A Global Assessment of Nitrate Contamination in Groundwater

Internship report

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Abstract

This study provides information on the occurrence of nitrate contamination in groundwater. Furthermore, it gives insights in the sources and negative effects of nitrate contamination. In addition, the study gives a broad overview of possible technical, scientific, managerial and institutional method that effectively reduce and mitigate the risk of groundwater nitrate contamination. A global transboundary aquifer pollution vulnerability map is presented based on the GOD method. A global overview of groundwater nitrate contamination level is shown by GIS maps and regional maps.

Key words: global overview, groundwater, nitrate contamination, aquifer pollution vulnerability, GIS

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1. Introduction

Groundwater is an important natural resources with high economic value and social significance. Groundwater supplies almost half of all drinking water in the world (WWAP, 2009), and plays a key role in food production, accounting for over 40% of the global consumptive use in agricultural irrigation (Siebert et al., 2010). Furthermore, in the environmental aspect, groundwater resources directly support rivers, lakes and wetlands. The last decades have witnessed an increased pressure on groundwater resources globally, which in many cases induced abstraction beyond sustainable levels and increased levels of pollution (Groundwater Governance, 2013). Climate change, land use and population growth are posing a variety of threats to groundwater resources globally thereby impacting both quantity and quality of the water.

Agricultural land use represents the largest diffuse pollution threat to groundwater quality on a global scale (Haller, 2013). As a result of decades of fertilizer application and surface spreading of animal manure, significant increases in nutrient concentrations have been documented in both private and municipal well systems (Hallberg and Keeney, 1993). Nitrate (NO_3^-) is one of the main groundwater pollutants. High nitrate concentrations in groundwater can cause public health risk and environmental pollution that have already become a common problem in many parts of the world. Nitrate threats depends on scales which can take on chronic or acute forms (Sousa et al., 2013).

Consuming water containing high nitrate concentrations can have almost immediate effect on a person (acute toxicity), and could cause the risk of methemoglobinemia (sometimes referred to as "blue baby syndrome"), in which blood lacks the ability to carry sufficient oxygen to the individual body cells (Uhlman and Artiola, 2011). Long term exposure to high nitrate levels in drinking water has been found in some studies to be a risk factor for several types of cancer including gastric, colorectal, bladder, urothelial and brain tumor (CDPH, 2013). In other words, it is of vital importance to regulate nitrate concentration in drinking water to minimize public health risk. It is therefore expedient to mitigate the impact of nitrate pollution in groundwater and understand the global impact of nitrate contamination.

This reports focus on nitrate contamination in groundwater and its global appearance. It provides a perspective on its current state of knowledge, best practices and future challenges of nitrate contamination, and an overview of the severity of groundwater pollution worldwide.

2. Research Aim

The aim of this project is to investigate nitrate contamination in groundwater on a global scale in order to communicate the negative effects of nitrate contamination in groundwater systems to water experts, decision makers as well as the general public. By reviewing, integrating and analyzing available information, an overview of the current state of nitrate pollution will be provided in the form of groundwater vulnerability maps. These maps will enable to identify the vulnerability of global groundwater systems to nitrate contamination. The objective is to raise public and institutional awareness in terms of the effectiveness of nitrogen management policies. The information could be beneficial for groundwater management worldwide.

3. Background information

3.1 Source of nitrate

Nitrate contamination in groundwater systems is caused by various processes and sources. Identifying the various sources of nitrate contamination and understanding system dynamics is fundamental to address groundwater quality problems. In general, sources of nitrate pollution can be divided into two main groups, nonpoint (diffuse) and point-source pollution. Agricultural fertilizers application is the largest nonpoint source pollution affecting groundwater quality. This form of pollution is extended over a wide area, as opposed to point sources, which are single and identifiable sources of contamination mainly affecting localized areas. The diffuse sources of nitrate include long-term, widespread overuse of chemical or manure fertilizers (cropland, lawns or golf courses) and long-term leaks in sewer lines (Viers et al., 2012). Examples of point sources include the areas of concentrated livestock confinement, leaky septic or sewer systems and areas of chemical or manure storage (Haller et al, 2013). In particular, point sources may result in extremely high nitrate concentration in localized areas.

3.1.1 Diffuse sources

Diffuse sources pollution is mainly caused by the extensive use of synthetic and organic nitrogen fertilizers. The development of synthetic fertilizer production is mainly based on the Haber- Bosch process (Smil, 2001). It catalyzes atmospheric nitrogen gas with hydrogen to produce ammonia, which can then be further oxidized to produce nitrate.The Haber-Bosch process has facilitated the production of agricultural fertilizers on an industrial scale, thereby it has radically increased global agricultural productivity in most regions of the world (Erisman et al., 2011). It is estimated that nearly 2 billion people are sustained with fertilizers generated by the Haber-Bosch process (Borkovich, 2010; Schmoll et al., 2006).

Plants do not necessarily use all the nitrate in (chemical) fertilizers or all the nitrate produced when organic matter decomposes. Therefore, nitrate can accumlate in the soil when the nitrate supply is more than the amount plants use. With high nitrogen inputs to increase crop yields, the efficiency of nitrogen use may reduce and increase the potential for nitrate leaching to the groundwater.

The main nitrogen transformation processes in soil are shown in Figure 1. Nitrate can be lost from the system in various ways. Excessive nitrates may leach through the root zone and contaminate groundwater resources. The potential of nitrate leaching depends on the soil types and the amount of water in the form of precipitation and/or irrigation (Mahler et al., 2007). The movement of nitrate in the soil is a natural processs and not always harmful for the environment. However, excessive use of fertilizer and improper management of nitrogen sources increases the leaching rate and the magnitude of groundwater contamination.

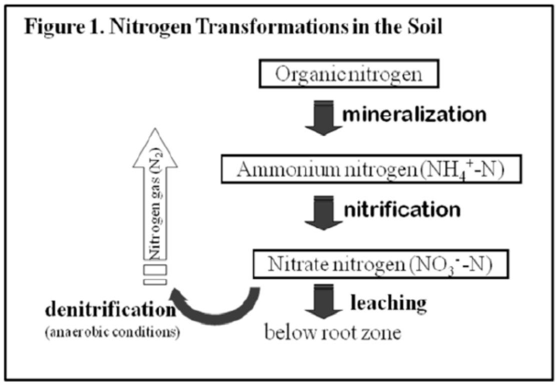

Figure 1 Nitrogen transformations in soil (Source: Frate, 2007)

Nitrogen can be found in various froms. An overview of various nitrogen forms in the soil and the corresponding conversion processes are presented in Table 1. Organic nitrogen cannot be used by plants directly. However, as organic matter decomposes, it releases nitrogen in the form of nitrate that can be used by plants. The conversion of organic nitrogen into inorganic, plant-available forms occurs in all natural ecosystems. Organic nitrogen fertilizers used in agriculture include animal manures, human wastes, composts, sewage slude, legume crops and green manure crops.

Nitrogen types	Chemical forms	Chemical process	Crops availability
Organic nitrogen	Organic N	Mineralization	Non-plant available nitrogen
Ammonium nitrogen	(NH_4^+-N)	Nitrification	Plant available nitrogen
Nitrate nitrogen	(NO_3^-N)	Leaching to root zone	Plant available nitrogen

Table 1 Nitrogen form in soil (Sources: Frate, 2007)

3.1.2 Point sources

Point source pollution results from accidental spills of nitrogen-rich compounds, absence of slurry storage facilities and manure tanks in rural areas. Examples of point sources include areas of concentrated livestock confinement, leaky septic or sewer systems and areas of chemical or manure storage. Moreover, unplugged abandoned wells and boreholes, improperly constructed wells and sinkholes can allow rapid contamination of groundwater from point sources at the surface. They are most often causing the amount of nitrate to rise to a harmful level (Hallberg and Keeney, 1993).

