GROUNDWATER QUALITY VULNERABILITY ASSESSMENT IN NORTH DAKOTA

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

MASTER OF SCIENCE

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ABSTRACT

In North Dakota, arsenic and nitrate are two major groundwater contaminants. These contaminants originate from either natural geologic or anthropogenic sources. Differences in geology, hydrology, geochemistry, and chemical use explain how and why concentrations of these groundwater contaminants vary across the regions. Based on these properties, a research was carried out to identify the potential groundwater quality vulnerable regions. For vulnerability assessment, modified DRASTIC-G and Susceptibility Index model were used for arsenic and nitrate, respectively. Our research showed that approximately 21 and 28 % of the study area fall within high arsenic and nitrate vulnerable areas, respectively. Our study also identified 33 out of the 84 high risk arsenic and 16 out of 28 high risk nitrate observation wells fall within the high arsenic and nitrate vulnerability areas, respectively. These developed maps can be used as a starting point for identifying probable groundwater vulnerable areas and future decision making.

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DEDICATION

Dedicated to my Beloved Family.

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1. INTRODUCTION

Groundwater is the most important natural resource for reliable and economic source of water supply around the world. It is one of the most widely extracted natural resource as it is intensively consumed to meet various domestic, agricultural and industrial demands. Its use has significantly increased in recent decades and global groundwater withdrawal rate was about 700-800 km^3/year in 2004 (Zektser and Everett, 2004). With the increasing demand and withdrawal worldwide, groundwater systems are experiencing increasing threats and risk of pollution. These threats are coming from various natural as well as anthropogenic sources. Contaminations of groundwater from these sources affect its suitability for different uses.

In the United States, one out of every five groundwater wells sampled were found to be potentially human health concerning due to the contaminants from either geologic or anthropogenic sources (USGS, 2015a). Most of these contaminants originate from natural geologic sources, such as manganese, radon, arsenic, and uranium. Nitrate is the only contaminant in the groundwater that comes from anthropogenic sources that exceeded its human-health risk benchmark in more than 1 percent of the studied wells. Although groundwater is still considered to be a safe and reliable source of drinking water for millions of people nationwide, presence of high concentrations of some of these contaminants can pose potential human-health risks (USGS, 2015a).

In the United States, there are currently 62 major aquifer systems (USGS, 2015a). Among these aquifer systems, the glacial aquifer system underlies much of the northern United States including North Dakota. Approximately 1/6 of the United States population (more than 41 million people) count on the glacial aquifer system for drinking water. In the glacial aquifer system regions, the major groundwater contaminants from geologic source includes arsenic and manganese. In these regions, elevated concentrations of nitrate and pesticides in groundwater were observed even in areas of intensive agriculture practices (USGS, 2015b).

Among the currently available contaminants in groundwater, arsenic is one of the most hazardous reoccurring heavy metal pollutants found worldwide. Long-term consumption of drinking water containing high levels of arsenic can lead to serious health problems such as increased risk of cancer in the skin, lungs, bladder, and kidney (Smith et al., 2000). Due to its serious health effects, the World Health Organization (WHO) has set a maximum concentration level (MCL) of 10 μg/L of arsenic in drinking water (Berg et al., 2006).

High arsenic concentrations in groundwater have been documented in many areas of the United States. Within the last decade, parts of Maine, Oklahoma, Michigan, Wisconsin, Minnesota, and South Dakota have been found to have widespread arsenic concentrations exceeding 10 μg/L (Welch et al., 1999). In North Dakota, arsenic in groundwater has become an issue recently when Leonard-area residents suffered from high levels of poisonous arsenic (Inforum, June 29, 2015). The residents complained that there is scant regulation of private wells in North Dakota, and rural residents are on their own to test not only for bacteria but also for trace elements like arsenic in their well water, with little guidance from state health officials. After a detailed test, it was observed that arsenic that occurs naturally in the ground was leaching into the water well on Wadeson's farmstead southwest of Leonard, just inside the Ransom County line. Arsenic concentration in some well water of the area were almost 4½ times higher than the MCL deemed safe for community water supplies. The concentration in the affected person’s blood was slightly higher, 5½ times the safe level for drinking water exposure (Inforum, June 29, 2015).

