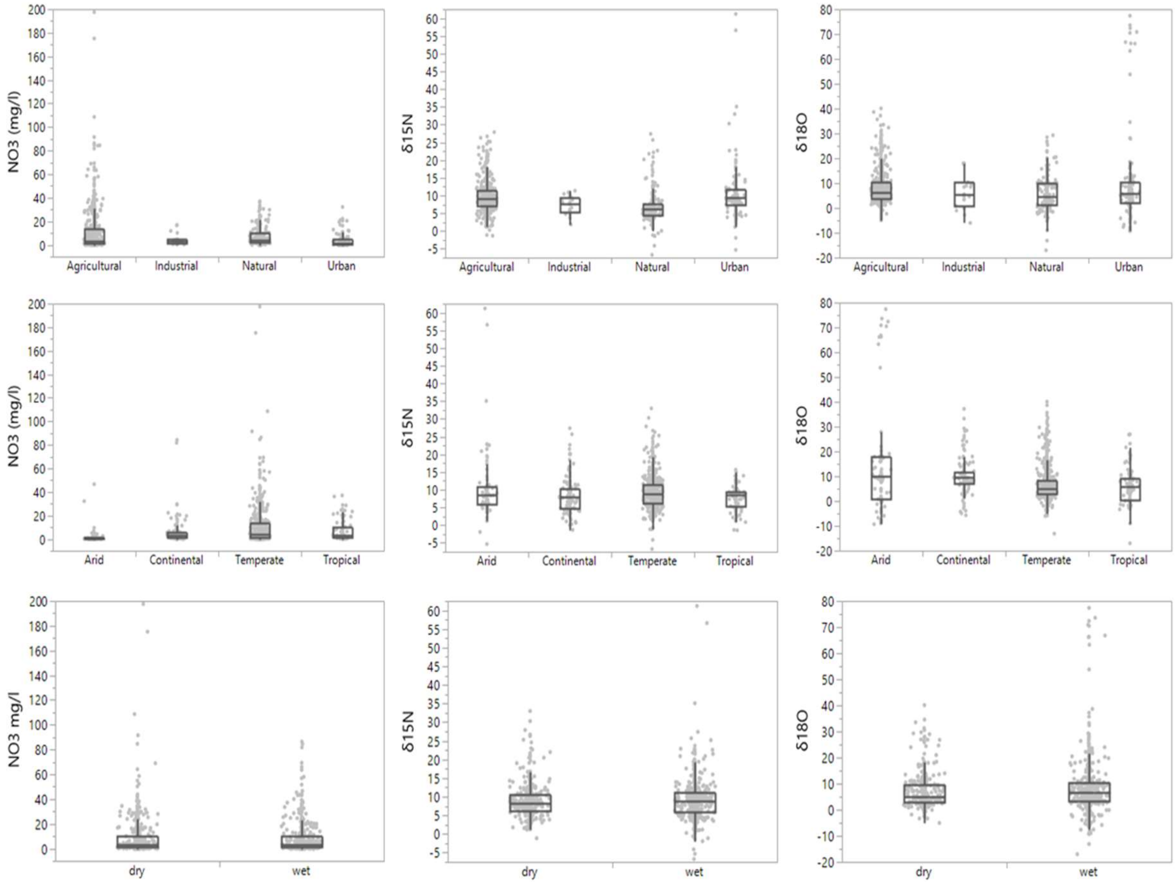

Figure 5: Boxplots across all variables in surface water. Variables from top row to bottom are; land use, climate, moisture regime

Table 5
Median ($N(\delta^{18}O_{-NO3}$(‰))) across variables within the global database. Interquartile ranges in brackets. If a significant difference exists between categories, this is represented with the same letter next to the median values of both categories. Statistical analysis was done with the Steel-Dwass method used for climate and land use, while the Wilcoxon method was used for moisture regime.

	Climate			
Water Type	**Tropical**	**Temperate**	**Arid**	**Continental**
Surface water	5.8 (8.78)[a]	5.0 (5.57)[b,c]	8.95 (17.7)[b]	7.95 (4.35)[a,c]
Groundwater	11.01 (7.9)[a,b,d]	6.5 (8.01)[a,c]	6.12 (5.48)[b,c,e]	8.4 (10.1)[d,e]
	Land use			
	Natural	**Agricultural**	**Urban**	**Industrial**
Surface water	4.62 (8.37)[a]	6.2 (6.71)[a]	5.61 (7.95)	5.6 (9.5)
Groundwater	4.35 (6.8)[b,c,d,f]	6.6 (8.70)[a,f]	7.7 (6.28)[b,c,e]	17 (7.18)[a,d,e]
	Moisture Regime			
	Wet	**Dry**		
Surface water	6.38 (7.37)	5.08 (6.70)		
Groundwater	6.56 (8.2)	6.91 (7.35)		
	Overall			
Surface water	5.8 (6.88)			
Groundwater	6.8 (8.0)			

Referring to Table 1 and the hypothesis proposed, the null hypothesis can be rejected while H_1 can be accepted. There were significant differences in nitrate concentrations and isotopic values found in several variables in both surface and groundwater.

4.2 Nitrate Source Identification

4.2.1 Shotgun Approach

Nitrate source identification was first completed using the 'shotgun approach' where the same source values obtained from the literature were used across each site, and every possible source was considered present at each site. With this approach the most frequently observed nitrate source in groundwater around the world is manure and sewage (n=32) followed by microbially produced soil N (n=12) while the least frequently observed likely source was nitrate precipitation and ammonium fertiliser/rain (n=1). Again, in surface water manure + sewage was the most commonly identified most likely nitrate source (n=18) followed by soil N (n=8). The most likely sources for the shotgun approach can be seen by the orange bars in Figures 6 and 7.

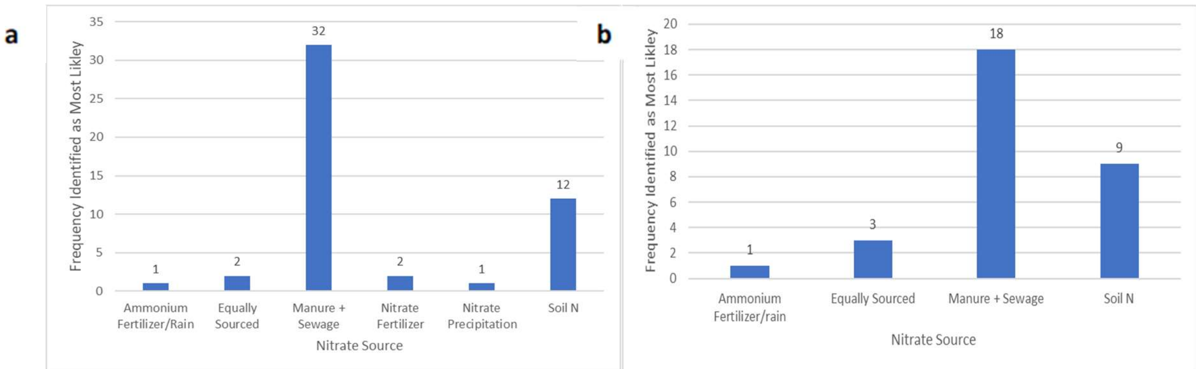

Figure 6: frequency plot each source is the most likely source of nitrate in a)groundwater and b) surface water for the shotgun model run

4.2.2 Intelligent Approach

Following this, in an attempt to reduce the uncertainty that arises as a result of the 'shotgun approach' each site was individually considered for presence or absence of each nitrate source along with any site-specific end-member values for nitrate sources; this was termed the 'intelligent approach'. Out of the total 71 studies included in this research, 40 had unique source considerations where either only a certain number of the sources were considered, or sources had site-specific end member values. The remaining 31 used the standard sources reported in the literature, along with the standard source ranges. As can be seen in Figures 7 the most common source was again manure and sewage in both surface (n=14) and groundwater(n=31). In surface water studies, there were no locations where synthetic nitrate fertiliser was identified as the most likely source. Soil N was the second most common source in surface water (n=13) and in groundwater (n=10). When a result is termed equally sourced, this is when none of the five sources had a contribution above 25%.

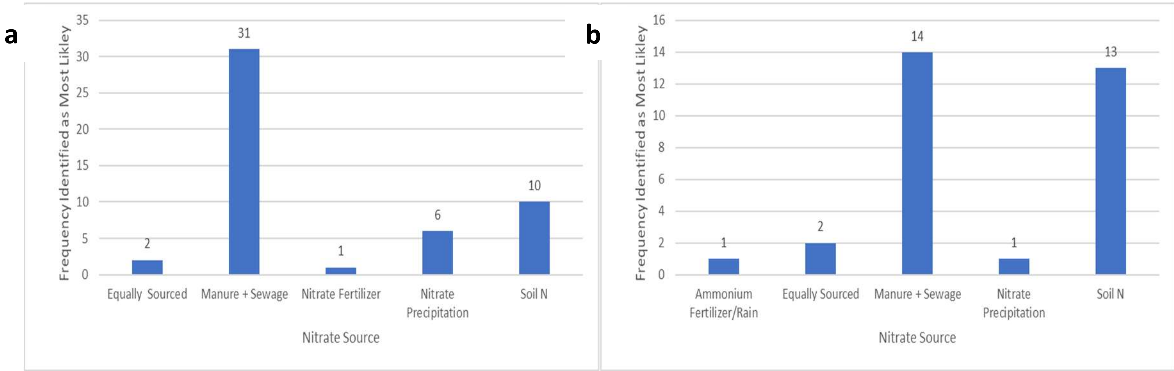

Figure 7: frequency plot each source is the most likely source of nitrate in a) groundwater and b) surface water for the Intelligent model run

4.2.3 Comparison of Approaches

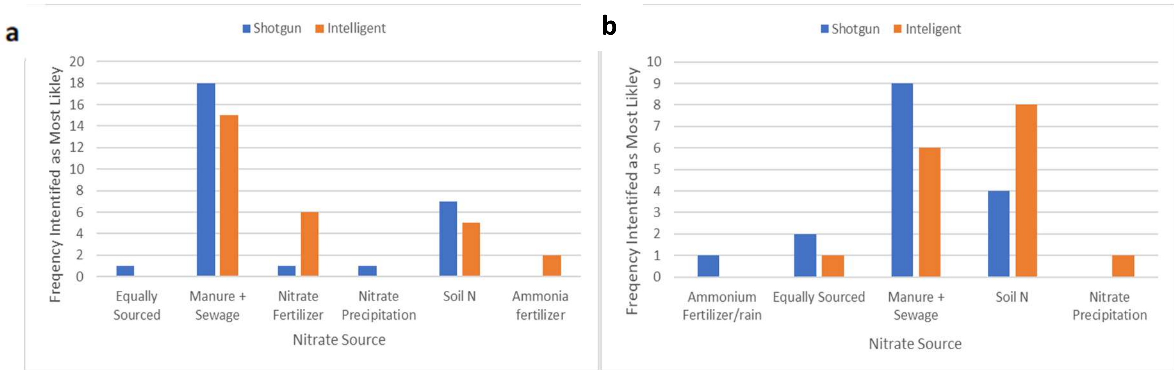

Figure 8: differences in the most likely source of nitrate between model runs when source specific information was included for a) groundwater b) surface water

In total 16 surface water and 28 groundwater studies had different source considerations and/or source end-member values. In groundwater 11 out of the 28 (39%) studies yielded a different most likely source between model runs. In surface water, this was 7 out of 16 (43%). These differences can be seen above in Figure 8. These differences suggest the inclusion of site-specific information can impact the source identified as the most likely pollution source. Looking back to the hypothesis in Table 1, the null hypothesis can be rejected for the second research question, and the alternative hypothesis can be accepted. Manure + sewage was, in fact, the most frequent likely nitrate pollution source in both surface and groundwaters. For sub-question 2.1 the null hypothesis can be rejected and the alternative accepted, there were differences in the most likely source when the modelling approach changed in both surface and groundwater. The full results from both modelling runs can be seen in appendices B, C and D.