Many studies have shown that poorly designed manure storage pits, lagoons and storage tanks can contribute significant amounts of nitrate to groundwater. In additon, the potential of nitrate leaching from barnyards is great when they are located on sandy soils or on thin soils over creviced bedrock. In these situation, yards tend to stay porous and aerboic that allowing nitrogen to convert to nitrate and leach rapidly into groundwater (Bundy et al., 1980).

Furthermore, septic systems are examples of anthropogenic sources of nitrogen contamination of the groundwater (Haller et al., 2013). In unsewered areas, most people use septic systems to dispose household wastewater. The systems discharge waste into a tank and then into an underground disposal field. Nitrogen remains in ammonium and organic forms until it reaches the aerobic zone below the disposal field. Once reached the aerobic zones, it is oxidized to nitrate and transported with water into the groundwater.

Box 1. The difference between groundwater contamination and pollution

Although the terms contamination and pollution are often used interchangeably in colloquial speech, they are distinct environmental concepts. Contamination is simply the presence of a substance that is normally not present or at a concentration above natural background level. When contamination reaches a level that results in or can causing negative biological effects to resident communities it becomes pollution (Chapman, 2007). All pollutants are contaminants, however, not all contaminants are pollutants. Pollution can produce highly damage or disturb ecosystem while contaminant should be supported by system without stopping general life cycle.

There are many different reasons causing groundwater pollution, which is important to clarify two broad categories, "point source" - occurs when harmful substances are emitted directly into a body of water and "non-point source"- delivers pollutants indirectly through transport or environmental change.

3.2. Negative impacts of nitrate pollution in groundwater

In many parts of the world, groundwater is the single most important supply for the production of drinking water, particular in areas with limited or polluted surface water sources (Schmoll et al., 2006). Half of all drinking water in the world is extracted from groundwater resources (WWAP, 2009). Groundwater contamination can directly affect human health because excessive levels of nitrate in drinking water can produce negative health impacts on human well-being.

3.2.1 Human health

Excessive levels of nitrate in drinking water can produce negative health impacts on human well-being. Especially infants below the age of six months could become seriously ill from intake of water with a concentration higher than 10 mg/L of nitrate. Infant nitrate poisining has been recognized as a concern since the problem was first reported in 1945. Infants consuming water containing high nitrate levels can result methemoglobinemia, also referred to as "blue baby syndrome". The name derives from the characteristically blue or lavendar skin color of infants suffering from the syndrome. Normally, the distinctive blue color is caused by the red blood cells which is not able to carry oxygen from the lungs to the rest of the body. Symptoms can occur rapidly over a period of days with the shortness of breath and blueness of the skin. Furthermore, this condition occurs when bacteria in a baby's mouth and stomach convert nitrate to highly toxic nitrite. Methemoglobineamia generally does not affect older children or healthy adults. Healthy adults can consume fairly large amounts of nitrate with few known health effects. In fact, people consume nitrate on a daily basis, particulary from raw or cooked vegetables. This nitrate is readily abosorbed and excreted in the urine. However, prolonged intake of high levels of nitrate are linked to gastric problems due to the formations of nitrosamines. N-nitrosamine compounds have been shown to cause cancer in test animals (Self and Waskom, 2013). However, some information suggests that ingesting nitrate-contaminated drinking water during early pregnancy may increase the risk of certain birth defects (Bundy et al., 1980). Various studies conducted in Australia, Canada and U.S.A. found a higher incidence of neural tube defects and cleft palates in areas where nitrate levels were elevated (Bundy et al., 1980). Additional problem related to nitrate exposure during pregnancy have been raised concerns because research shows nitrites may cross the placenta and potentially increase methemoglobin levels in the developing fetus.

3.2.2 Environmental impacts

Water quality is a major concern throughout the world. Excessive nitrogen use stimulates growth of aquatic plants and algae. Excessive growth of these organisms can result in eutrophication, which may cause harmful algal blooms, water column anoxia, and fish mortality, all of which have a negative impact on humans in terms of reduced environmental quality, potential health risks and increased management cost (Wetzel, 2001; Wilson and Carpenter, 1999).. Eutrophication is the enrichment of surface water with plant nutrients. While eutrophication occurs naturally, it is normally associated with anthropogenic sources of nutrients. Eutrophication cause some undersirable consequences. For instance, penetration of light into the water is diminished. This occurs because the algae forms as a result of being produced faster than they are consumed. Diminished light penetration decreases the productivity of plants living in the deeper waters. Secondly, the water becomes depleted in oxygen. When the abundant algae die and decompose, much oxygen is consumed by those decomposers. Oxygen in the water is also lowered by the lack of primary production in the darkened deeper water. Essentially, the entire aquatic ecosystem changes with eutrophication.

Box 2 Chemical conversion process between nitrate and nitrite

Nitrate is an inorganic compound composed of one atom of nitrogen (N) and three atoms of oxygen (O). The chemical symbol for nitrate is NO_3^-. In the atmosphere, the major sources of nitrate include reactions caused by lightning, photochemical oxidation in the stratosphere. Other sources of nitrate are chemical oxidation of ammonia, soil production of NO_3^- by microbial processes and fossil fuel combustion (Gaillard, 1995). Natural sources of the formation of reactive nitrogen consists of four primary processes that are nitrogen fixation, ammonification, denitrification and nitrification. All these processes are predominantly facilitated by micro-organisms. Nitrification is a significant process in the production of nitrite (NO_2^-) and nitrate (NO_3^-). This process takes place naturally and is carried out in two steps. The first step is nitrification that uses a type of bacteria called nitrosomonas. During the process of nitrification, NH_4^- (ammonium) is oxidized into NO_2^- (nitrogen dioxide). The chemical equation for this process is summarized below:

$$NH_3 + 1.5 \cdot O_2 \rightarrow NO_2^- + H^+ + H_2O$$

The second part of nitrification process is called nitration. Nitration uses the enzyme nitrite oxidoreductase to complete the nitrification process. The chemical equation shows how this reaction occurs:

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^-$$

When all of these processes are completed, nitrate can be converted back into elemental nitrogen by the process of denitrification. It also takes place in the soil through the activity of bacteria.

3.3 Methods to reduce nitrate risks

Nitrate contamination in the groundwater system, and thereby the drinking water supply, has become a serious global problem. Therefore, many studies have been put emphasis on finding effective treatment processes to control and mitigtate nitrate pollution.

3.3.1 Prevention method

One of the most important steps to reduce the nitrate leaching in area is to limit the amount of nitrogen applied. It is better to use slow-release nitrogen sources, or low rates of soluble nitrogen applied more often. In addition, the farmers should be more cautious about adding nitrogen during periods in which the ground is not yet frozen but the grass is not growing. The farmers should also avoid over-irrigation, which increases the chance of nitrate leaching. By following these steps the agricultural areas will greatly reduce the chance of nitrate leaching into groundwater. If proper measures are taken, the fertilizing of golf courses, and athletic fields will not result in nitrogen pollution of groundwater (Hallberg and Keeney, 1993).

3.3.2 Environmental protection policies and regulations

Nitrate pollution has been addressed by governmental policy measures related to reduce atmospheric pollution and limiting nitrogen contamination of groundwater and surface water resources. It includes several European directives, such as the Nitrate Directive, Water Framework Directive, Groundwater Directive, Ambient Air Quality, National Emissions Ceilings Directive, Urban Waste Water Treatment Directive (Sutton et al., 2011).