Another important groundwater quality contaminant is nitrate. Due to continued higher yield demands and relatively low cost of nitrogenous fertilizers per unit of yield increase, the use of nitrogenous fertilizers has increased substantially. This has resulted in increased nitrate concentrations in the groundwater, especially in regions with coarse-textured soils and shallow groundwater (Burkart and James, 1999). The application of fertilizer and pesticides on croplands has often been shown to result in deterioration of the quality of the groundwater and increasing health concerns, such as blue baby syndrome, gastric cancer and non-Hodgkin's lymphoma (Knobeloch et al., 2000; Karkouti et al., 2005). Natural resource managers are increasingly concerned about human health and ecological effects of contaminants such as nitrates and pesticides (Merchant, 1994; Sampat, 2000).

Differences in geology, hydrology, geochemistry, and chemical use explain how and why aquifer vulnerability and concentrations of contaminants vary across the nation. Factors such as the mineral composition of aquifer materials, how groundwater moves through an aquifer, geochemical conditions like redox, and what chemicals are used and disposed of on the land surface all affect contaminant occurrence and vary among principal aquifers (USGS, 2015a). As a consequence, different contaminants occur more or less frequently in some aquifers than others. Understanding how these factors act is used to predict concentrations in some aquifers, such as arsenic and nitrate in the southwest, through in-depth assessments of regional groundwater quality (USGS, 2015a). Based on the understandings of these factors, a number of models for identifying and mapping groundwater vulnerability have been developed (Focazio et al., 2005). These models typically consider all of the natural hydro-geologic characteristics that are thought to be involved in aquifer vulnerability such as depth of water, soils, aquifer hydrogeology, and groundwater recharge.

An understanding of the status and vulnerability assessment of groundwater arsenic concentrations can help with the following: (1) assist water managers and users in overcoming adverse health effects through avoidance or treatment, (2) provide a basis for evaluating the costs of adopting a particular value for a drinking-water standard (or MCL), and (3) assist epidemiologists interested in evaluating the intake of arsenic from drinking water, which can contribute much of the human exposure to inorganic arsenic (Welch et al., 1999).

1.1. Objectives

Objectives of our study will be to:

a) Evaluate groundwater quality vulnerability for arsenic in North Dakota using the modified DRASTIC-G model.

b) Analyze groundwater quality vulnerability for nitrates in North Dakota using the modified DRASTIC model, i.e., SI Index model (Stigter et al., 2006; Bartzas et al., 2015).

2. LITERATURE REVIEW

2.1. Groundwater Quality in North Dakota

Groundwater is an important resource for North Dakota. Approximately 62% of the people here rely on groundwater, and almost all of the rural population depends on groundwater for their daily domestic needs (Radig, 1997). Currently in North Dakota, groundwater provides 51% of all drinking water for the total population and 99% for the rural population (NDDoH, 2016). It also provides 37% of the irrigation water in North Dakota (NDDoH, 2016).

North Dakota is mostly an agricultural state. But there is a very little information available to determine whether agricultural chemicals have widely impacted groundwater quality in the state or not. However, there is a potential that groundwater quality may be impacted from agricultural chemicals, based on water quality monitoring conducted in other states. Groundwater quality may also be impacted from the geologic aquifers (NDDoH, 2016).

In North Dakota, approximately 40 million acres of land are used for agricultural farming and ranching (USDA, 2017). Therefore, the effects of agricultural chemicals like nitrate on groundwater quality are a major concern. In 1986 Water Supply and Pollution Control Division of North Dakota Department of Health (NDDoH) analyzed 218 samples of water from private and municipal groundwater wells for a suite of synthetic organic chemicals. Among those, groundwater was found to contain trace concentrations of pesticides in 14 sites (Nelson, 1987). However, none of the concentrations were large enough to pose a health hazard. The most commonly detected chemical was picloram (Nelson, 1987). They also observed nitrate concentrations in excess of 10 mg/L in 22 private, irrigation and observation groundwater wells south of the Town of Oakes. Groundwater contamination of nitrate has also been detected in many farmlands, feedlots, and corrals (Nelson, 1987).