4.2.4 Other Likely Sources of Nitrate in Surface and Groundwater

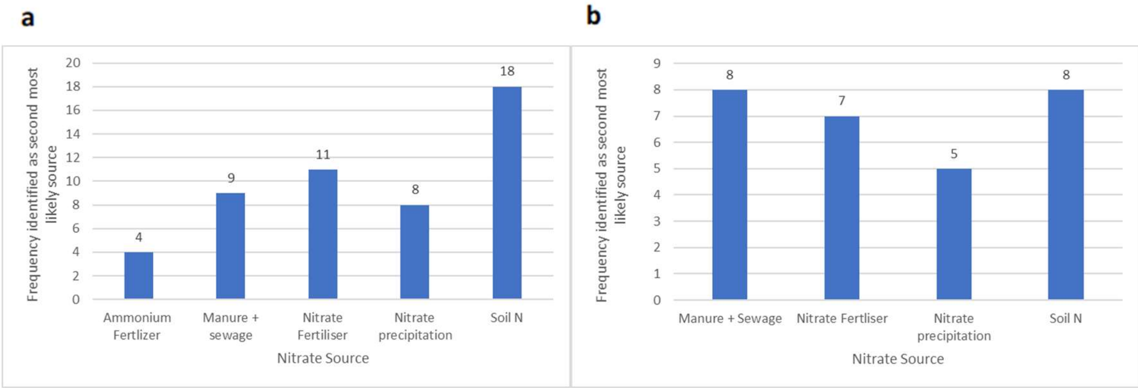

Figure 9: frequency each source was identified as the second most likely source of nitrate in a)groundwater and b)surface water

The results from SIMMR also allows for a rank order of nitrate sources from most likely to least likely. The results of the intelligent run were used for this. As can been seen in Figure 9a the second most common likely contributor of nitrate in groundwater around the world is soil N (n=18). In surface water soil N (n= 8) and manure +sewage (n=8) were tied for second most likely source. Nitrate fertilisers were also identified as the second most common nitrate source frequently in both surface and groundwater. There was a much wider spread between sources than the most likely nitrate contributors as seen in Figure 9.

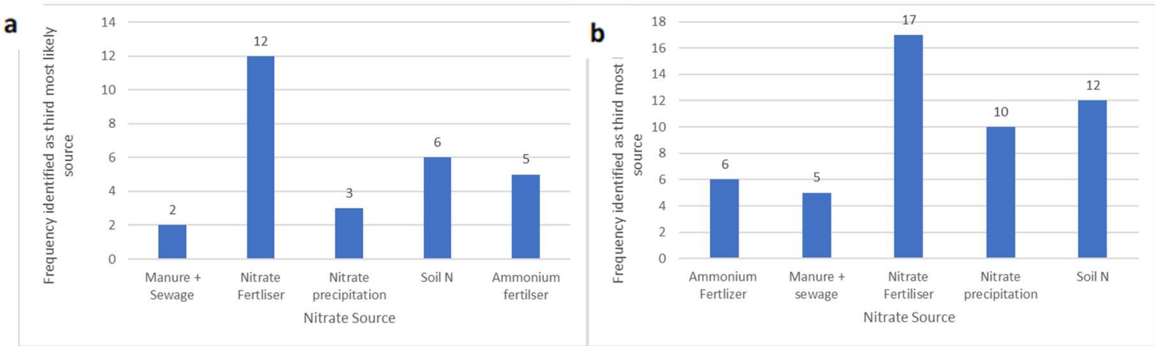

Figure 10: frequency each source was identified as the third most likely source of nitrate in a)groundwater and b)surface water

As can be seen in Figure 10 above nitrate fertilisers dominated as the third most likely source of nitrate around the world, in both surface and groundwater. Again, the spread across other sources is more even, with all other sources contributing.

4.2.2 Nitrate Pollution Sources Around the World

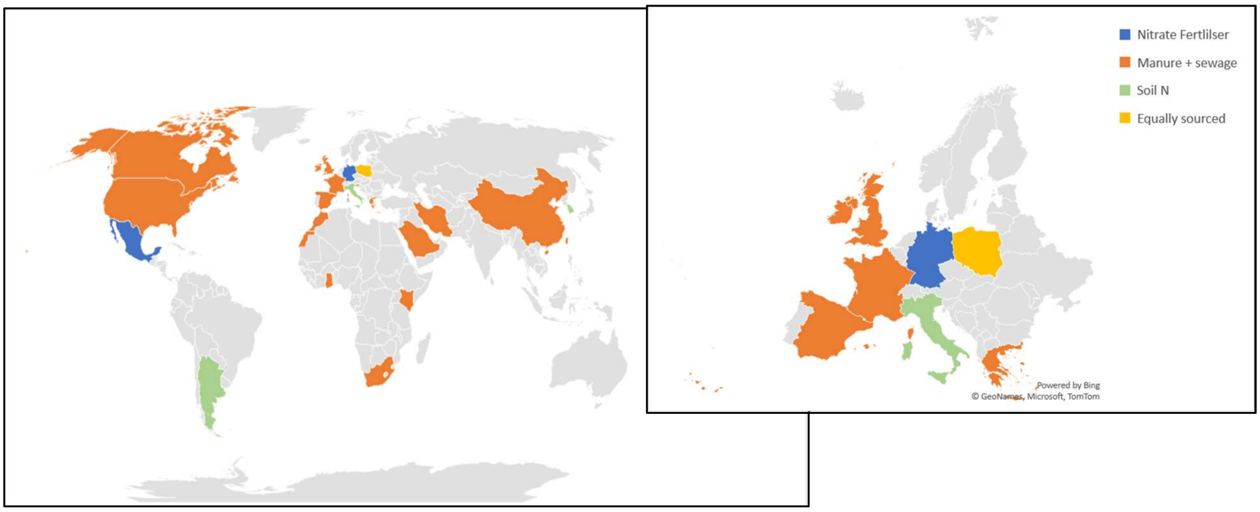

Figure 11: The most likely source of nitrate in groundwater per country across the globe and zoomed in on Europe

The spatial spread of the most likely sources of nitrate in groundwater can be seen in Figure 11. It is clear that manure + sewage dominates as the most likely source around the globe in nearly every continent. In surface water there is also a wide spread of manure and sewage as the most likely nitrate source (Figure 12). In Europe however, there is more variation, with soil N and ammonium fertilisers contributing.

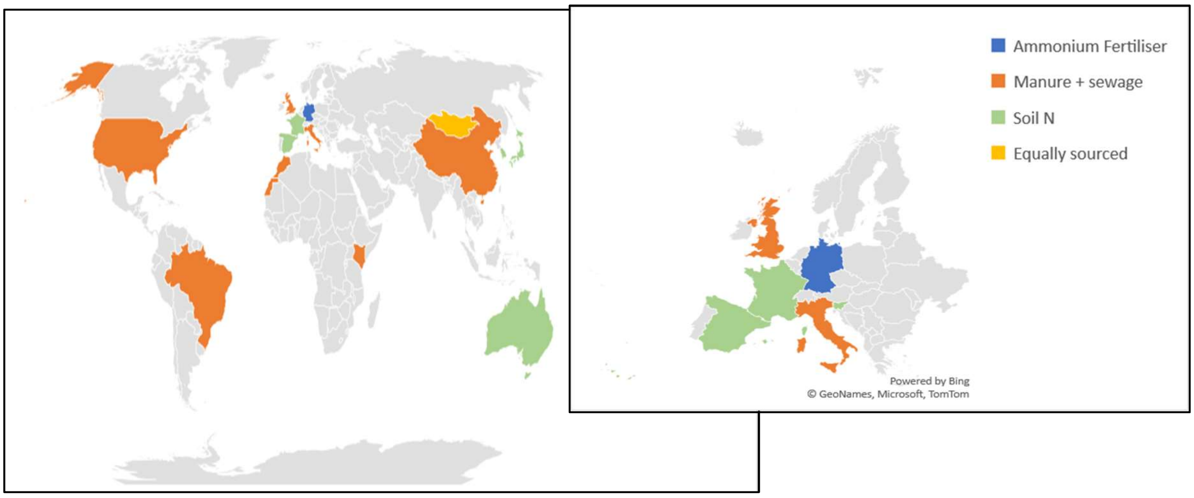

Figure 12: The most likely source of nitrate in surface water per country across the globe and zoomed in on Europe

As can be seen in Figure 13a, in surface water the split of most likely nitrate sources is reasonably even across all climate types with manure and sewage being the most common nitrate source identified as the most likely. Microbially produced soil N remains the most likely source around 30% of the time across all climates while in temperate and tropical environments other sources such as ammonium-based fertilisers were identified as the most likely source but much more infrequently. Looking at Figure 13b, for groundwater again manure and sewage is the most commonly observed most likely nitrate source across all climate types, with similar proportions of being the most likely source. In tropical climates, however, manure and sewage was the most likely source 100% of the time. Other sources such as fertilisers were more frequently identified as the most likely source in groundwater than in surface water.