3.3.3 Drinking water standards

In order to regulate the nitrate concentration to minimize public health risk, the World Health Organization (WHO) has published the guideline value for nitrate (NO_3^-) in drinking water which should not exceed 50 mg/l (WHO, 2004). Furthermore, local environmental protection agency of various countries have created standards for maximum contaminant level for nitrate in drinking water supply. For example, the Environmental Protection Agency (EPA) in United States established standards and limits for nitrate in public water supplies. The maximum contaminant level for drinking water supplies should not contain more than 10 mg/l of nitrate (as nitrogen) and 1 mg/L of nitrite (as nitrogen) (Borkovich, 2010). The chemical conversion between nitrate and nitrite is referring to the Box 2.

3.3.4 Sewage system management

Wastewater is necessary to be treated before discharged in order to minimize environmental pollution. Many developed countries has invested large amount of money and resources in the aspect of wastewater treatment and disposal technology (WHO, 2004). Sewerage networks transport wastewaters to treatment plants where organic matter, nutrients and harmful substances are removed from the sewage before the effluent is discharged back into the environment. The aim of sewage treatment is to purify the effluent by removal of harmful and hazardous substances and plant nutrients contained in sewage as solids and as dissolved matter. The United Nations Environment Program (UNEP) has publised national policies and measures to ensure that all waste disposal conforms with national and international quality guideline by the year 2025. The specific measures is to identifiy the major sewage sources and areas where sewage poses major environmental and health-related hazards. Providing sufficient training and education for local administration to plan and building the adequate sewage treatment facilities in rural areas. Then, formulation and implementation of awareness campaigns for the general public to gain general recognition for the need for the installation of appropriate and environmentally sound sewage facilities.

3.3.5 Beneficial management practices for agriculture

Effective prevention measures to reduce the nitrate pollution is to minimize the leaching of nitrate from the soil. Furthermore, it suggests that effectively managing nitrogen is a multi-faceted task and requires an integrated approach based on the adoption of benefical management practices (BMP) (Di and Cameron, 2002). This technique is a practical and afforable activity that can achieve the goals including protecting and conserving farm resources, facilitation the reduction of greenhouse gas emission or encourage carbon sequestration (Mussell et al, 2011). BMP techniques can be applied to minimize nitrate leaching from croplands and/or to make crops use nitrogen fertilizer as efficiently as possible. For instance, better timing and placement of fertilizers could improve efficient use (Bundy et al., 1980). Many studies have shown that benefical management practices significantly improve the potential to maximize crop yield while minimizing the quantity of nitrate leaching into groundwater (Keeney, 1991; Ritter, 2001; McKague, 2005). Many research projects have invested in the BMP to reduce the nitrate pollution from agricultural activities. For example, in Ontario, Canada, the application of nitrogen BMP scenario's developed to improve existing nitrogen management practices (such as soil N test, N balance and max N balance) or remove key sources of nitrogen (drop manure) in agricultural fields. It represents effective environmental strategies to ensure the groundwater obtained in drinkingwater production wells will meet the Ontario Drinking Water Standard (ODWS) for nitrogen (10 mg/L) now and in the future (Mussell et al., 2011).

3.3.6 Prevention techniques

Manure lagoons is a large contaminant source in many farming areas. One technique to prevent this contaminant is building manure storage for storing manure in concrete pits. Another possible solution is the installation of a storage facility termed a slurrystore. These facilities are proven to store manure without leaking and are actually more convenient for the farmer once they are installed.

3.3.7 Water treatment techniques

Nitrate contaminated groundwater is primarily a problem once water is abstracted and used for drinking water supply. In order to deal with nitrate contaminiation in subsurface water, there are various alternative treatment methods to reduce the concentration of nitrate before it is used as drinking water. The most important once are described.

Blending drinking water is a method to mix contaminated water with clean water from another source to lower overall nitrate concentration.This method is not safe for infants but is acceptable for livestock and adults (Self and Waskom, 2013). The method is also referredto as a non-treatment technique. The benefits of non-treatment method is the spread of the costs of water quality monitoring in the different regions so that it significantly reduces expenses and helps to provide safe(r) drinking water to the majority of the people. The disadvantage of this method is however that it can only be applied when the nitrate contamination is limited to a specific area. Other alternatives are the use of treatment processes, such as ion exchange, reverse osmosis and biological denitrification (Haller et al., 2013).

Ion exchange needs a substance such as chloride to exchange with nitrate in the water. The ion exchange unit is a tank filled with special resin beads that are charged with chloride. Once contaminated water passes over the tank, the nitrate is substituted with the chloride. The resin is recharged by backwashing it using a sodium chloride solution. Ion exchange method is very effective method, except for water that contains high amounts of sulfate. In this case the sulfate compete with nitrate in the exchange process (Self and Waskom, 2013).

Reverse osmosis is another method that can be used tho reduce nitrate concentration. Water is move under high pressure through a membrane. The membrane contains many microscopic pores that allow only water molecules to pass through, and as such, will stop nitrate and other inorganic chemicals such as calcium and magnesium. The membrane can reject nitrate which estimates around 83-92 % of the incoming nitrate. Consequenctly, it is important to know the orginal nitrate concentration in the water. If nitrate-nitrogen levels are extremely high (greater than 110 mg/l) up to 90 % may be removed. Although reverse osimosis can be an effective nitrate remover, this method is relatively expensive and removing the useful chemicals (Mahler et al., 2007).

Biological denitrification is using denitrifying bacteria and microbes so that nitrate ions are converted into its elemental state of nitrogen. Nitrate can be removed by using a chemical material like ethanol. Besides special bacteria, photosynthetic algae can be used to remove nitrates from water. This method does not produce concentrated brine streams, however, biofilm growth have to be managed. The important drawback of biological systems are requiring start-up time after prolonged periods of closure. For instance, the response of seasonal water demand need more operator support than nonbiological systems (Mahler et al., 2007).

4. Review of global and regional nitrogen assessment maps

This chapter presents several different global and regional maps related nitrate contamination in groundwater and the current states of nitrogen fertilizer application.

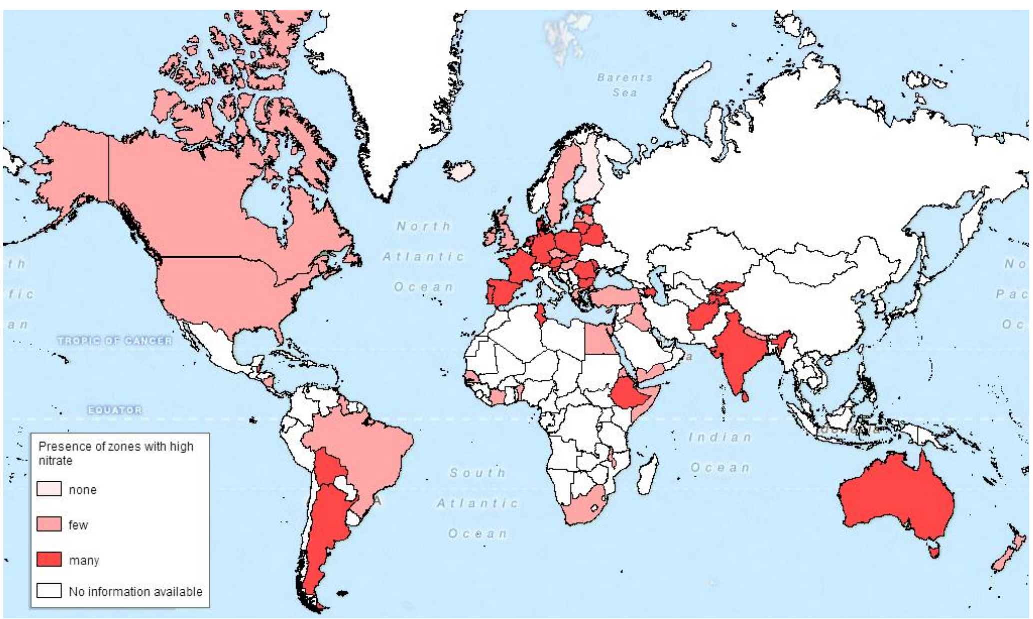

Figure 2 Global map with the presence of zones with high nitrate in groundwater (source: IGRAC, 2012)

The global map with presence of zones with high nitrate in groundwater is obtained from IGRAC's Global Groundwater Information System (GGIS). The map shows aggregated data per country, classified from none, few and many zones where high concentration of nitrate have been reported. The map is based on a literature study that demonstrated the percentage of regions with high nitrate contamination in the world. However, one drawback of this map is that the legend is of qualitative range, without specifying quantitative definition for "high nitrate", "many" and "few."