Under their groundwater monitoring program, NDDoH collected groundwater samples from 756 wells during their first five years (NDDoH, 1999). Of those samples, 62 wells (8 % of the wells sampled), contained noticeable concentrations of one or more pesticides. Approximately half of all pesticide detections occurred in two aquifers: Elk Valley and Sheyenne Delta. They observed 21 pesticide species during the monitoring period; picloram was the pesticide detected most often, accounting for 39 of 83 detections. Groundwater samples from 295 wells (39 % of the wells sampled) had nitrate plus nitrite concentrations greater than or equal to 0.05 mg/l. Approximately half of the nitrate detections occurred at concentrations less than 1.0 mg/l. Thirty-eight of the wells (5% wells) had nitrate concentrations greater than or equal to the MCL of 10.0 mg/l (N). NDDoH assumed that most of these pesticide and nitrate detections were associated with point sources of contamination (NDDoH, 1999).

In North Dakota, groundwater arsenic concentrations of greater than 50 μg/L were observed in four areas in Ransom, Sargent, and Richland Counties (Roberts et al., 1985). These regions are located in the southeastern part of the State, where the dominant aquifer system is glacial aquifer. These areas cover approximately 170 square miles and are close to the town of Lidgerwood. The sources of arsenic are considered to be from natural leaching from earth materials and from the application of arsenic-laced grasshopper bait used in the area through 1947 (Roberts et al., 1985). The arsenic contamination was examined during a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund remedial investigation (Roberts et al., 1985).

2.2. Sources of Arsenic and Nitrate in Groundwater

2.2.1. Sources of Arsenic

Arsenic (atomic number 33; relative atomic mass 74.91) is a metalloid widely distributed in the earth's crust. It may occur in trace quantities in all rock, soil, water and air (WHO, 2001). It is the main constituent of more than 200 mineral species, of which about 60% are arsenate, 20% sulfide and sulfosalts and the remaining 20% include arsenides, arsenites, oxides and elemental arsenic. The most common of the arsenic minerals is arsenopyrite (FeAsS), and arsenic is found associated with many types of mineral deposits, especially those including sulfide mineralization (Alloway, 1995).

These hazardous reoccurring heavy metal pollutants may be released into groundwater or surface water sources either naturally from geologic formations or by means of various anthropogenic human activities. Mining, smelting of non-ferrous metals and burning of fossil fuels are the major industrial processes that contribute to anthropogenic arsenic contamination of air, water and soil. Historically, use of arsenic-containing pesticides has left large tracts of agricultural land contaminated. The use of arsenic in the preservation of timber has also led to contamination of the environment.

In North Dakota, large concentrations of arsenic, dissolved solids, molybdenum and selenium are introduced to groundwater from fly-ash residues and flue-gas desulfurization wastes from lignite-fired electricity generating plants. Another important anthropogenic source of arsenic is considered to be from the application of arsenic-laced grasshopper bait used in the area through 1947 (National Water Summary, 1986).

Naturally occurring arsenic is common in North Dakota groundwater due to glacial deposits (USGS, 2015b). The concentrations of arsenic vary throughout the state. Arsenic contamination of well water is a longstanding problem throughout much of the Midwest due to glacial deposits. Arsenic concentrations exceeded the WHO maximum concentration level of 10 μg/L in 18 North Dakota towns from 2006 to 2012 (Inforum, May 28, 2015). Those communities included LaMoure, Lidgerwood and Oakes in southeastern part of North Dakota.