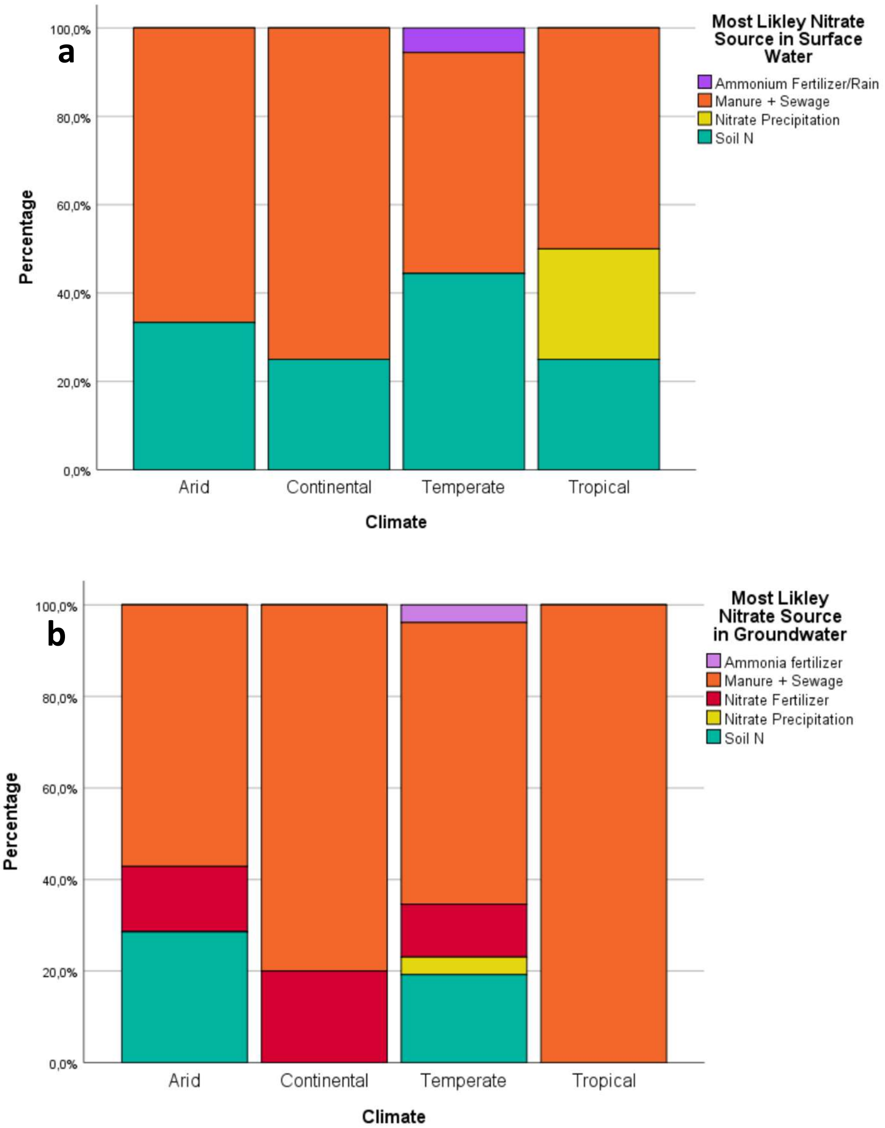

Figure 13: percentages of the most likely source of nitrate in each climate type in a) surface water and b) groundwater

Correspondingly to climate, manure and sewage dominate as the most likely source across all land use types in both surface and groundwater, this can be seen in Figures 14a and b below. In urban surface water environments and industrial groundwater environments, manure + sewage was the only source to be identified as most likely. There was most variation in the most likely source in areas where agricultural land use dominates.

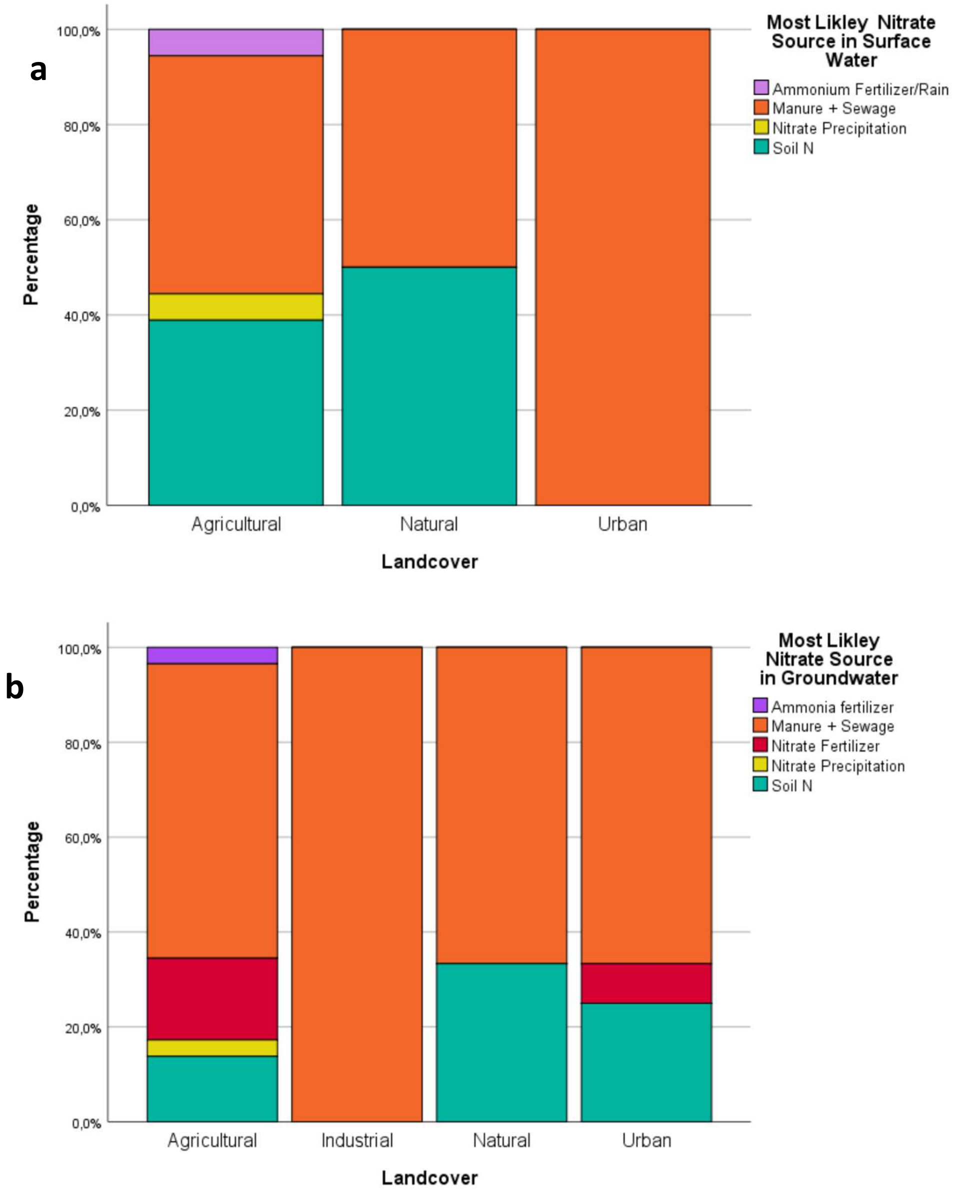

Figure 14: percentages of the most likely source of nitrate across dominant land use types in a) surface water and b) groundwater.

To test if any relationships existed between dominate land use and most likely source identified as well as climate type and most likely source statistical tests were used. A Fisher exact test showed that there was no significant relationship between the climate and most likely nitrate source in both surface water ($p=0.584$) and groundwater ($p=0.764$). There was also no relationship found between land use and most likely nitrate source in both surface water ($p=0.361$) and groundwater ($p=0.954$). These results can be related to the hypotheses in Table 1. Here the null hypothesis can be accepted, and the alternative rejected as there were no significant relationships between any of the variables and most likely nitrate source.

4.3 Water Quality Management of Nitrate and its Relation to Source Identification and Economic Complexity.

Finally, a second database was created to assess the current state of practice of water quality management of nitrate around the world. This was done by relating UCW to type of nitrate source and economic development on a country level. In Table 6 below, the top 10 performing countries regarding

UCW scores are shown. As can be seen in Table 6, European countries make up most of the top performing nations, with North American nations also featuring. Although these countries are performing very well according to their UCW scores, the results from the isotope data suggest that despite high levels of wastewater treatment manure + sewage is a frequently observed source of nitrate in surface and groundwater.

Table 6
Top 10 performing countries for UCW score and the most likely nitrate pollution sources per water type at a country level.

Country	UCW score	Untreated Water	Most Likely Source SW	Most Likely Source GW
Germany	0.1516	Low (<30%)	Ammonium fertiliser	Nitrate fertiliser
UK	0.1616	Low (<30%)	Manure + sewage	Manure + sewage
Spain	0.2002	Low (<30%)	Soil N	Manure + sewage
Australia	0.6340	Low (<30%)	Soil N	n/a
Greece	0.7332	Low (<30%)	n/a	Manure + sewage
Canada	0.7363	Low (<30%)	n/a	Manure + sewage
France	0.8678	Low (<30%)	Soil N	Manure + sewage
USA	0.8806	Low (<30%)	Manure + sewage	Manure + sewage
Italy	1.0333	Low - Medium (30-60%)	Manure + sewage	Soil N
Korea	1.0887	Low - Medium (30-60%)	Soil N	Soil N

Table 7 shows the worst performing nations regarding UCW. Unsurprisingly with poor levels of wastewater treatment, manure + sewage is the most likely source of nitrate in both water types for all but one of the bottom 10 nations. Only 8 out of the 28 countries in the database have <30% of water treated.

Table 7
Bottom 10 performing countries for UCW score and the most likely nitrate pollution sources per water type at a country level.

Country	UCW score	Untreated Water	Most Likely Source SW	Most Likely Source GW
South Africa	2.0053	Medium - High (60-90%)	n/a	Manure + sewage
Saudi Arabia	2.4	Medium - High (60-90%)	n/a	Manure + sewage
Morocco	2.5605	Medium - High (60-90%)	Manure + sewage	Manure + sewage
Brazil	2.8121	Medium - High (60-90%)	Manure + sewage	n/a
China	3.2836	High (90-100%)	Manure + sewage	Manure + sewage
Iran	3.8813	High (90-100%)	n/a	Manure + sewage
Kenya	3.9653	High (90-100%)	Manure + sewage	Manure + sewage
Djibouti	5	Extremely High (100%)	n/a	Soil N
Ghana	5	Extremely High (100%)	n/a	Manure + sewage
Mongolia	5	Extremely High (100%)	Equally sourced	n/a

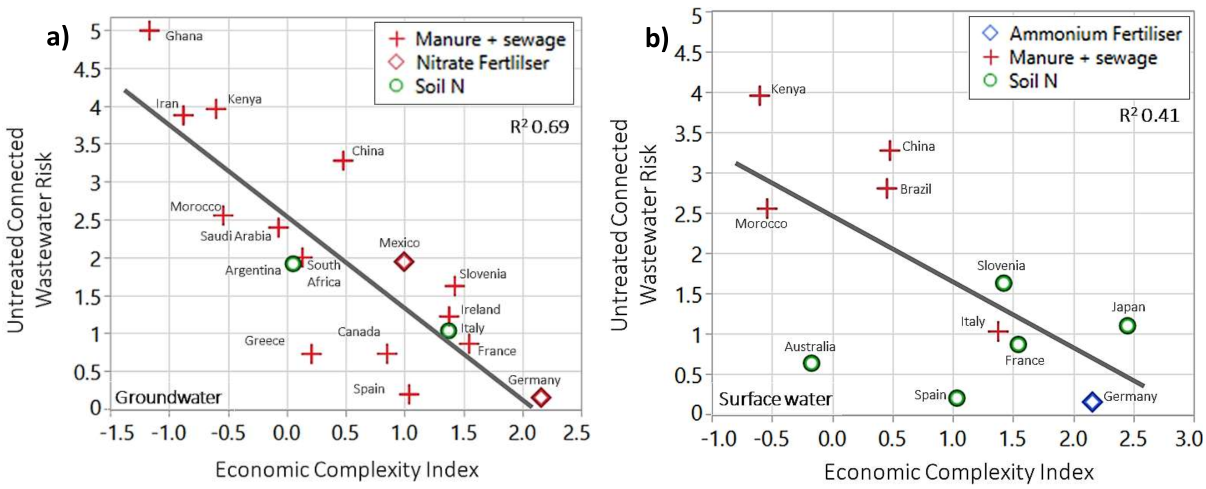

Figure 15: Scatter plots of UCW score vs ECI with most likely nitrate source in a) groundwater and b)surface water

Next, any potential relationships between nitrate pollution sources, economic complexity and water quality management of nitrate were investigated. As is clear from the scatter plots in Figure 15, there is a relationship between economic complexity and level of wastewater treatment in both surface and groundwater, with high ECI scores usually indicating a low UCW risk score. This is confirmed by the trendline and R^2 values. With groundwater, ECI is a much stronger predictor of UCW (R^2= 0.69) than surface water (R^2= 0.41). The surface water plot shows that countries with low ECI and high UCW scores show manure+ sewage as the likely sources of nitrate, while countries with high ECI scores and low UCW scores tend to show other sources, such as soil N and ammonium fertiliser. Conversely, with groundwater, ECI is much stronger predictor of UCW scores, indicating that a countries economic prowess is a good indicator of how well it manages its wastewater infrastructure. However, with groundwater, no matter if a country has a low ECI and high UCW, or if a country has high ECI and low UCW, manure + sewage tended to prevail as the most likely source of nitrate.