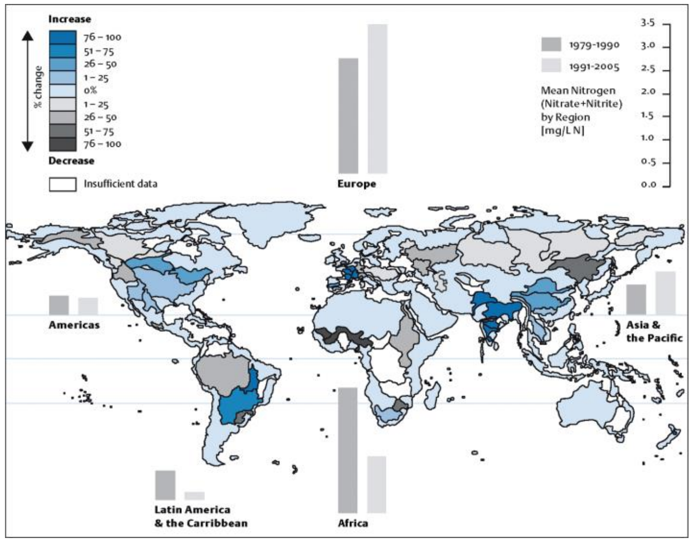

Figure 3 Changes in nitrogen concentration for significant global watersheds (%) and by region: 1979-1990 and 1991-2005 (source: UNEP, 2007)

The changes in nitrogen concentration for significant global watersheds are shown in Figure 5. It focuses on the change of nitrogen concentration in the watersheds between the period of 1979-1990 and 1991-2005. During these two different time periods, the significantly increasing of nitrogen level occurred in Europe and Asia from 1991 to 2005. In contrast, Africa and Latin America reduced the nitrogen concentration in this period. Americas does not show a large difference in the different phases.

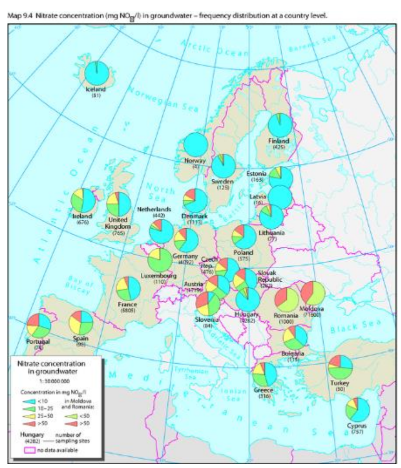

Figure 4 Nitrate concentration (NO_3^- in mg/L) in groundwater at a country level (source: EEA, 2002)

Nitrate concentration in groundwater in European countries is presented in Figure 8. The frequency distribution of nitrate concentration are presented for most European countries. The majority of countries show nitrate levels higher than 50 mg L^{-1}. The data value was measured by a number of sampling sites in different countries.

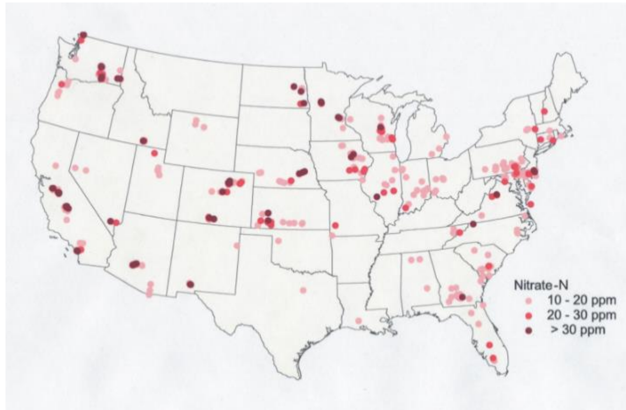

Figure 5 Groundwater nitrate-N concentration in United States (source: Townsend et al., 2003)

In Figure 9, nitrate-N concentration in groundwater is presented for the United Sates. The concentrations are classified into three different ranges. Most of the sampling points of nitrate-N concentration with large than 30 ppm are located in the west and central part of America. The range of concentration variation mainly exists between 10 to 20 ppm. However, the legend with greater than 30 ppm does not give the maximum limited value.

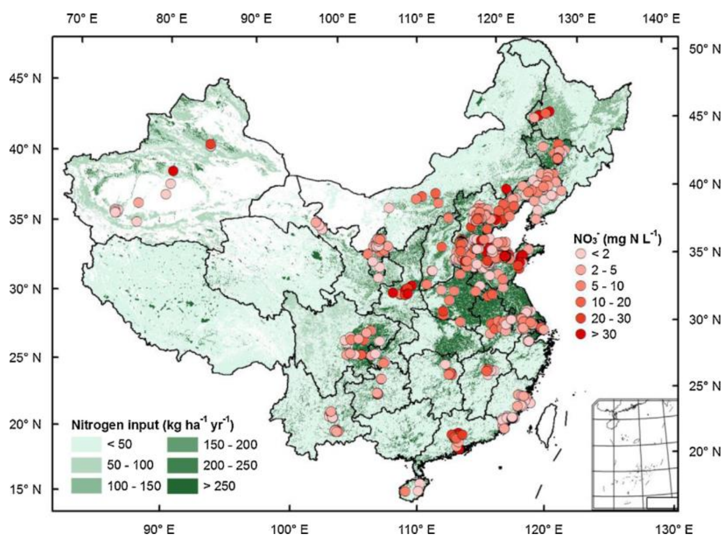

Figure 6 Groundwater nitrate concentration in the sampling sites of China during 2000-2012 (source: Gu et al., 2013)

Groundwater nitrate concentration in China is illustrated in Figure 8. The dark green area represents the region with annual nitrogen input large than 250 kg ha^{-1}, which appear mostly in the east part of China. The red points represents the distribution of nitrate concentration in groundwater. The concentration varies between 20 and 30 mg L^{-1} in the east region of China that correspond to the high nitrogen input area. The low nitrate concentration usually occurs along the coastal region with the variation of 2-5 mg L^{-1}. The map data consists of a total of 628 valid data of groundwater nitrate concentration from the literature analysis (Gu et al., 2013). The majority of nitrate sampling sites distribute in the north east of China, and no information available in the south west region.