2.2.2. Sources of Nitrate

Nitrate is a naturally-occurring ion and is a major part of the nitrogen cycle. Because it is very soluble, nitrate is the most usable form of nitrogen for plants. Nitrate is a common surface water and groundwater contaminant that can cause health problems in infants and animals, as well as eutrophication in surface waters (Fennessy and Cronk, 1997). Nitrate is an effective fertilizer and is used in agricultural activities due to the use of fertilizers and manure application. However, there are other nitrate sources related to urban development that can increase nitrate concentrations in groundwater. Some studies in the last few years have found that nitrate concentrations in some urban aquifers are similar or even higher to those in their surrounding agricultural areas (Ford and Tellam, 1994; Lerner et al., 1999).

Agriculture is the major source of nitrate, but it is not the only one. There are several sources including sewage and mains leakage, septic tanks, industrial spillages, contaminated land, landfills, river or channel infiltration, fertilizers used in gardens, house building, storm water and direct recharge. An overview of these sources is presented in Table 2.1 (Aljazzar, 2010). Within the last decades, nitrate use has gone beyond the plants needs and the capacity of the biosphere to assimilate or eliminate it. Nitrate is carried with the flowing groundwater and might undergo different biochemical processes.

Table 2.1. Source and origins of nitrate in soils and groundwater (Aljazzar, 2010).

Sources	Non-point sources	Point sources
Agriculture	• Use of nitrogenous fertilizers • Use of organic manures	• Accidental spills of N-rich chemicals • Leakage from slurry/manure storage facilities
Domestic	• Chemical combustion • Improper disposal of municipal effluents	• Poorly designed landfills • Septic tanks and leakage from sewage systems
Industrial	• Atmospheric emissions from energy production • Disposal of industrial effluents	• Disposal of N-rich effluents • Poorly designed industrial landfills

2.3. Human Health Effects of Arsenic and Nitrate Exposures

2.3.1. Arsenic

Arsenic is known as carcinogen (IARC, 1987) and has mutagenic and teratogenic effects (ATSDR, 1993). Arsenic occurs in two oxidation states: a trivalent form, arsenite ($As_2O_3^-$, As III) and a pentavalent form, arsenate ($As_2O_5^-$, As V). Trivalent arsenic is 60 times more toxic than pentavalent arsenic and organic arsenic is non-toxic whereas inorganic arsenic is. Trivalent arsenic exerts its toxicity usually by binding thiol or sulfhydryl groups in tissue proteins of the liver, lungs, kidney, spleen, gastrointestinal mucosa, and keratin-rich tissues (skin, hair, and nails)(Cobo and Castineira, 1997).

Arsenic exposure occurs primarily by ingestion of contaminated drinking water. Other ways of exposures are inhalation or absorption through the skin. Arsenic intakes are usually higher from solid foods than from liquids including drinking water (Tripathi et al., 1997). Organic and inorganic arsenic compounds may enter the plant food chain from agricultural products or from soil irrigated with arsenic contaminated water. The major site of absorption is the small intestine by an electrogenic process involving a proton (H^+) gradient (Ratnaike and Barbour, 2000).

Arsenic affects people regardless of sex. Symptomatology of arsenical toxicity may develop insidiously after 6 months to 2 years or more, depending on the amount of water intake and the arsenic concentration in the water sample. The higher the concentration of arsenic in water and the higher the amount of daily water intake, the earlier one of clinical features may appear. Darkening of skin (diffuse melanosis) in the whole body or on the palm of the hand is the earliest symptom. People suffering from arsenic toxicity do not necessarily show symptoms of diffuse melanosis. Spotted pigmentation (spotted melanosis) is an early symptom that is common and is usually seen on the chest, back, or limbs. Leucomelanosis (white and black spots side by side) is also seen on many patients (Smith et al., 1992). Leucomelanosis is common in persons who have stopped drinking arsenic-contaminated water but who previously had spotted melanosis. Buccal mucus membrane melanosis (diffuse, patchy, or spotted melanosis) on the tongue, gums, lips, etc. may also be manifestations of arsenic toxicity (Khan et al., 2003).