5. Discussion

Nitrate pollution of surface and groundwater is a pressing contemporary issue that affects nearly every region of the globe (He et al.,2011). This thesis aimed to provide a global analysis of nitrate pollution in surface and groundwater to better understand and assess the spatial variability around the world with different climates and land use types. It found that nitrate concentrations and isotopic values differed significantly between several groups of climate and land use in both surface and groundwater. Nitrate source identification reviled that manure + sewage is the most common source of nitrate in both surface and groundwaters around the world, and by a considerable margin. However, no relationships between the type of nitrate source identified, and climate and land use existed. It was also found that in groundwater environments, even though countries had good scores for water quality management of nitrate and wastewater treatment, manure and sewage was still identified as a likely source of nitrate. In this section, the key results relating to each research question will be put into the context of the broader scientific literature, while the policy implications of such results will also be discussed. Following this any limitations and avenues for future research will be discussed per research question.

5.1 Spatial Variations of Nitrate Concentrations and Isotopic Values

There were significant differences in nitrate concentrations between groups of land use in both surface and groundwater. Other studies, such as one in Japan, have found that concentrations of nitrate in shallow groundwater and rivers tended to increase with the ratios of agriculture and urban land use while decreasing with a higher ratio of forests (Yoshikawa et al., 2014). Other studies have also found that when the proportion of natural land use is high nitrate concentrations tend to be lower in stream waters (Jacobs et al., 2017 & Li et al., 2016). This is logical as when land use that involves human activity is high more nitrate is inputted into the system and will be released into the environment. This is true for groundwater in this study, with significantly higher nitrate concentrations in urban and agricultural groundwater environments than natural areas. However, median values of concentrations in surface water show that naturally dominated catchments have the highest nitrate concentrations, the opposite to what has been observed in the literature. One explanation for this may be the methodology used in this research. Here the dominate land use was taken; this does not mean that the region solely contained this land use type. For example, a catchment might be 90% forested but could contain a small farm with a few houses which intensively uses fertiliser and manure that could directly run-off into surface water after precipitation events. This could raise concentration levels to a high level despite the catchment being dominated by natural land use types.

There were significant differences between nitrate concentrations across climate types, with especially high concentrations in groundwater arid environments. Climate influences water availability through variations in precipitation and temperature. It can also impact the capacity of systems to transport pollutants and the ability to dilute concentrations of these pollutants (Whitehead et al., 2009). This could explain why arid groundwater environments, which receive low average precipitation, have high median nitrate concentrations; due to a lack of dilution and groundwater recharge. Climate also has a role in the ability of the land to be used by humans in different ways, especially agriculture. The productivity of the land is highly dependent on the climate of an area. The productivity of the land then influences how intensive agriculture or urbanisation may be, which then leads to more pollution (Dunn et al., 2012). Consequently, even though climate influences the distribution of natural vegetation and precipitation amounts and, in turn groundwater recharge, this influence indirectly facilitates anthropogenic responses in how the land is used. Therefore, although climate and land use on their own have small impacts on nitrate concentrations, the indirect relationship between climate land use may have a much more significant effect. The coupled association between land use and climate type is highly complex, and for effective management of nitrate pollution, a multi-disciplinary approach is required to analyse any future changes and sensitivities (Dunn et al., 2012).

There were also significant differences between isotopic compositions of nitrate in surface and groundwater between groups of climates. The level of fractionation caused by various biogeochemical reactions is influenced by ambient conditions of hydrogeological systems (Nikolenko et al., 2018). One of these conditions, which is varied between climate types, is temperature. Microbial activity levels are controlled by water temperature, which also influences the dissolved oxygen content of groundwater (Nikolenko et al., 2018). Any differences in temperature could affect the $\delta^{15}N$ of NO_3^-, with higher values of isotopic enrichment in warmer groundwater environments where denitrification occurs compared to cooler groundwater environments (Nikolenko et al., 2018). The differences in temperature could be the driver behind the differences in isotopic values between climate classes. Tropical climates had significantly higher $\delta^{15}N$ values in groundwater compared to temperate and continental climates, and as tropical environments are characterised by high temperatures all year round (Kottek et al., 2006) this could explain these differences.

Significant differences in $\delta^{15}N$ and $\delta^{18}O$ were also observed between different land use types in both surface and groundwater. Other studies have also observed the differences in isotopic values between land use classes. Burns et al. (2010), found that watersheds with high proportions of agricultural land had higher $\delta^{15}N$ values in stream water than watersheds with urban or forested land. Barnes & Raymond (2010), also found that $\delta^{15}N$ and $\delta^{18}O$ in streams varied significantly between watersheds with forested, urban and agricultural land use types. The same study also found there was much more variation in $\delta^{15}N$ values in stream water across different land use types compared to $\delta^{18}O$ values. As $\delta^{18}O$ consistently fell in the ranges of microbially produced nitrate it was determined that $\delta^{18}O$ reflects the biogeochemical processes in the area while $\delta^{15}N$ values reflect the nitrate sources in the area (Barnes & Raymond, 2010). This was also true for this study, with differences between three categories of land use for surface water $\delta^{15}N$ and only one for surface water $\delta^{18}O$ values.

One of the key limitations of this global analysis of nitrate pollution in surface and groundwater is the geographic spread of data in the database. Much of the available dual isotope literature is taken from China where pollution of water sources is an extremely pressing issue (Xing and Liu, 2016) and highly developed regions such as Europe and North America. Although there were several studies scattered in other regions of the globe such as Africa, South America and South-East Asia, there were not enough studies in these areas to give a truly global representation of nitrate pollution around the world. Despite this limitation, this research still gives a solid insight to nitrate pollution in surface and groundwaters around the globe and the creation of the database will allow for any future studies in the less examined regions to be quickly added to the database in the future.

5.3 Nitrate Source Identification

The most commonly identified most likely source of nitrate around the world in both surface and groundwater was manure + sewage. This is the first-time nitrate source identification with a Bayesian mixing model has been completed across a range of regions around the world with different climates, and land uses. Previous studies have only used a mixing model on a regional or local level (Xue et al., 2012 & Li et al., 2019). One possible explanation for sewage being a common nitrate source in surface and groundwaters is that water treatment infrastructure may not be of a high enough standard or even present at all in many regions of the globe. Many estimates suggest that over 80% of global wastewater is untreated (UN, 2017). To mitigate the lack of wastewater treatment, local water quality management should make use of new technologies available and attempt to bring treatment to an acceptable standard.

The dual isotope technique does not allow for the separation of manure and sewage as individual sources due to their near-identical isotopic ranges (Kendall et al., 2007). Hence, it must be assumed that manure may also be a common pollution source, especially since many of the studies in the database were taken in agriculturally dominated regions. Manure nitrogen has been estimated to have increased from 21.4 Tg N yr^{-1} in 1860 to 131 Tg N yr^{-1} in 2014 globally (Zhang et al., 2017), which indicates global manure use is high. Local water quality management must work with local farmers to attempt to reduce the amount of manure used and minimise the run-off and leaching to water sources to combat the impacts of pollution from manure. One caveat with assuming manure is a common nitrate source is that the high proportions of regions with large amounts of agricultural land use in this study would suggest that fertilisers would also be identified frequently as a common nitrate source. Despite this, there were only a few studies which identified fertilisers as the most likely nitrate source. This suggests that sewage is the more likely candidate for being the common source of nitrate around the globe rather than manure.

This study also highlighted the importance of source selection and source end-member values when using a Bayesian mixing model for nitrate source identification. When using site-specific data, several studies most likely nitrate sourced changed compared to when the standard literature sources and values were used. This was also found by Davis et al. (2016) who used known source mixtures to assess the uncertainties with mixing model assumptions. When site knowledge was incorporated into the model run, there were significant improvements in the model's ability to predict the mixing ratios, with results much closer to the true mixing ratios. This highlights the importance of incorporating site knowledge into the model to achieve reliable results. Using the literature-based source values may give a good general idea of the nitrate sources present; however, without prior site knowledge results must be taken with caution.

There are limitations concerning the SIMMR model. As previously stated, the source apportionment calculated by SIMMR carries a high degree of uncertainty, indicated by the large standard deviations in source values. This leads to the five potential NO_3^- sources having overlapping ranges, which can be seen in Figure 5, and any small variations in isotopic values in a sample may result in a large change in source apportionment estimated by SIMMR (Xue et al., 2012). As the stable isotope values of nitrogen vary across different regions of the globe because of various regional conditions, using the same literature-based values for source end-members can create a high degree of uncertainty. To reduce this uncertainty, site-specific data should be included to reduce the overlapping of source ranges and reduce the standard deviation (Davis et al., 2016). Although the two modelling techniques used in this study aimed to address this uncertainty through the inclusion of site-specific data, not all studies had this information available, which could potentially cause issues in source identification. Furthermore, the output from SIMMR only reflects the contribution of each nitrate source at the specific time the sample was taken, but the contribution of each source is expected to vary temporally (Matiatos, 2016).

Another limitation to do with source identification is that effects of biogeochemical processes on isotopic values were not included in this study. Nitrogen goes through multiple biogeochemical processes as it passes from source to sink. Processes such as denitrification and others that were stated in section 2.6 can cause isotope fractionation which can modify the dissolved N species isotopic composition (Kendall and McDonnell, 1998). These processes are also affected by local factors such as climate, land use and hydrogeological conditions (Zhang et al., 2018). All the biogeochemical processes have some sort of fractionation however, fractionation is relatively low during nitrification, ammonia volatilisation, mineralisation, assimilation and nitrogen fixation, while fractionation associated with denitrification is relatively high (Zhang et al., 2018). Currently, the research into isotopic fractionation lacks quantitative foundations as they can only analyse if fractionation has occurred. The quantitative evaluation of the fractionation processes is less understood, and currently, denitrification effects can only be estimated (Zhang et al., 2018). Analysing the plots produced by SIMMR, several studies showed evidence, where the slope was ca. 0.5-0.8, that denitrification may be present.