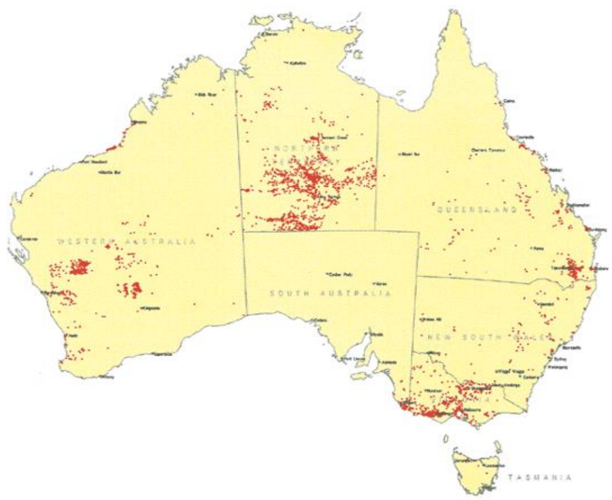

Figure 7 The distribution of bores across Australia with nitrate level greater than 10 mg L-1 (source: LWRRDC, 2001)

Nitrate contamination of groundwater (indicated by > 10 mg L^{-1} nitrate) in Australia is widespread and occurs over regional and local scale. Each red point represents the measuring bores with nitrate level higher than 10 mg L^{-1}. The data points are clustered in the centre, west and southeast regions. In many areas, the concentration is larger than Australia Drinking Water Guidelines level of 50 mg L^{-1} nitrate (NO_3^-), resulting in groundwater that is unfitting for drinking. The concentration in some of the contaminated areas even excess above 100 mg L^{-1}.

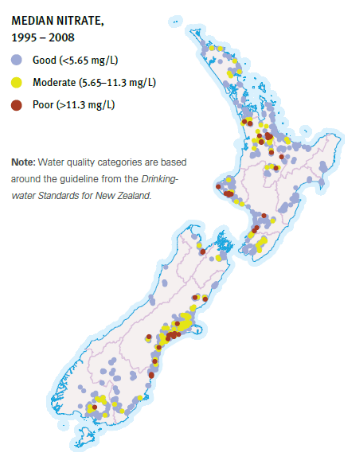

Figure 8 Median nitrate level in groundwater in New Zeeland during 1995-2008 (Source: MFE, 2010)

This map demonstrates the median nitrate levels for the period 1995 to 2008 for 914 groundwater sites in New Zealand. The majority of sites (80%) have median nitrate level less than 5.65 mg/l. Forty four (5%) sites have median nitrate levels that exceed the health-related drinking water guideline of 11.3 mg/L according to the Drinking Water Standards for New Zealand in 2005 (MFE, 2010). Regions with a significant proportion of sites that have median nitrate exceeding 5.65 mg/L such as Canterbury, Manawatu, Southland, Taranaki, Waikato and Wairarapa.

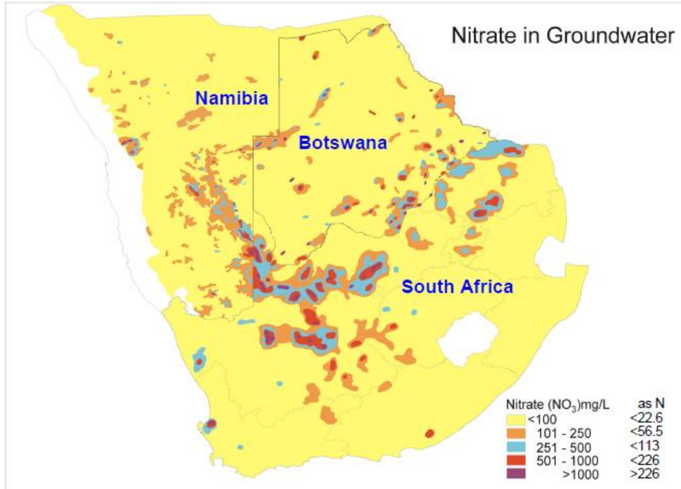

Figure 9 Groundwater nitrate distribution in southern Africa (source: Tredoux et al., 2009)

This regional map represents the distribution of nitrate concentration in groundwater between Namibia, Botswana and South Africa. Based on this map, the highest nitrate concentration is found in the central part of these three countries, the Stampriet Kalahari/ Karoo aquifer systems, around 500 mg L^{-1} in the groundwater. Because the transboundary aquifers is covering in that region with stretching over an area of 14,000 km^2. It is, that consists of two confined regional sub-artesian aquifer located in the Karoo sediments and one overlying unconfined aquifer system of Kalahari sediments. The dataset on this map was collected from the analytical information of more than 50,000 groundwater sources (Tredoux et al., 2009). The contour maps were overlain to produce a simplified groundwater nitrate map for each country. The coverage for Namibia is based on work completed much earlier than those for Botswana and South Africa, which are derivied from currently active databases. The Botswana data coverage is sparse at this stage since only a limited number of chemical analysis have been satisfactory linked to geographical locations.

Many research have been done on groundwater contamination by nitrate in Europe and North America.

Box 2 Interconverting Nitrate as Nitrate (Nitrate-NO_3) and Nitrate as Nitrogen (Nitrate-N)

The atomic weight of nitrogen is 14.0067 and the molar mass of nitrate anion (NO_3^-) is 62.0049 g/mole. In order to convert Nitrate-NO_3 (mg/L) to Nitrate-N (mg/L):

$$Nitrate - N(mg/L) = 0.2259 \times Nitrate - NO_3(mg/L)$$

And to convert Nitrate-N (mg/L) to Nitrate-NO_3 (mg/L):

$$Nitrate - NO_3(mg/L) = 4.4268 \times Nitrate - N(mg/L)$$

The nitrate concentrations are expressed in various ways depending on method used and/or concentration in the water. Actually, nitrate can be expressed as either NO_3 (nitrate) or NO_3-N (nitrate-nitrogen). Both two expression forms are correct, however, there is a slight difference in the aspect of concentration converting.

In addition, the nitrate concentration unit is usually defined as milligram per litre. At Figure 9, the Nitrate-N concentration was measured by ppm (part per million). It is a way of expression very dilute concentrations of substances. It is used to describe the concentration of a substance in water or soil. One ppm is equivalent to 1 milligram per litre of water (mg/L). Hence, all these different chemical expression about nitrate can be converted as uniform standard in Table 4.

Table 2 Nitrate chemical expression interconverting

NO_3^--N (mg/L)	*NO_3^- (mg/L)*	*NO_3^- (ppm)*	*NO_2^--N (mg/L)*
10	*45*	*45*	*1*

5. Methodology

The research consists of a literature review and data collection/analysis on nitrate contamination in groundwater systems globally. The literature study identified the current state of knowledge on nitrate contamination in relation to groundwater. In addition, the drinking water standard and guideline values for nitrate (NO_3^-) concentration in drinking water for have been collected. Data is collected from literature, online databases and by contacting IGRAC's international network. In order to make a groundwater vulnerability map by nitrate contamination, various methodologies exist.

5.1. Methodology for vulnerability mapping

A research has been done into various frameworks for vulnerability mapping of groundwater. Based on suitability and data availability a selection has been made. Two main methodologies, DRASTIC method (Aller et al., 1985) and GOD method (Foster et al., 1987) will be explained briefly. For this project, the GOD method has been applied on data available from the Transboundary Water Assessment Programme (TWAP). TWAP is a two year project funded by the Global Environment Facility (GEF) and aims at conducting the first global baseline assessment of transboundary water systems. The data collection is done by IGRAC and stored in the Global Groundwater Information System (GGIS).

5.1.1. DRASTIC method

The DRASTIC approach was proposed by the US Environmental Protection Agency (Aller et al., 1985), which allows the assessment of vulnerability of the vertical aquifer pollution caused by parametric systems. It is based on the estimation of the following seven parameters in particularly: depth to water (D), net recharge (R), aquifer media (A), soil media (S), topography (T), vadose zone impact (I) and hydraulic conductivity (C) (see Figure 2).