In chronic arsenic ingestion, arsenic accumulates in the liver, kidneys, heart, and lungs and smaller amounts in the muscles, nervous system, gastrointestinal tract, and spleen. Though most arsenic is cleared from these sites, residual amounts remain in the keratin-rich tissues, nails, hair, and skin. After about two weeks of ingestion, arsenic is deposited in the hair and nails (Ratnaike, 2003).

Keratosis is a late feature of arsenical dermatosis. Diffuse or nodular keratosis on the palm of the hand and the sole of the foot is a sign of moderately severe toxicity. Rough dry skin, often with palpable nodules (spotted keratosis), in dorsum of hands, feet, and legs are symptoms seen in severe cases (Rahman et al., 1998). However, pigmentation or nodular rough skin alone may not confirm arsenic patients until hair/nail samples show elevated levels of arsenic, but a combination of pigmentation (melanosis) and nodular rough skin (spotted palmoplantar keratosis) in a victim is a sure sign of arsenic toxicity.

Arsenic in drinking water has also been found to affect the pregnancy of the women. In their study Ahmad et al. (2001) observed significantly higher adverse pregnancy outcomes in terms of spontaneous abortion, stillbirth, and preterm birth rates in the arsenic exposed group than those in the non-exposed group. Arsenic toxicity causes the abnormal development of the embryos. Exposure to arsenic also exerted direct adverse effects on explanted rodent embryos exposed to arsenic outside the maternal system. However, there was a poor correlation between maternal and developmental toxicity in an extensive literature analysis (Abul et al., 2005).

2.3.2. Nitrate

Nitrate has a low toxicity except at massive doses and is generally of no concern with respect to human health. However, under certain circumstances nitrate can be reduced to nitrite and acts as a main cause of blue-baby disease and might have some contributions to stomach and colon cancer (WHO, 2004; Yang et al., 2007). The immediate health concern of nitrate is therefore through its reduction to nitrite in the digestive tract by the active nitrate reducing bacteria. Thus, nitrite and N-nitrosamines compounds coexist often with nitrate and are biologically active in human body (Sprent, 1987; McLay et al., 2001). Nitrite is readily absorbed into the blood where it combines with the haemoglobin and converts it into 40 metahemoglobine which is not able to carry oxygen. This phenomenon is a well-known disease especially among infants and is known as blue-baby syndrome or methemoglobinemia (Curry, 1982; White and Weiss, 1991). Ingestion of NO_3 in drinking water has caused methemoglobinemia in infants under 6 months of age and caused the death of a South Dakota infant (Johnson et al., 1987). The noncancerous acute toxicity of NO_3 is the U.S. Environmental Protection Agency's (USEPA) basis for establishing a maximum contaminant level (MCL) for NO_3-N in drinking water. Although acute toxicity generally has been documented at concentrations greater than 50 mg/L NO_3-N, the MCL has been set at 10 mg/L (Spalding and Exner, 1993).

The relationship between nitrate levels in drinking water and cancer has been inconclusive. Nitrogen-nitrosamine compounds are some of the strongest known carcinogens. They have been found to induce cancer in variety of organs in various animal species including higher primates (Jalali, 2005). Consequently, nitrates may also have a possible role as procarcinogenics (Almasri and Kaluarachchi, 2004). It was documented that there was no significant difference in stomach cancer rates between a high nitrate area and a similar low nitrate area in the UK. A study on the incidence of cancer in Britain farmers working in a fertilizer plant showed that no significantly higher cancer rates were observed in a control group of similar workers (Croll and Hayes, 1988).

2.4. Groundwater Quality Vulnerability Assessment Models

A number of groundwater quality vulnerability assessment models are currently available. Each model has its specific objectives and data requirements. Some of the currently available models are briefly discussed below with their specific objectives and data requirements.

2.4.1. DRASTIC Model

DRASTIC method, developed by the USEPA, is one of the most frequently used approaches to assess vulnerability to groundwater contamination (Bartzas et al, 2015). It includes seven parameters, specifically, namely depth to water (D), net recharge (R), aquifer media (A), soil media (S), topography (T), impact of vadose zone (I) and hydraulic conductivity (C), as weighted layers to enable a reliable assessment of vulnerability.