To overcome the limitation of the lack of site-specific nitrate source values around the world, a complementary database to the one in this study should be created. Here isotopic values of different nitrate sources in regions of the world should be gathered. This would allow for regional source isotope values to be inputted into the model even if no site data had been collected. For example, if a study in a region on the UK had collected stable isotope data from an aquifer but did not measure any nitrate source end-member values, then the source database could be used to find regional values. This would greatly reduce the uncertainty of using literature-based values. In addition to site-specific source values, correctional factors should be applied to studies which show evidence of denitrification. Rayleigh equations can be used to evaluate the role of denitrification on isotopic values (Osaka et al., 2018). Enrichment factors for ^{15}N and ^{18}O must be assigned to calculate this equation. This is one of the biggest challenges in quantifying denitrification, as there has been a wide range of enrichment factors reported by the literature (Osaka et al., 2018). Now it is agreed that there is no one size fits all value for enrichment factors and actual values are dependent on ambient conditions such as temperature, and to truly quantify denitrification site-specific data is needed (Osaka et al., 2018). Therefore, future studies should include site data to calculate specific enrichment factors so denitrification can be quantified as accurately as possible.

To further distinguish nitrate sources in water stable boron isotopes may be used. Boron has two stable isotopes, ^{11}B and ^{10}B. Boron is present as a minor or trace constituent in and is highly soluble in aqueous solutions (Xue et al., 2009). Boron is also unaffected by the various biogeochemical process that causes fractionation mentioned previously. $\delta^{11}B$ values ranges for sewage and manure are different with a range of −7.7‰ to +12.9‰ in sewage and +6.9‰ to +42.1‰ in manure (Xue et al., 2009). This unique $\delta^{11}B$ can then be used to distinguish between sewage and manure. So far, only a sparse amount of studies have measured $\delta^{11}B$ values; however, every study that did record this data has been taken down in the global database. Future research could make use of $\delta^{11}B$ values for further source discrimination.

5.4 Water Quality Management of Nitrate in Surface and Groundwater

All the top performing nations regarding water quality management of nitrate were developed nations, while the worst performing nations were from developing nations. This was confirmed by assessing the relationship between UCW scores and economic complexity. This supports the UN report which stated low-income countries are disproportionally affected by wastewater pollution in comparison to high-income countries, with 70% of all municipal and industrial wastewater treated in high-income countries, 38% in middle-income countries and only 8% in low-income countries (UN, 2017). This is unsurprising as in developed countries there are strict directives that monitor and regulate nitrate pollution, such as the Nitrate Directive in the EU (CEC, 2000) and standards set by the Environmental Protection Agency in the US (EPA, 2015). On the contrary, most African and Latin American countries have a severe lack of groundwater quality monitoring, regions which contain many less-developed nations (Zhou, 2015). Therefore, countries with already low economic power will be further burdened when implementing improvements to wastewater treatment to reach the levels that more developed nations are currently at.

In surface water, countries with low economic complexity and poor levels of wastewater treatment show manure + sewage as the likely nitrate source. This is unsurprising as lack of wastewater treatment will lead to much more sewage being released into the environment. Conversely, countries that are performing well according to level of wastewater treatment and have high economic power nearly always showed alternative nitrate sources, such as soil N and fertilisers in surface water. This shows that countries with the infrastructure and technological capacity available to them are effectively managing wastewater and, in turn, pollution of surface waters by nitrate. The prevalence of manure + sewage as the source of nitrate in surface water for nations with low economic complexity compounds the need for improved wastewater treatment to mitigate sewage as a pollution source to surface water and improve standards of water quality to reduce the likelihood of harmful affects on human and ecosystem health.

For groundwater, ECI was a strong predictor for UCW, with high ECI scores usually corresponding to low UCW scores while low ECI scores usually correspond to high UCW scores. Despite this manure + sewage is a prevalent source of nitrate in groundwater across all countries and all ECI scores. This suggests that even in countries with high ECI and low UCW such as France or Ireland, manure + sewage pollution of groundwater is an equal problem and countries with low ECI and high UCW, such as Ghana or Iran. This can create problems for drinking water in many areas of the world as many regions rely soley on potable water being extracted from groundwater (Carrard et al., 2019). In these regions, even though levels of water treatment may be high, this does not prevent manure and sewage from being a problematic nitrate source in groundwater. The risks to groundwater drinking supplies are compounded by the high levels of nitrate concentrations observed in this study, as concentrations were much higher in groundwater than surface water across every variable. This combination of the high prevalence of sewage as a nitrate source and observed high nitrate concentrations, highlight the need for caution in regions of the globe which depend on groundwater for drinking water supplies. In the future as water scarcity becomes a more pressing issue, more freshwater will be extracted from groundwater for drinking water supplies (Turner et al., 2019). This could lead to over extraction of groundwater, which can cause continuous decline of the water table, leading to arrival of water from many different directions that many contain high concentrations of harmful substances (Katsanou & Karapanagioti, 2019). If this problem is not mitigated nitrate pollution of groundwaters will become a serious issue in regions which relay on groundwater, regardless of the economic prowess of a nation.

There are some limitations that need to be addressed regarding the analysis of water quality management of nitrate. As mentioned previously, UCW scores does not specifically distinguish between primary, secondary and tertiary treatment, although it still has validity in assessing a nation's infrastructure and institutional knowledge for treating wastewater. UCW does not account for other sources of nitrate such as agricultural run-off and does not capture on-site water treatment such as private septic tanks (Hofste et al., 2019). A limitation regarding ECI is that for larger countries economic development may not be uniform across the whole country. China is an example of this, with some cities being much wealthier than others (Solinger & Hu, 2012). This could lead to some areas having the capacity to mange nitrate pollution while others lack the economic power. Overall however, ECI is a good indicator for most nations.

An area for future research in water quality management of nitrate would be to investigate the environmental externalities, in the form of economic costs, from NO_3^- pollution in surface and groundwater systems. The economic burdens for water quality management of nitrate are likely higher in developing nation than in developed nations. The monetary costs associated with dealing with nitrate pollution could be assessed with programs such as web browser-based Water Risk Monetizer (WRM) from Ecolab (Ecolab, n.d). The program quantifies the value of incoming and outgoing water of a chosen location calculated using the local conditions of quality and quantity of water. This would allow for an estimate of costs in dealing with nitrate pollution and better assess how costs may vary around the world and highlight the potential difference in costs between developed nations and less developed nations.

6. Conclusion

The rapidly increasing global population and the coupled demand for food and sanitation means nitrogen is being released into the environment at a vast rate, and this will only increase in the future (Zhang et al., 2015). Identifying and assessing the sources of nitrate pollution in surface and groundwater around the world is vital in mitigating the devastating impacts of nitrogen pollution on human and ecosystem health. This thesis found that nitrate concentrations and isotopic are significantly different between many groups of climate and land use. Nitrate source identification found manure + sewage is the most common source of nitrate in both surface and groundwaters around the world. The need for site-specific data when using mixing models for source identification was also highlighted. Finally, the relationship between nitrate sources, economic complexity and water quality management of nitrate was assessed. It was found that even in nations with high levels of wastewater treatment and economic complexity, sewage was still commonly observed as a likely source of nitrate in groundwater. A relationship between low levels of economic development and low levels of wastewater treatment was also found.

The identification of manure and sewage as the most common source of nitrate pollution in surface waters of nations with low economic complexity highlights the need for improved sanitation and wastewater treatment in these regions of the world. As less developed nations have a low level of water quality management of nitrate, this emphasises the fact that more economic resources will be required to reduce the levels of nitrate pollution and bring water treatment up to an acceptable level. In groundwater, even the top performing nations for UCW and ECI had a likely nitrate source of manure + sewage. This underlines the need for caution in areas which depend on groundwater for potable water, regardless of economic development or levels of wastewater treatment. In the future with increased water scarcity, without proper monitoring, groundwater nitrate levels could rise above the safe thresholds and become damaging to human and ecosystem health. If developing nations are unable to afford the necessary improvements to infrastructure to mitigate the effects of nitrate pollution in water, the adverse effects will become worse. The Sustainable Development Goal Target 6.3 states 'By 2030, improve water quality by reducing pollution, eliminating dumping and minimising release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally' (UN, 2017). Results from this thesis show much more needs to be done in improving wastewater treatment around the world before this target is met.

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Appendix A: SIMMR Script

```
# Insert Isotpe data
mix = as.matrix()
#Name isotopes
colnames(mix) = c('d15N','d18O')
#Name Sources
s_names=c('Ammonium Fertilizer/Rain','Nitrate Fertilizer','Precipitation','Soil N', 'Manure + Sewage')
#source values
s_means = matrix(c(-0.89, 1.079, -1.16, 4.19, 10.53, 0.8, 20.1, 50, 0.1, -2), ncol=2, nrow=5)
s_sds = matrix(c(2.62, 2.5, 3.75, 1.1, 4.8, 2.3, 1.1, 12.5, 1.3, 8), ncol=2, nrow=5)


# Load into simmr
simmr_in = simmr_load(mixtures=mix,
                      source_names=s_names,
                      source_means=s_means,
                      source_sds=s_sds)


# Plot
plot(simmr_in, xlab=expression(paste(delta^15, "N (\u2030)",sep="")),
     ylab=expression(paste(delta^18, "O (\u2030)",sep="")),
     title='DILITA')

#Run the model
simmr_out = simmr_mcmc(simmr_in)

#Numerical output
summary(simmr_out,type='diagnostics')
summary(simmr_out,type='statistics')
summary(simmr_out,type='quantiles')

#Graohical output
plot(simmr_out_combine$input, xlab=expression(paste(delta^15, "N (\u2030)",sep="")),
     ylab=expression(paste(delta^18, "O (\u2030)",sep="")),
     title='')
#plot(simmr_out,type='density')
compare_sources(simmr_out,source_names=c('Ammonium Fertilizer/Rain','Nitrate Fertilizer',
                                         'Precipitation','Soil N', 'Manure + Sewage'))