Each mapped factor is classified into ranges (continuous variables) or significant media types (thematic data) having an impact on pollution potential. Each parameter was divided to an interval range of significant values and assigned by a numerical rating based on its growing importance in the vulnerability. Seven parameters are used to define the different hydrological units, variously influenced by transport processes and attenuation of contamination in the soil. Numerical value called a weight parameter, between 1 to 5 is assigned to each parameter and reflects its influence degree. Each parameter is listed based on the associated scores ranging from 1 to 10, the lowest score represents the condition of the lower vulnerability contamination; also to describe the vulnerability degree of each hydrologeological unit, the numerical value called DRASTIC vulnerability index should be determined.

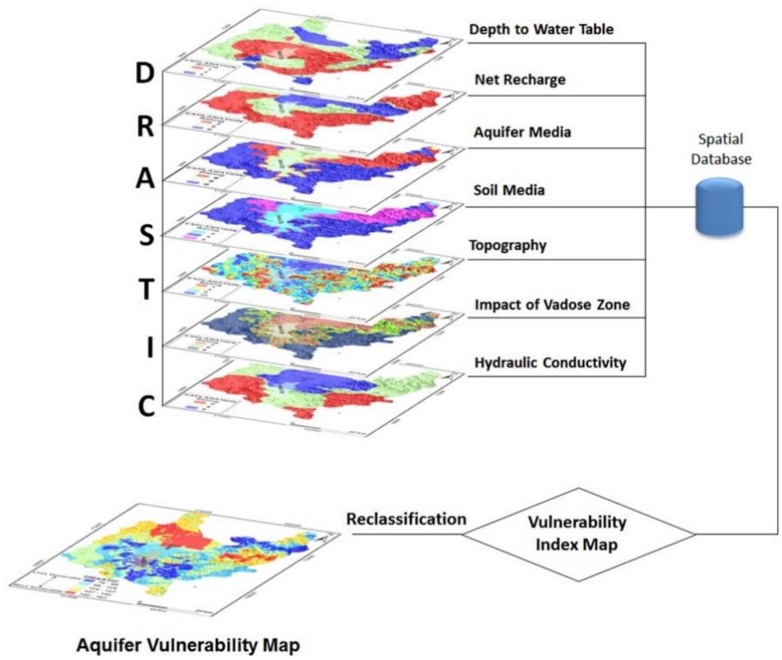

Figure 10 DRASTIC method flowchart (source: Gultekin and Ersoy, 2013)

The DRASTIC index (Di) can be computed using the following expression (1):

$D_i=(D_r \times D_w) + (R_r \times R_w) + (A_r \times A_w) + (S_r \times S_w) + (T_r \times T_w) + (I_r \times I_w) + (C_r \times C_w)$ (1)

Where r represents the range for the parameters, and w is an assigned weight for the parameter. Therefore, the DRASTIC index is defined by the scores of the all vulnerability parameters multiplied by their respective weights. The DRASTIC weight parameters was defined in Table 2. The range of vulnerability of the aquifer hydrological is defined by the indices DRASTIC. These indices are divided into four classes in Table 3.

Symbol	Parameter	Weight
D	Water depth	5
R	Effective recharge	4
A	Middle aquifer	3
S	Soil type	2
T	Topography	1
I	Impact of the vadose zone	5
C	Hydraulic Conductivity	3

Table 3 Weight setting of DRASTIC (Source: Aller et al., 1987)

Class vulnerability	Low	Average	High	Very high
Index	<101	101-140	141-200	>200

Table 4 Criteria of the vulnerability assessment by using DRASTIC method (Source: Engel et al., 1996)

5.1.2 GOD method

The approach is formulated by a rapid assessment of the aquifer vulnerability. It was developed by Foster in 1987 and 1988 for studying the vulnerability of the aquifer against the vertical percolation of pollutants through the unsaturated zone, without considering their lateral migration in the saturated zone (Ferreira et al., 2004). The GOD index is used to evaluate and map the aquifer's vulnerability to pollution. Three parameters have to be considered for this approach: a) Groundwater occurance, b) Overall aquifer class, and c) Depth of the groundwater table. The GOD index is calculated by multiplication of the influence of the three parameters using the following equation:

$$GOD\ index = C_I \times C_a \times C_d$$

Where C_I is the lithology of the unsaturated zone, C_a is the aquifer type and C_d is the depth to groundwater table. The GOD indexes are divided into five classes and vary between the extreme values ranging from 0 to 1 (Boufekane et al., 2013).

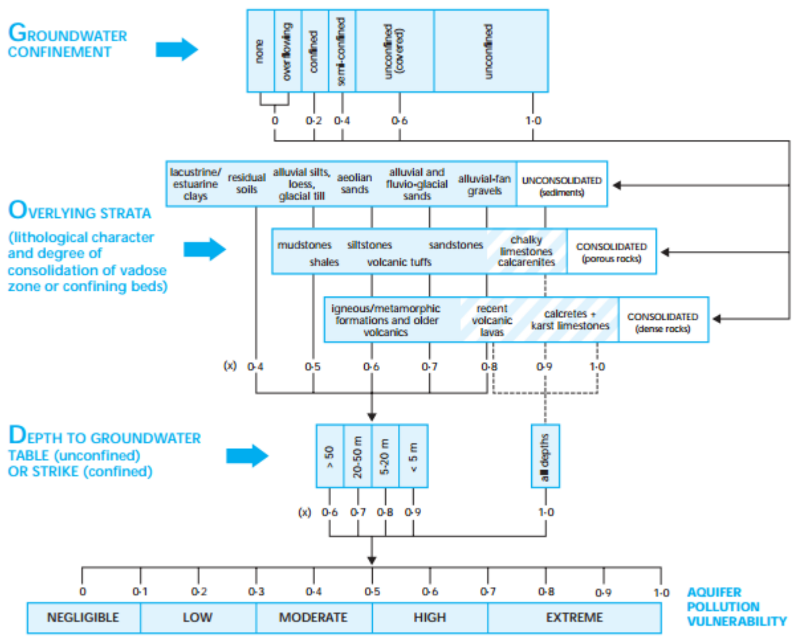

Figure 11 GOD empirical system for the rapid assessment of aquifer pollution vulnerability (source: Duijvenooden and Waegeningh, 1987)

The GOD flowchart and corresponding rating of each parameter is illustrated in Figure 2. The flowchart shows the three input steps to compute the aquifer vulnerability index by choosing first the rating of groundwater occurrence parameter, and then multiplying by the overlying lithology rating as well as with the depth to groundwater table parameter rating. The final value represents the aquifer pollution vulnerability. The GOD indexes are divided into five classes and vary between the extreme values ranging from 0 to 1 (Abdelmadjid and Omar, 2013).

The dataset of the parameters in the GOD principle have been collected from the TWAP database. Then, the basic groundwater vulnerability map was created by using ArcGIS tool.

6. Results

The global aquifer vulnerability map and the collected sampling points with nitrate concentration in groundwater are illustrated in this chapter. In addition, the global nitrogen fertilizer application and maps are collected from literature study, which was used to analyse the potential possibility of nitrate leaching in some areas of the world.