The DRASTIC index is often used to standardize the evaluation of groundwater pollution potential within various hydrogeological settings. For the calculation of the DRASTIC index it assumes that, (1) the contaminant is introduced at the ground surface; (2) the contaminant is flushed into the groundwater by precipitation; (3) the contaminant has the mobility of water; and (4) the area evaluated is 0.4 km2 or larger (Aller et al., 1987, Neukum et al., 2008). The DRASTIC method calculates an index derived from ratings and weights assigned to the seven parameters mentioned earlier. The DRASTIC index is quantified by a linear combination of ratings and weights of the seven parameters and is expressed in Eq. (2.1):

$$DRASTIC = D_r D_w + R_r R_w + A_r A_w + S_r S_w + T_r T_w + I_r I_w + C_r C_w \qquad (2.1)$$

where, D is the depth of water, R is recharge, A is the aquifer, S is soil, T is topography, I is the impact of vadose zone, and C is the conductivity. In the equation, r denotes the rating for the particular property and w is the weight for that property.

Each of the seven parameters are classified into several classes and assigned scores from 1 to 10, while the seven parameters are assigned weights ranging from 1 to 5 depending on their impact significance (Table 2.2). There are two weighting models in DRASTIC methodology, first one is for normal circumstances (Generic DRASTIC) and the second one is for intensive agricultural activities (Pesticide DRASTIC). The higher the values of the DRASTIC index, the greater the groundwater vulnerability to contamination.

Table 2.2. Parameters and weights for DRASTIC index.

Parameter	Acronym	Generic DRASTIC Weight	Pesticide DRASTIC Weight
Depth of water	D	5	5
Net recharge	R	4	4
Aquifer media	A	3	3
Soil media	S	2	5
Topography	T	1	3
Impact of vadose zone	I	5	4
Hydraulic conductivity	C	3	2

2.4.2. Susceptibility Index

Susceptibility Index (SI) (Stigter et al., 2006, Bartzas et al., 2015) is a modification of the well-established DRASTIC method by including a new parameter called land use and eliminating the DRASTIC parameters of soil media (S), impact of vadose zone (I) and hydraulic conductivity (C). This new parameter considers the impact of agricultural activities (such as fertilizer and pesticide application) on groundwater quality. In their studies, Stigter et al. (2006) mentioned that even though soil media can largely effect the attenuation potentiality of certain contaminants, its effect on groundwater vulnerability can be indirectly estimated by considering land use. This is because the quality of natural soils often changes during land cultivation. The SI is quantified by a linear combination of ratings and weights of the four parameters and is expressed using Eq. (2.2):

$$SI = D_r D_w + R_r R_w + A_r A_w + T_r T_w + LU_r LU_w \tag{2.2}$$

where, again D is for the depth of water, R is recharge, A is the aquifer, T is topography, LU is the land use. In the equation, r denotes the rating for the particular property and w is the weight for that property. Table 2.3 presents the assigned weights for each of these parameters according to the SI method (Bartzas et al., 2015). The principal classes of land use and their assigned ratings according to the SI approach are given in Table 2.4.

Table 2.3. Parameters and weight settings in SI method

Parameter	Acronym	SI Index Weight
Depth of water	D	0.186
Net recharge	R	0.212
Aquifer media	A	0.259
Topography	T	0.121
Land use	LU	0.222

Table 2.4. Ratings for land use/land cover parameter in the Confined Animal Feeding Operations (CAFO) DRASTIC model (Dickerson, 2007).