```

Appendix B: Shotgun Modelling Results

Paper	Country	SW Most Likely Source	SW Magnitude	GW Most Likely Source	GW Magnitude
Qin - Using nitrogen and oxygen isotopes to access sources and transformations of nitrogen in the Qinhe Basin, North China	China	Soil N	0.41		
Hosono et al -Multiple isotope (H, O, N, S and Sr) approach elucidates complex pollution causes in the shallow groundwaters of the Taipei urban area	Taiwan			Manure + Sewage	0.677
Bailey et al - Spatial and temporal variations in groundwater nitrate at an intensive dairy farm in South-East Ireland: Insights from stable isotope data	Ireland			Manure + Sewage	0.679
Vitoria et al - Environmental isotopes (N, S, C, O, D) to determine natural attenuation processes in nitrate contaminated waters: Example of Osona (NE Spain).	Spain			Soil N	0.519
Wexler et al- Microbial and hydrological influences on nitrate isotopic composition in an agricultural lowland catchment	UK	Soil N	0.644		
IHLENFELD et al - Isotopic Fingerprinting of Groundwater Nitrate Sources around Anglo Platinum's RPM Mogalakwena Operation (Limpopo Province, South Africa)	South Africa			Manure + Sewage	0.276
Chen et al - Nitrate sources and watershed denitrification inferred from nitrate dual isotopes in the Beijiang River, south China.	China	Manure + Sewage	0.433		
Duetch et al - Quantification of diffuse nitrate inputs into a small river system using stable isotopes of oxygen and nitrogen in nitrate	Germany	Manure + Sewage	0.595	Ammonium Fertilizer/Rain	0.447
Hales -Isotopic signature of nitrate in two contrasting watersheds of Brush Brook, Vermont, USA	USA	Equally Sourced			
Di Lorenzzo - Nitrate source and fate at the catchment scale of the Vibrata River and aquifer	Italy			Manure + Sewage	0.448

(central Italy): an analysis by integrating component approaches and nitrogen isotopes					
Urresesti estala et al - Application of stable isotopes (δ34S-SO4, δ18O-SO4, δ15N-NO3, δ18O-NO3) to determine natural background and contamination sources in the Guadalhorce River Basin (southern Spain)	Spain			Manure + Sewage	0.487
Sacoon et al - Multi-isotope approach for the identification and characterisation of nitrate pollution sources in the Marano lagoon (Italy) and parts of its catchment area.	Italy	Manure + Sewage	0.538	Soil N	0.736
Seiler - Combined use of 15N and 18O of nitrate and 11B to evaluate nitrate contamination in groundwater	USA			Manure + Sewage	0.349
Sanchez et al - Determining sources of nitrate in the semi-arid Rio Grande using nitrogen and oxygen isotopes.	USA	Manure + Sewage	0.659	Manure + Sewage	0.82
Puig et al - Characterizing sources and natural attenuation of nitrate contamination in the Baix Ter aquifer system (NE Spain) using a multi-isotope approach	Spain			Manure + Sewage	0.352
Puig - Multi-isotopic study (15N, 34S, 18O, 13C) to identify processes affecting nitrate and sulfate in response to local and regional groundwater mixing in a large-scale flow system.	Spain			Soil N	0.474
Pittalis et al - Hydrogeological and multi-isotopic approach to define nitrate pollution and denitrification processes in a coastal aquifer (Sardinia, Italy).	Italy			Manure + Sewage	0.555
Pastén-Zapata et al - Assessment of sources and fate of nitrate in shallow groundwater of an agricultural area by using a multi-tracer approach	Mexico			Soil N	0.413

Panno et al - Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators	USA	_	_	Manure + Sewage	0.409
Ohte - Spatial distribution of nitrate sources of rivers in the Lake Biwa watershed, Japan: Controlling factors revealed by nitrogen and oxygen isotope values	Japan	Soil N	0.724		
Ogrinc - Evaluation of geochemical processes and nitrate pollution sources at the Ljubljansko polje aquifer (Slovenia): A stable isotope perspective	Slovenia			Manure + Sewage	0.352
Nyilita - Tracking Sources and Fate of Groundwater Nitrate in Kisumu City and Kano Plains, Kenya	Kenya			Manure + Sewage	0.485
Murgulet - Understanding the sources and fate of nitrate in a highly developed aquifer system	USA			Soil N	0.65
G. Mongelli - Assessing nitrate origin in a volcanic aquifer using a dual isotope approach	Italy			Soil N	0.757
Mingzhu et al - Tracking sources of groundwater nitrate contamination using nitrogen and oxygen stable isotopes at Beijing area, China	China			Manure + Sewage	0.601
Merchan et al - Main sources and processes affecting dissolved sulphates and nitrates in a small irrigated basin (Lerma Basin, Zaragoza, Spain):	Spain	Soil N	0.375	Manure + Sewage	0.33
Matiatos- Nitrate source identification in groundwater of multiple land-use areas by combining isotopes and multivariate statistical analysis: A case study of Asopos basin (Central Greece).	Greece			Manure + Sewage	0.42
Liu et al - Using δ15N- and δ18O-values to identify nitrate sources in karst ground water, Guiyang, Southwest China	China	Equally Sourced		Manure + Sewage	0.488

Li et al - Identifying nitrate sources and transformations in Taizi River Basin, Northeast China.	China	Manure + Sewage	0.541		
Lee et al - Tracing the sources of nitrate in the Han River watershed in Korea, using δ15N-NO3- and δ18O-NO3- values	Korea	Soil N	0.486		
Koh et al - Hydrogeochemistry and Isotopic Tracing of Nitrate Contamination of Two Aquifer Systems on Jeju Island, Korea.	Korea			Manure + Sewage	0.482
Kaowan et al - Identification of nitrate and sulfate sources in groundwater using dual stable isotope approaches for an agricultural area with different land use (Chuncheon, mid-eastern Korea)	Korea			Soil N	0.306
Itoah et al -Evaluation of wastewater nitrogen transformation in a natural wetland (Ulaanbaatar, Mongolia) using dual-isotope analysis of nitra	Mongolia	Ammonium Fertilizer/rain	0.413		
Heaton - An isotope study of the sources of nitrate in Malta's groundwater.	Malta			Soil N	0.633
Amiri et al - Assessing sources of nitrate contamination in the Shiraz urban aquifer (Iran) using the δ 15 N and δ 18 O dual-isotope approach	Iran			Manure + Sewage	0.711
Fukada et al - A dual-isotope approach to the nitrogen hydrochemistry of an urban aquifer	UK			Equally Sourced	
Fukuda et al - A dual isotope approach to identify denitrification in groundwater at a river-bank infiltration site.	Germany			Nitrate Fertilizer	0.293
Erostae et al - Delayed nitrate dispersion within a coastal aquifer provides constraints on land-use evolution and nitrate contamination in the past	France			Manure + Sewage	0.405
Varga - Nitrogen and oxygen isotopes as indicators of pollution sources in the Faxinal Dam watershed, Southern Brazil	Brazil	Manure + Sewage	0.405		

Briand et al - Legacy of contaminant N sources to the NO3-signature in rivers: A combined isotopic (δ15N-NO3-, δ18O-NO3-, δ11 B) and microbiological investigation.	France	Soil N	0.527		
Anoru et al - Tracking nitrate sources in groundwater and associated health risk for rural communities in the White Volta River basin of Ghana using isotopic approach (δ15N, δ18O[sbnd]NO3 and 3H).	Ghana	Equally Sourced		Manure + Sewage	0.442
Albertin et al - Identification of nitrogen sources and transformations within karst springs using isotope tracers of nitrogen	USA			Manure + Sewage	0.392
Vrzel et al - Determination of the sources of nitrate and the microbiological sources of pollution in the Sava River Basin	Slovenia	Soil N	0.398		
Singleton et al - Tracking Sources of Unsaturated Zone and Groundwater Nitrate Contamination Using Nitrogen and Oxygen Stable Isotopes at the Hanford Site	USA			Manure + Sewage	0.588
Xu et al - Estimating the Proportional Contributions of Multiple Nitrate Sources in Shallow Groundwater with a Bayesian Isotope Mixing Model	China			Manure + Sewage	0.5
Yu - Tracking nitrate sources in the Chaohu Lake, China, using the nitrogen and oxygen isotopic approach	China	Manure + Sewage	0.61		
Zhang et al - Tracing nitrate pollution sources and transformation in surface- and ground-waters using environmental isotopes	China	Manure + Sewage	0.426	Manure + Sewage	0.471
Zendehbad et al - Source identification of nitrate contamination in the urban aquifer of Mashhad, Iran	Iran			Soil N	0.583

Jakóbczyk-Karpierz et al -Geochemical and isotopic study to determine sources and processes affecting nitrate and sulphate in groundwater influenced by intensive human activity - carbonate aquifer Gliwice (southern Poland)	Poland			Equally Sourced	
Martinez et al - Distribution and origin of nitrate in groundwater in an urban and suburban aquifer in Mar del Plata, Argentina	Argentina			Soil N	0.583
Otero et al - Monitoring groundwater nitrate attenuation in a regional system coupling hydrogeology with multi-isotopic methods: The case of Plana de Vic (Osona, Spain).	Spain			Manure + Sewage	0.776
Moore et al - Sources of groundwater nitrate revealed using residence time and isotope methods	USA			Manure + Sewage	0.415
Liu et al - Using 15 N, 17 O, and 18 O To Determine Nitrate Sources in the Yellow River, China.	China	Manure + Sewage	0.552		
Garrad - A stable isotope and hydrochemical approach to examining denitrification along a shallow groundwater - surface water continuum in an agriculturally-impacted catchment	UK	Manure + Sewage	0.776	Manure + Sewage	0.713
Aravena & Robertson - Use of Multiple Isotope Tracers to Evaluate Denitrification in Ground Water: Study of Nitrate from a Large-Flux Septic System Plume	Canada			Manure + Sewage	0.507
Battaglin et al - Chemical and isotopic evidence of nitrogentransformation in the MississippiRiver, 1997 – 98	USA	Manure + Sewage	0.577		
Biddau et al - Source and fate of nitrate in contaminated groundwater systems: Assessing spatial and temporal variations by hydrogeochemistry and multiple stable isotope tools	Italy			Nitrate Fertilizer	0.509

Bottcher et al - Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer	Germany			Nitrate Precipitation	0.28
jin et al - Determination of nitrate contamination sources using isotopic and chemical indicators in an agricultural region in China	China			Manure + Sewage	0.514
Jin et al - Using dual isotopes to evaluate sources and transformations of nitrate in the West Lake watershed, eastern China	China	Manure + Sewage	0.627	Manure + Sewage	0.698
Danni et al - Assessment of water quality and nitrate source in the Massa catchment (Morocco) using δ 15N and δ 18O tracers	Morocco	Manure + Sewage	0.331	Soil N	0.448
SiLiang et al - Assessment of the Sources of Nitrate in the Changjiang River, China Using a Nitrogen and Oxygen Isotopic Approach	China	Manure + Sewage	0.681		
Wassenaar et al - Decadal Geochemical and Isotopic Trends for Nitrate in the Transboundary Abbotsford-Sumas Aquifer and Implications for Agricultural Beneficial Management Practices	USA			Manure + Sewage	0.546
Xing & Liu - Using dual isotopes to identify sources and transformations of nitrogen in water catchments with different land uses, Loess Plateau of China	China	Manure + Sewage	0.596		
Yue et al - Using dual isotopes to evaluate sources and transformation of nitrogen in the Liao River, northeast China	China	Manure + Sewage	0.78		
Wong et al - Stable isotopes of nitrate reveal different nitrogen processing mechanisms in streams across a land use gradient during wet and dry periods	Australia	Soil N	0.481		
Nyiliyta - Land use controls Kenyan riverine nitrate discharge into Lake Victoria – evidence from Nyando, Nzoia and Sondu Miriu river catchments*	Kenya	Manure + Sewage	0.7		