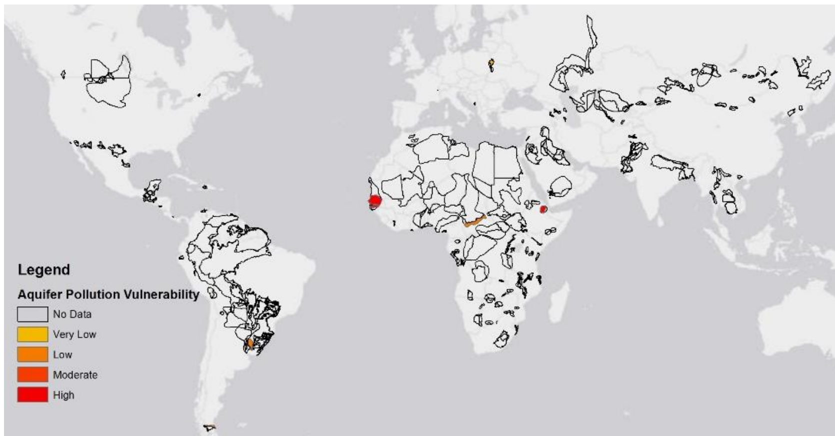

Figure 12 Vulnerability map of the main transboundary aquifers of the world

The GOD method is used to evaluate the global aquifer pollution vulnerability. The final GOD index is calculated by the rating the parameters for each aquifer according to the GOD flowchart. The map of aquifer's vulnerability to pollution is shown in Figure 12. Because the TWAP database does not is not yet a completed dataset, only for ten aquifers a GOD index showing the vulnerability could be calculated. The high aquifer vulnerability occurs in Uruguay, Senegal and Ethiopia which is assigned 0.45, 0.63 and 0.54 GOD index. Argentina and Zimbabwe present the low aquifer vulnerability with indices of 0.14 and 0.135. The moderate degree exists in Mexico and Central African Republic.

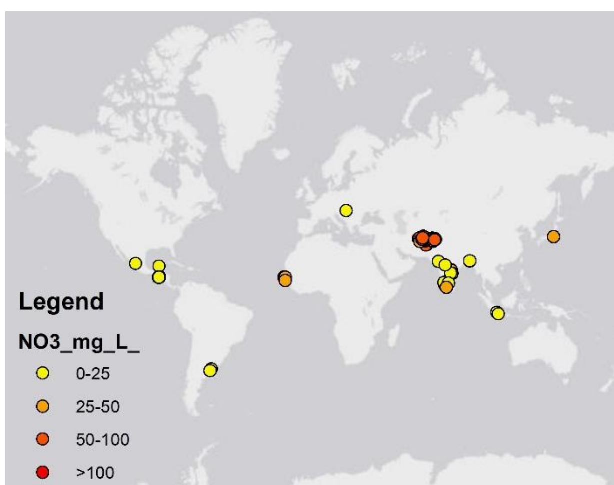

Figure 13 Groundwater nitrate concentration in the sampling wells around the world

Figure 13 shows data coming from GEMstat provided by the Federal Institute of Germany. Around 700 well point data were measured during the period from 1990 to 2013. The majority of data point was measured in Asia, especially in Afghanistan and India. In the map, most of points with nitrate concentration above 100 mg/L in the groundwater is in Afghanistan. The rest of points present the nitrate level below 25 mg/L in America and Asia countries.

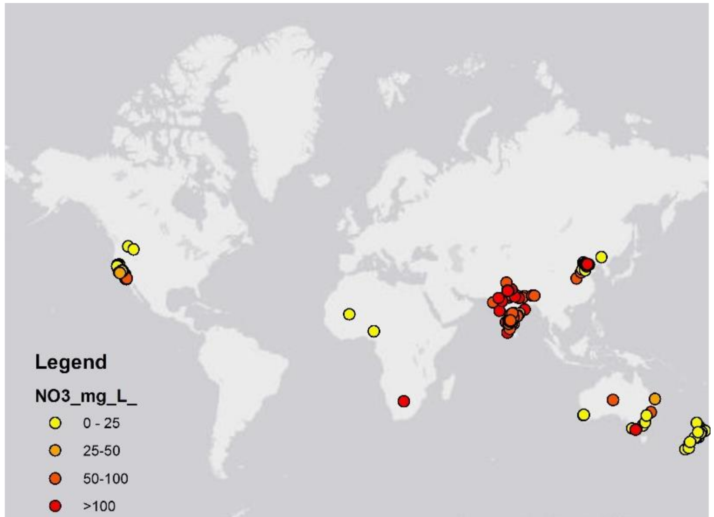

Figure 14 Groundwater nitrate concentration in the different regions of the world

The distribution of nitrate level in groundwater is presented in Figure 14. The data points represent the nitrate concentration in the certain region of the country. The data was collected from the annual report of different environmental protection authorities. Many data was found from the developed and developing countries, such as United States, India, Australia and New Zealand. These data points only represented the nitrate level in the local regional groundwater system. The high nitrate concentration is located in India with the most of points between 50 mg/L and 100 mg/L, or even higher than 100 mg/L. In contrast, most nitrate levels in New Zealand and Australia were below 50 mg/L, which is the standard for safe drinking water for human health. In some areas of China and United States, nitrate concentration is exceeding the 50 mg/L.

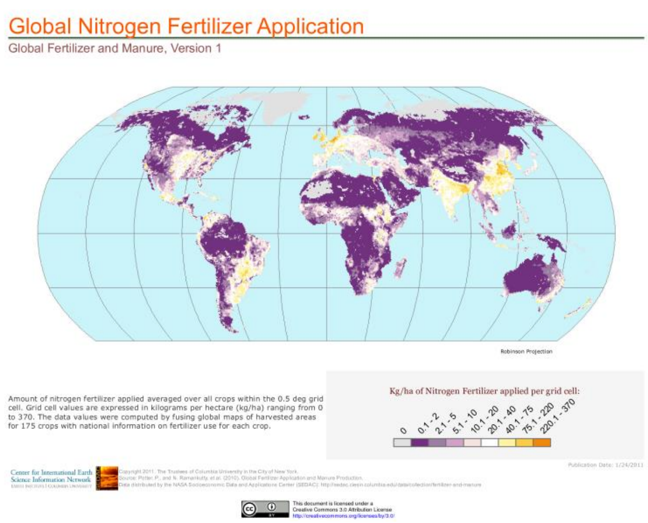

Figure 15 Global nitrogen fertilizer application (source: Potter et al., 2010)

Figure 15 demonstrates the application of nitrogen fertilizer globally. The high nitrogen fertilizer application usually occurs in the same regions of high nitrogen manure production, especially in Asia, Europe and South America. For the majority areas in the world, nitrogen fertilizer application keeps a normal level. The map is computed by combining global map of harvested areas for 175 crops with national information on fertilizer use for each crop.

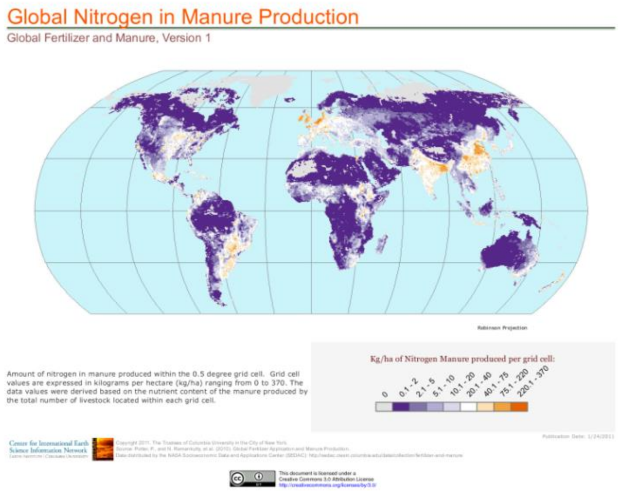

Figure 16 Global nitrogen in manure production (source: Potter et al., 2010)

Figure 16 describes the nitrogen in manure production in the world. The highest concentration of nitrogen manure occurs in Asia and Europe with 220 - 370 kg/ha. This figure corresponds to Figure 15 on the application of nitrogen fertilizer. The data values are derived based on the nutrient content of the manure produced by the total number of livestock located within each grid cell.