Land Use/Land Cover	Rating
Cultivated Crops	10
Barren Land (Rock/Sand/Clay)	8
Developed – High Intensity	5
Shrub/Scrub	4
Grassland/Herbaceous	4
Pasture/Hay	4
Developed – Open Space	3
Developed – Low Intensity	3
Developed – Medium Intensity	3
Deciduous Forest	2
Evergreen Forest	2
Mixed Forest	2
Open Water	1
Woody Wetlands	1
Emergent Herbaceous Wetland	1

2.4.3. PSR Sustainability Framework

Pressure-States-Response (PSR) based risk index development framework was first proposed by Rapport and Friend (1979) and then fully developed by the Organization for Economic Cooperation and Development (OECD, 1993). It is a systematic mechanism that helps to monitor the status of an environment or sustainable development of natural resources and environmental ecology. The PSR model divides the risk factors in terms of pressure, state, and response, following the logic that “pressure on the environment from human and economic activities, leads to changes in the state (or environmental conditions) that prevail as a result of that pressure, and may provoke responses by society to change the pressure and state of the environment" (OECD, 1999).

For any specific region, the risk factors to be included in the PSR framework are mainly dependent upon contaminant transport processes and data availability for that specific landscape. Therefore, there is no universal set of risk factors that should apply to all regions or countries (Huang et al., 2010). In principle, the selected indicators should be policy-relevant, understandable, easily available, and measurable (Huffman et al., 2000; Niemeijer and de Groot, 2008). The biggest advantage of selecting the risk factors under the PSR framework is to purposely select a set of risk factors rather than randomly select a bunch of individual factors. In other words, the risk factors will be chosen to be complementary rather than redundant to each other and the whole set will reflect all aspects of the groundwater pollution.

Once a set of risk factors are selected for a specific study area under the PSR framework, a composite risk index (CRI) for groundwater contamination at assessment unit (usually grid cell) i can be calculated using a weighted linear model (Gilfedder and Walker, 2001):

$$CRI_i = \sum_{j=1}^{m} r_{ij} \times w_j \tag{2.3}$$

where m is the total number of risk factors selected; w_j is the weight assigned to the jth risk factor; and r_{ij}'s are the so-called grey relational coefficients between two normalized comparable sequences x_{i0} and x_{ij} (Rao and Yadava, 2009; Zhou et al., 2013). The grey relational coefficients reflect the degree of closeness between the two sequences.

Grey relational coefficients (r_{ij}'s) of a grey model are calculated using the formula below (Zeng et al., 2007; Rao and Yadava, 2009):

$$r_{ij} = \frac{min_i min_j \{|x_{ij} - x_{i0}|\} + b max_i max_j \{|x_{ij} - x_{i0}|\}}{|x_{ij} - x_{i0}| + b max_i max_j \{|x_{ij} - x_{i0}|\}} \tag{2.4}$$

here the value of r_{ij}'s ranges between 0 and 1, with higher values indicating stronger affiliation between the two sequences. In the equation, b is a unique coefficient with a value ranging between 0 and 1. The purpose of this coefficient is to weaken the effect of the maximum absolute difference between the two sequences (i.e., $\{|x_{ij} - x_{i0}|\}$ in Eq. (2.4)). In many studies the value of b was assumed to be 0.5 (Pai et al., 2007).

2.4.4. Health Risk Assessment of Arsenic Contaminated Groundwater

Potential health risk from arsenic contaminated groundwater can be estimated using the valid methodological principles and procedures of health risk assessment provided by USEPA (1999). In this method, a screening procedure is used based on the evaluation of two of the most important factors contributing to potential effects of chemicals - analytical concentration and toxicity:

$$R_r = \frac{C_{ij} \times T_{ij}}{\sum_{i=1}^{n} C_{ij} \times T_{ij}} \tag{2.5}$$

where R_r is risk rate of the chemical i in medium j on total risk (–), C_{ij} is (the highest) concentration of the chemical i in medium j (mg l–1), T_{ij} is toxicity value for a chemical i in medium j. The toxicity value for any chemical is equivalent to the ratio between its chronic effects [$(1/RfD)$, mg/ kg-day] and carcinogenic effects or cancer slope factor [CSF, (mg/kg-day)-1. For this purpose we can use potentially toxic elements and significant groundwater contaminants like As, Ba, Cd, Cu, Hg, Pb, Sb, Se and Zn in the risk rate calculation.