Awaleh et al - Geochemical, multi-isotopic studies and geothermal potential evaluation of the complex Djibouti volcanic aquifer (republic of Djibouti)	Dijbouti			Soil N	0.354
Bratek et al - Nitrate sources and the effect of land cover on the isotopic composition of nitrate in the catchment of the Rhône River	France	Soil N	0.59		
Saeed et al - Application of Multi-Tracer Methods to Evaluate Nitrate Sources and Transformation in Sabkha Matti(Saudi Arabia)	Saudi Arabia			Manure + Sewage	0.66
Parades et al - Agricultural and urban delivered nitrate pollution input to Mediterranean temporary freshwaters	Spain	Manure + Sewage	0.509		

Appendix C: Intelligent Modelling Results Groundwater

Study	Most likely source	2nd most likely	3rd most likely	4th most likely	Least likely	Sources Considered	Site Specific values
Hosono et al -Multiple isotope (H, O, N, S and Sr) approach elucidates complex pollution causes in the shallow groundwaters of the Taipei urban area	Manure + sewage	Soil N	Nitrate Fertiliser	Ammonium Fertiliser		No precipitation	
Bailey et al - Spatial and temporal variations in groundwater nitrate at an intensive dairy farm in South-East Ireland: Insights from stable isotope data	Manure + sewage	Nitrate Fertiliser	Soil N	Ammonium Fertiliser	Nitrate precipitatio n	All	
Vitoria et al - Environmental isotopes (N, S, C, O, D) to determine natural attenuation processes in nitrate contaminated waters: Example of Osona (NE Spain).	Soil N	Nitrate Fertiliser	Ammonium Fertiliser	Nitrate precipitatio n		No sewage due to two WWTP	
IHLENFELD et al - Isotopic Fingerprinting of Groundwater Nitrate Sources around Anglo Platinum's RPM Mogalakwena Operation (Limpopo Province, South Africa)	Manure + sewage	Soil N	Nitrate precipitatio n			No Fertiliser	

Chen et al - Nitrate sources and watershed denitrification inferred from nitrate dual isotopes in the Beijiang River, south China.	Manure + sewage	Nitrate Fertiliser	Nitrate precipitatio n	Soil N	Ammonium Fertiliser	All	
Duetch et al - Quantification of diffuse nitrate inputs into a small river system using stable isotopes of oxygen and nitrogen in nitrate	Ammonium Fertiliser	Soil N	Manure + sewage	Nitrate Fertiliser	Nitrate precipitatio n	All	
Di Lorenzzo - Nitrate source and fate at the catchment scale of the Vibrata River and aquifer (central Italy): an analysis by integrating component approaches and nitrogen isotopes	Manure + sewage	Soil N	Nitrate Fertiliser	Nitrate precipitatio n	Ammonium Fertiliser	All	
Urresesti estala et al - Application of stable isotopes (δ34S-SO4, δ18O-SO4, δ15N-NO3, δ18O-NO3) to determine natural background and contamination sources in the Guadalhorce River Basin (southern Spain)	Manure + Sewage	Nitrate Fertiliser	Soil N	Ammonium Fertiliser	Nitrate precipitatio n	All	
Sacoon et al - Multi-isotope approach for the identification and characterisation of nitrate pollution sources in the Marano lagoon (Italy) and parts of its catchment area.	Soil N	Nitrate Fertiliser	Manure + sewage	Ammonium Fertiliser	Nitrate precipitatio n	All	
Seiler - Combined use of 15N and 18O of nitrate and 11B to evaluate nitrate contamination in groundwater	Nitrate Fertiliser	Soil N	Manure + sewage			wastewater, fertilizers, and decaying organic	

						material in soils	
Sanchez et al - Determining sources of nitrate in the semi-arid Rio Grande using nitrogen and oxygen isotopes.	Manure + sewage	Soil N	Ammonium Fertiliser	Nitrate Fertiliser	Nitrate precipitatio n	All	
Puig et al - Characterizing sources and natural attenuation of nitrate contamination in the Baix Ter aquifer system (NE Spain) using a multi-isotope approach	Nitrate Fertiliser	Soil N	Manure + sewage			Manure + sewage, mineral fertilizers, Soil N	
Puig - Multi-isotopic study (15N, 34S, 18O, 13C) to identify processes affecting nitrate and sulfate in response to local and regional groundwater mixing in a large-scale flow system.	Soil N	Manure + sewage	Nitrate Fertiliser	Ammonium Fertiliser	Nitrate precipitatio n	All	
Pittalis et al - Hydrogeological and multi-isotopic approach to define nitrate pollution and denitrification processes in a coastal aquifer (Sardinia, Italy).	Manure + sewage	Soil N	Nitrate Fertiliser	Ammonium Fertiliser		All but Nitrate Precip	
Pastén-Zapata et al - Assessment of sources and fate of nitrate in shallow groundwater of an agricultural area by using a multi-tracer approach	Nitrate Fertiliser	Soil N	Manure + sewage	Ammonium Fertiliser		All but Nitrate Precip	
Panno et al - Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators	Nitrate Fertiliser	Manure + sewage	Soil N	Ammonium Fertiliser		soil organic matter, agrichemicals (N-fertilizers), livestock wastes and	

						effluent from septic systems	
Ogrinc - Evaluation of geochemical processes and nitrate pollution sources at the Ljubljansko polje aquifer (Slovenia): A stable isotope perspective	Manure + sewage	Soil N	Nitrate precipitatio n	Nitrate Fertiliser	Ammonium Fertiliser	All	
Nyilita - Tracking Sources and Fate of Groundwater Nitrate in Kisumu City and Kano Plains, Kenya	Manure + Sewage	Nitrate precipitatio n	Nitrate Fertiliser	Soil N	Ammonium Fertiliser	All	
Murgulet - Understanding the sources and fate of nitrate in a highly developed aquifer system	Ammonia fertilizer	Manure + sewage	Nitrate Fertiliser			Only Fertilizers and Manure + Sewage	
G. Mongelli - Assessing nitrate origin in a volcanic aquifer using a dual isotope approach	Soil N	Manure + sewage	Nitrate Fertiliser	Ammonium Fertiliser	Soil N	All	
Mingzhu et al - Tracking sources of groundwater nitrate contamination using nitrogen and oxygen stable isotopes at Beijing area, China	Manure + Sewage	Nitrate precipitatio n	Nitrate Fertiliser	Ammonium Fertiliser		Synthetic Fertilizer, Manure/Sew age, Nitrate Precipitation	
Merchan et al - Main sources and processes affecting dissolved sulphates and nitrates in a small irrigated basin (Lerma Basin, Zaragoza, Spain):	Manure + Sewage	Soil N	Nitrate Fertiliser	Ammonium Fertiliser	Nitrate precipitatio n	Only Manure as no urban areas in basin	

Matiatos- Nitrate source identification in groundwater of multiple land-use areas by combining isotopes and multivariate statistical analysis: A case study of Asopos basin (Central Greece).	Manure + Sewage	Ammonium Fertiliser	Soil N	Nitrate Fertiliser	Nitrate precipitation	All	
Liu et al - Using δ15N- and δ18O-values to identify nitrate sources in karst ground water, Guiyang, Southwest China	Manure + Sewage	Nitrate precipitation	Soil N	Nitrate Fertiliser	Ammonium Fertiliser	All but with site specific measurements of 15N for sewage	Sewage- δ15N- 18.8
Koh et al - Hydrogeochemistry and Isotopic Tracing of Nitrate Contamination of Two Aquifer Systems on Jeju Island, Korea.	Manure + Sewage	Soil N	Ammonium Fertiliser			NH4 in fertilizer, Soil N, Manure + sewage	
Kaowan et al - Identification of nitrate and sulfate sources in groundwater using dual stable isotope approaches for an agricultural area with different land use (Chuncheon, mid-eastern Korea)	Soil N	Manure + sewage	Ammonium Fertiliser			NH4 in fertilizer/Rain, Soil N, Manure + Sewage	
Heaton - An isotope study of the sources of nitrate in Malta's groundwater.	Soil N	Manure + sewage	Nitrate Fertiliser	Nitrate precipitation	Ammonium Fertiliser	All	
Amiri et al - Assessing sources of nitrate contamination in the Shiraz urban aquifer (Iran) using the δ 15 N and δ 18 O dual-isotope approach	Manure + Sewage	Nitrate precipitation	Nitrate Fertiliser	Soil N	Ammonium Fertiliser	All, specific end member values for precipitation.	Precipitation δ15N -10.8 and δ18O - 4.5

Fukada et al - A dual-isotope approach to the nitrogen hydrochemistry of an urban aquifer	Manure + Sewage	Nitrate precipitatio n	Soil N			No Fertiliser	
Fukuda et al - A dual isotope approach to identify denitrification in groundwater at a river-bank infiltration site.	Nitrate Fertilizer	Soil N	Nitrate precipitatio n	Ammonium Fertiliser		No Urban areas so sewage not considered	
Erostae et al - Delayed nitrate dispersion within a coastal aquifer provides constraints on land-use evolution and nitrate contamination in the past	Manure + Sewage	Soil N	Nitrate Fertiliser	Ammonium Fertiliser	Nitrate precipitatio n	All	
Anoru et al - Tracking nitrate sources in groundwater and associated health risk for rural communities in the White Volta River basin of Ghana using isotopic approach (δ15N, δ18O[sbnd]NO3 and 3H).	Manure + Sewage	Nitrate Fertiliser	Soil N	Nitrate precipitatio n	Ammonium Fertiliser	All	
Albertin et al - Identification of nitrogen sources and transformations within karst springs using isotope tracers of nitrogen	Soil N	Manure + sewage	Nitrate precipitatio n	Ammonium Fertiliser		No Nitrate Fertilizer	
Singleton et al - Tracking Sources of Unsaturated Zone and Groundwater Nitrate Contamination Using Nitrogen and Oxygen Stable Isotopes at the Hanford Site	Manure + Sewage	Soil N	Nitrate precipitatio n			No Fertiliser	

Xu et al - Estimating the Proportional Contributions of Multiple Nitrate Sources in Shallow Groundwater with a Bayesian Isotope Mixing Model	Manure + Sewage	Nitrate Fertiliser	Soil N	Nitrate precipitation	Ammonium Fertiliser	All	
Zhang et al - Tracing nitrate pollution sources and transformation in surface- and ground-waters using environmental isotopes	Manure + Sewage	Nitrate precipitation	Soil N	Nitrate Fertiliser	Ammonium Fertiliser	All	
Zendehbad et al - Source identification of nitrate contamination in the urban aquifer of Mashhad, Iran	Manure + Sewage	Soil N	Nitrate precipitation			No Fertilisers	
Jakóbczyk-Karpierz et al - Geochemical and isotopic study to determine sources and processes affecting nitrate and sulphate in groundwater influenced by intensive human activity - carbonate aquifer Gliwice (southern Poland)	Equally Sourced					All	
Martinez et al - Distribution and origin of nitrate in groundwater in an urban and suburban aquifer in Mar del Plata, Argentina	Soil N	Manure + sewage	Nitrate Fertiliser	Ammonium Fertiliser	Nitrate precipitation	All	
Otero et al - Monitoring groundwater nitrate attenuation in a regional system coupling hydrogeology with multi-isotopic methods: The case of Plana de Vic (Osona, Spain).	Manure + Sewage	Nitrate Fertiliser	Ammonium Fertiliser	Soil N	Nitrate precipitation	All	