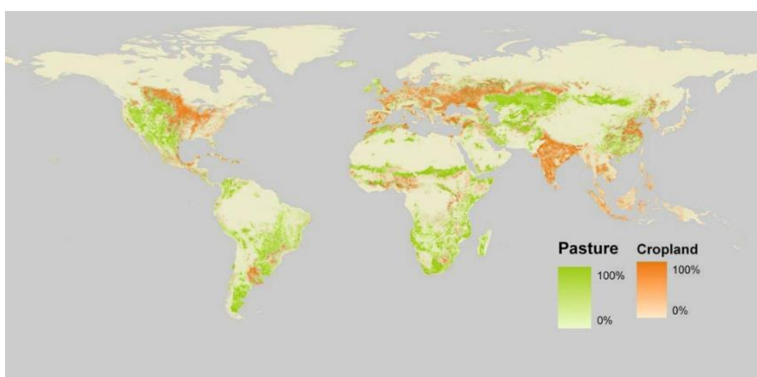

Figure 17 Landuse percentage in the world (source: SAGE, 2005)

Figure 17 shows the percentage of global landuse as pasture and cropland. It is clearly seen the high percentage of cropland exists in the North America, Europe and Asia with orange areas. In addition, the high percentage of pasture appears in North/ South America, Africa and Middle East. Both two land uses have the potential effects for the nitrate leaching to the groundwater. Cropland is normally used to agricultural activities with the high possibility of nitrogen fertilizer application. Once the excessive nitrogen fertilizer applied, the region with cropland covering will have high potential nitrate contamination effects.

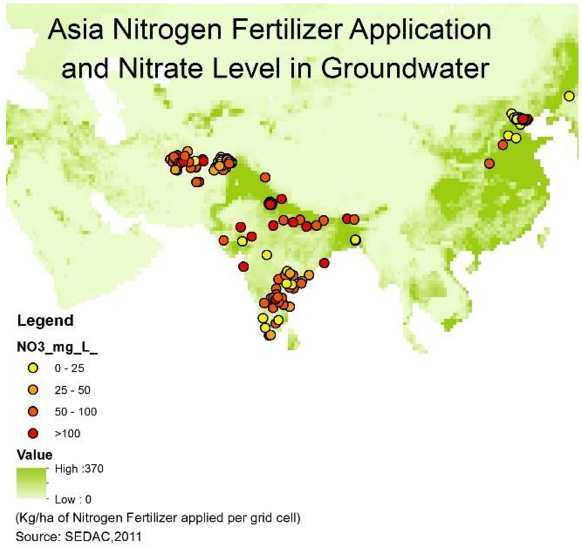

Figure 18 Asia nitrogen fertilizer application and nitrate level in groundwater

Figure 18 present an overlapped map with nitrogen fertilizer application and nitrate level of sampling wells. The background map represents the nitrogen fertilizer application in Asia, with high value in dark green. All the sampling points represent the nitrate concentration in groundwater. Each sampling point was computed by average level. It was measured through the certain local or regional case study. Obviously, the high nitrate level occurs in India, Afghanistan and north part of China. Furthermore, the majority of point is corresponding to the area with high nitrogen fertilizer input.

7. Discussion

Due to time limitation and lack of data availability, the final result does not present a completed global overview for nitrate contamination in groundwater. Although many studies on nitrate contamination are available online, they are mostly focusing on developed countries. In addition, although many researchers study nitrate contamination in groundwater, the majority focuses on local study areas. It is challenging to integrate all the available regional studies, to a national or global level. Based on the collected data from literature studies, high nitrate contamination in groundwater was found in Asian countries (see Figure 13 and 14).

On the other hand, the potential for nitrate contamination in groundwater can be analyzed by various indicators. The aquifer's vulnerability to pollution is a significant indicator to assess the potential for groundwater pollution. The aquifer vulnerability map presented in this report was computed using the GOD method. The data for the various parameters were taken from the TWAP database. Unfortunately, the database still contains many data gaps and hence does not contain all required information to provide a global vulnerability map using the GOD methodology. However, for the aquifers for which a GOD vulnerability index could be assigned, the potential of the TWAP database is shown. The DRASTIC method is another valuable method for the validation of the aquifer's vulnerability. The method contains seven parameters which was beyond the scope of the research to collect and analyse the data. The DRASTIC method was therefore not used for the vulnerability assessment. However, the principle of this methodology is very practical to model groundwater vulnerability, both on a regional, and continental scale.

There are many similarities between the global maps representing, nitrogen fertilizer application, nitrogen in manure production and land use (Figure 15, 16 and 17). For instance, the high nitrogen fertilizer application and production occurs in Europe, Asia and Latin America which correspond to high percentage of croplands. One of important reason resulted in the nitrate contamination in groundwater is excessive nitrogen fertilizer application. Therefore, the areas with high percentage in cropland covering could have high opportunity for nitrate leaching to groundwater. In Figure 5, the variation of nitrogen concentration in global watershed significantly occurred in Europe, Asia, Africa and Latin America. In particular, Europe and Asia have a sharply increase on nitrogen concentration compare with the decreasing in Africa and Latin America. In summary, the possibility with high risk of nitrate contamination in groundwater could exist in Europe, Asia and North America.

The challenge of this research is two-fold. The first barrier is lack of available data to make a good global overview. Even though data has been collected, not all countries make data available or have to the political will to share data. On the other hand, the data we have collected (received from among others GEMstat) is presented in various formats measuring units, measuring errors and range of methodologies to collect the data. Combining and comparing these data induces another challenges and might lead to errors in final results. The data presented in maps are average concentrations use for representing the nitrate level in that area. When it used to comparison, some data might have large deviation and influence the results.

8. Conclusion

Groundwater contamination by nitrate is a widespread problem in our world. By affecting the groundwater quality it can cause public health problems, and environmental degradation of ecosystems. All these negative effects can be minimized by proper groundwater management and good governance to mitigate the risks for nitrate contamination. However, in order to better manage nitrate contamination in groundwater systems, researchers, water resources specialists and policy makers do need information on the scope, distribution and severity of groundwater nitrate contamination. In other words, it would be better to facilitate early diagnosis of possible changes and widen their inspiration for selecting effective measures for interventions.

There is limited groundwater monitoring taking place in most African and Latin American countries. The state of development of groundwater quality monitoring globally is divergent. For the countries where data could be collected, the formats and quality of data and amount of metadata provided was highly diverse, thereby bringing additional uncertainty in data collected

Although the lack of data delayed this analysis of this project, it has been a good starting point for a global collection of groundwater quality data. The report has contributed to a first overview on data availability for various countries and the possibilities on vulnerability mapping of groundwater resources. IGRAC advocates an improvement of datasets on groundwater globally in order to acquire detailed observations of this vital natural resource. This internship has led to a successful starting point for a new project initiative from IGRAC to collect groundwater data and join forces with GEMstat (Koblenz, Germany) and the University of Louvain (Belgium).

9. Recommendations

Aquifer vulnerability is a good indicator to evaluate the potential risk of groundwater pollution. In this case, data collected within the TWAP project was used to GOD approach to find the hydrological property of the corresponding inputs. However, many information is missing so that we cannot make an aquifer vulnerability globally. It would be better to collect these missing data in TWAP database so that GOD index can be assigned to the different region for identifying the aquifer vulnerability.

Continue to collect the data of nitrate concentration in groundwater for the certain sampling wells globally, these data points could be used to validate with the nitrate contamination risk map. For example, the high nitrate leaching rate often occurs in the agricultural area. If one sampling spot with high nitrate level locate in the same region with high nitrogen fertilizer application, this region could have high potential risk of contamination.

Many regional or country map with nitrate contamination in groundwater available online, it can be digitized in the ArcGIS. I would suggest to digitize all these online available map first, and make a rough global overview. And then for some underdeveloped areas without any information about groundwater quality, aquifer vulnerability or nitrate leaching risk map can be used to explain the nitrate contamination problem.

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