Moore et al - Sources of groundwater nitrate revealed using residence time and isotope methods	Manure + Sewage	Nitrate Fertiliser	Soil N	Nitrate precipitation	Ammonium Fertiliser	All	
Garrad - A stable isotope and hydrochemical approach to examining denitrification along a shallow groundwater - surface water continuum in an agriculturally-impacted catchment	Soil N	Ammonium Fertiliser	Nitrate Fertiliser	Nitrate precipitation		No manure or sewage	
Aravena & Robertson - Use of Multiple Isotope Tracers to Evaluate Denitrification in Ground Water: Study of Nitrate from a Large-Flux Septic System Plume	Manure + Sewage	Soil N	Nitrate precipitation			No agriculture so no fertilizer	
Biddau et al - Source and fate of nitrate in contaminated groundwater systems: Assessing spatial and temporal variations by hydrogeochemistry and multiple stable isotope tools	Manure + Sewage	Nitrate Fertiliser	Nitrate precipitation	Soil N	Ammonium Fertiliser	All	
Bottcher et al - Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer	Ammonia fertilizer	Nitrate precipitation	Nitrate Fertiliser	Soil N		No manure or sewage	
jin et al - Determination of nitrate contamination sources using isotopic and chemical indicators in an agricultural region in China	Manure + Sewage	Ammonium Fertiliser	Soil N			No precipitation or Nitrate Fertiliser	

Jin et al - Using dual isotopes to evaluate sources and transformations of nitrate in the West Lake watershed, eastern China	Manure + Sewage	Ammonium Fertiliser	Soil N	Nitrate Fertiliser	Nitrate precipitatio n	All	
Danni et al - Assessment of water quality and nitrate source in the Massa catchment (Morocco) using δ 15N and δ 18O tracers	Manure + Sewage	Soil N	Nitrate Fertiliser	Ammonium Fertiliser	Nitrate precipitatio n	End member values for sewage	
Wassenaar et al - Decadal Geochemical and Isotopic Trends for Nitrate in the Transboundary Abbotsford-Sumas Aquifer and Implications for Agricultural Beneficial Management Practices	Manure + Sewage	Nitrate Fertiliser	Ammonium Fertiliser			Only fertilizers and Manure considered.	
Awaleh et al - Geochemical, multi-isotopic studies and geothermal potential evaluation of the complex Djibouti volcanic aquifer (republic of Djibouti)	Soil N	Manure + sewage	Nitrate precipitatio n			No agriculutral use in area for man years, so fertilizers not considered	
Saeed et al - Application of Multi-Tracer Methods to Evaluate Nitrate Sources and Transformation in Sabkha Matti(Saudi Arabia)	Manure + Sewage	Nitrate precipitatio n	Nitrate Fertiliser	Soil N	Ammonium Fertiliser	site specific rainfall measurement .	Precipitation- δ15N -6.1 δ18O-40

Appendix D: Intelligent Modelling Results Surface Water

Study	Most likely source	2nd most likely	3rd most likely	4th most likely	Least likely	Sources Considered	Site Specific values
Qin - Using nitrogen and oxygen isotopes to access sources and transformations of nitrogen in the Qinhe Basin, North China	Soil N	Manure + Sewage	Nitrate Fertiliser	Ammonium fertilser	Nitrate precipitation	All	
Wexler et al- Microbial and hydrological influences on nitrate isotopic composition in an agricultural lowland catchment	Soil N	Nitrate Fertiliser	Ammonium Fertiliser	Nitrate precipitation		No sewage	
Duetch et al - Quantification of diffuse nitrate inputs into a small river system using stable isotopes of oxygen and nitrogen in nitrate	Manure + Sewage	Soil N	Nitrate Fertiliser	Nitrate precipitation	Ammonium Fertiliser	All	
Hales -Isotopic signature of nitrate in two contrasting watersheds of Brush Brook, Vermont, USA	Soil N	Nitrate precipitation				Soil N, precipitation	
Sacoon et al - Multi-isotope approach for the identification and characterisation of nitrate pollution sources in the Marano lagoon (Italy) and parts of its catchment area.	Manure + Sewage	Soil N	Nitrate Fertiliser	Ammonium Fertiliser		All	
Sanchez et al - Determining sources of nitrate in the semi-arid Rio Grande using nitrogen and oxygen isotopes.	Manure + Sewage	Soil N	Ammonium fertiliser	Nitrate Fertiliser	Nitrate precipitation	All	
Ohte - Spatial distribution of nitrate sources of rivers in the Lake Biwa watershed, Japan: Controlling factors revealed by nitrogen and oxygen isotope values	Soil N	Manure + Sewage	Nitrate Fertiliser	Ammonium Fertiliser	Nitrate precipitation	All	

Merchan et al - Main sources and processes affecting dissolved sulphates and nitrates in a small irrigated basin (Lerma Basin, Zaragoza, Spain):	Soil N	Nitrate Fertiliser	Manure + Sewage	Ammonium Fertiliser	Nitrate precipitation	Only Manure as no urban areas in basin	
Liu et al - Using δ15N- and δ18O-values to identify nitrate sources in karst ground water, Guiyang, Southwest China	Nitrate Precipitation	Manure + Sewage	Soil N	Nitrate Fertiliser	Ammonium Fertiliser	All but with site specific measurements of 15N for sewage	Sewage- δ15N- 18.8
Li et al - Identifying nitrate sources and transformations in Taizi River Basin, Northeast China.	Manure + Sewage	Nitrate precipitation	Nitrate Fertiliser	Soil N	Ammonium Fertiliser	All	
Lee et al - Tracing the sources of nitrate in the Han River watershed in Korea, using δ15N-NO3- and δ18O-NO3- values	Soil N	Manure + Sewage	Nitrate Fertiliser	Nitrate Precipitation	Ammonium Fertiliser	All	
Itoah et al -Evaluation of wastewater nitrogen transformation in a natural wetland (Ulaanbaatar, Mongolia) using dual-isotope analysis of nitra	Equally Sourced					No Sewage due to proximity of WWTP and no agricultural so no fertilizer	
Varga - Nitrogen and oxygen isotopes as indicators of pollution sources in the Faxinal Dam watershed, Southern Brazil	Soil N	Nitrate Fertiliser	Ammonium Fertiliser	Nitrate precipitation		No sewage or manure	
Briand et al - Legacy of contaminant N sources to the NO3- signature in rivers: A combined isotopic (δ15N-NO3-, δ18O-NO3-, δ11 B) and microbiological investigation.	Soil N	Manure + Sewage	Nitrate precipitation			No Fertiliser	
Anoru et al - Tracking nitrate sources in groundwater and associated health risk for rural communities in the White Volta	Equally Sourced					All	

River basin of Ghana using isotopic approach (δ15N, δ18O[sbnd]NO3 and 3H).							
Vrzel et al - Determination of the sources of nitrate and the microbiological sources of pollution in the Sava River Basin	Soil N	Nitrate Fertiliser	Manure + Sewage	Nitrate precipita tion	Ammoni um Fertiliser	All	
Yu - Tracking nitrate sources in the Chaohu Lake, China, using the nitrogen and oxygen isotopic approach	Manure + Sewage	Nitrate precipita tion	Soil N	Ammoni um Fertiliser		No nitrate fertilizer applied in area	
Zhang et al - Tracing nitrate pollution sources and transformation in surface- and ground-waters using environmental isotopes	Manure + Sewage	Soil N	Nitrate Fertiliser	Nitrate precipita tion	Ammoni um Fertiliser	All	
Liu et al - Using 15 N, 17 O, and 18 O To Determine Nitrate Sources in the Yellow River, China.	Manure + Sewage	Soil N	Nitrate Fertiliser	Ammoni um Fertiliser		No Precipitatio n	
Garrad - A stable isotope and hydrochemical approach to examining denitrification along a shallow groundwater - surface water continuum in an agriculturally-impacted catchment	Soil N	Nitrate Fertiliser	Ammoni um Fertiliser	Nitrate precipita tion		No manure or sewage	
Battaglin et al - Chemical and isotopic evidence of nitrogentransformation in the MississippiRiver, 1997 – 98	Manure + Sewage	Nitrate precipita tion	Soil N	Nitrate Fertiliser	Ammoni um Fertiliser	All	
Jin et al - Using dual isotopes to evaluate sources and transformations of nitrate in the West Lake watershed, eastern China	Manure + Sewage	Soil N	Nitrate Fertiliser	Ammoni um Fertiliser	Nitrate precipita tion	All	
Danni et al - Assessment of water quality and nitrate source in the Massa catchment (Morocco) using δ 15N and δ 18O tracers	Manure + Sewage	Soil N	Nitrate Fertiliser	Ammoni um Fertiliser	Nitrate precipita tion	End member values for sewage	
SiLiang et al - Assessment of the Sources of Nitrate in the Changjiang River, China Using a Nitrogen and Oxygen Isotopic Approach	Manure + Sewage	Nitrate Fertiliser	Soil N	Nitrate precipita tion	Ammoni um Fertiliser	All, specific end member values for	Wastewa ter- δ15N- 8.9 δ18O 5.6

						wastewater .	
Xing & Liu - Using dual isotopes to identify sources and transformations of nitrogen in water catchments with different land uses, Loess Plateau of China	Soil N	Manure + Sewage	Nitrate precipita tion	Nitrate Fertiliser		No ammonium fertilizer considered and site specific end memnber values.	Sewage- δ15N- 26.1 δ18O- 13.1
Yue et al - Using dual isotopes to evaluate sources and transformation of nitrogen in the Liao River, northeast China	Manure + Sewage	Nitrate precipita tion	Soil N	Nitrate Fertiliser	Ammoni um Fertiliser	All considered but with site specific 15N data.	
Wong et al - Stable isotopes of nitrate reveal different nitrogen processing mechanisms in streams across a land use gradient during wet and dry periods	Soil N	Manure + Sewage	Nitrate Fertiliser			Three sources, artificial fertiliser, cow manure/or ganic fertiliser and soil organic matter with specific 15N values.	Inorganic Fertiliser- δ15N-0.5 Cow manure- δ15N-9.5
Nyiliyta - Land use controls Kenyan riverine nitrate discharge into Lake Victoria – evidence from Nyando, Nzoia and Sondu Miriu river catchments*	Manure + Sewage	Soil N	Nitrate precipita tion	Nitrate Fertiliser	Ammoni um Fertiliser	All	

Bratek et al - Nitrate sources and the effect of land cover on the isotopic composition of nitrate in the catchment of the Rhône River	Soil N	Manure + Sewage	Ammonium Fertiliser	Nitrate Fertiliser	Nitrate precipitation	All	
Parades et al - Agricultural and urban delivered nitrate pollution input to Mediterranean temporary freshwaters	Manure + Sewage	Nitrate Fertiliser	Soil N	Ammonium Fertiliser		No precipitation, site specific meausrements.	Wastewater- δ15N- 22.6 δ18O 10.5