Arsenic chronic risk level will be calculated using the formula below:

$$HQ \; = ADD/RfD \tag{2.6}$$

where HQ is the hazard quotient (–), ADD is the average daily dose (mg/kg-day), RfD is the reference dose (mg/kg-day); for As, this is 0.0003 mg/kg-day).

The carcinogenic risk level will be calculated as:

$$CR = ADD \times CSF \tag{2.7}$$

where CR is the cancer risk (–), ADD is the average daily dose (mg/kg-day), CSF is the cancer slope factor (mg/kg-day–1).

A list of currently available groundwater quality vulnerability assessment models with their data requirements and availability for North Dakota is provided in Table 2.5.

Table 2.5. Currently available groundwater quality vulnerability assessment models with their data requirements.

Model	Data Required	Data availability for ND	Output
PSR sustainability framework using grey relational coefficients (R_{ij}) (Zhou et al., 2013)	(1) Topography map	Available	Risk assessment
	(2) Monthly average ET to precipitation ratio	Available	
	(3) Remote sensing image to calculate i) Distance to irrigation channel ii) Distance to drainage channel iii) Normalized difference vegetation index (NDVI)	Available	
	(4) Depth of groundwater	Available	
	(5) Soil and groundwater salinity/As	Available	
	(6) Land use/Cropping index	Available	
	(7) Population density	Available	
	(8) Fertilizer/pesticide inputs	Available	
DRASTIC (Bartzas et al., 2015)	(1) Depth of groundwater	Available	Groundwater vulnerability
	(2) Net recharge	Available	
	(3) Aquifer media	Available	
	(4) Soil data	Available	
	(5) Elevation/topography	Available	
	(6) Impact of vadose zone	Not Available	
	(7) Hydraulic conductivity	Not Available	
Health Risk Assessment (RISC) (Rapant and Krcˇmova, 2007)	Arsenic concentration	Available	Human health risk assessment
	Reference dose (RfD) values of heavy metals	9 metal found	
	Water consumption rate		
SI (susceptibility index) (Bartzas et al., 2015)	Depth to water table from the soil surface	Available	Groundwater vulnerability
	Net recharge	Available	
	Aquifer media	Available	
	Topography	Available	
	Land use data	Available	

3. MATERIALS AND METHODS

3.1. Study Area

Our study area covered three counties of North Dakota that includes Ransom, Richland, and Sargent (Figure 3.1). Total area of the study area is 3176 mi2 (8225.8 km2), in which 864 mi2 (2237.7 km2) is in Ransom County, 1,445 mi2 (3742.5 km2) in Richland County, and 867 mi2 (2245.5 km2) in Sargent County. According to 2015 census data, total population of the study area were 25726 (Ransom: 5448, Richland: 16402, Sargent: 3876).

These areas are located on the southeastern corner of the state and are part of the Glaciated Plains, an area characterized by nearly level to undulating topography (Nolan et al., 1998). These areas are reported to have high nitrate vulnerability (Nolan et al., 1998) and high groundwater arsenic concentrations of greater than 10 µg/l in at least 25% or more of the wells (Ryker, 2001). In these study areas, nitrate contamination of groundwater has been detected at many feedlots, corrals, and farmsteads. Sources of groundwater arsenic in the study area are considered to be natural geologic formations of glacial drifts and application of arsenic-laced grasshopper bait used in these areas through 1947 (Garklavas, 1987). Leonard-area residents who suffered from high levels of poisonous arsenic falls within the study area.

3.2. Groundwater Well Arsenic and Nitrate

Our study site had a total of 849 groundwater observation wells. Of these 849 wells, 191 wells had arsenic concentration greater than 0 µg/l, and 84 well had arsenic concentration greater than maximum concentration limit of 10 µg/l. Of these 84 wells, maximum 47 wells fall within Sargent County, and Richland and Ransom had 26 and 11 wells respectively.

For nitrate, 130 out of 849 wells had some sorts of nitrate in the groundwater. Of these 130 wells, only 28 wells had nitrate concentrations greater than maximum concentration level of 10 mg/l. These 28 wells fall within two county, Ransom (23 wells) and Sargent (5 wells).

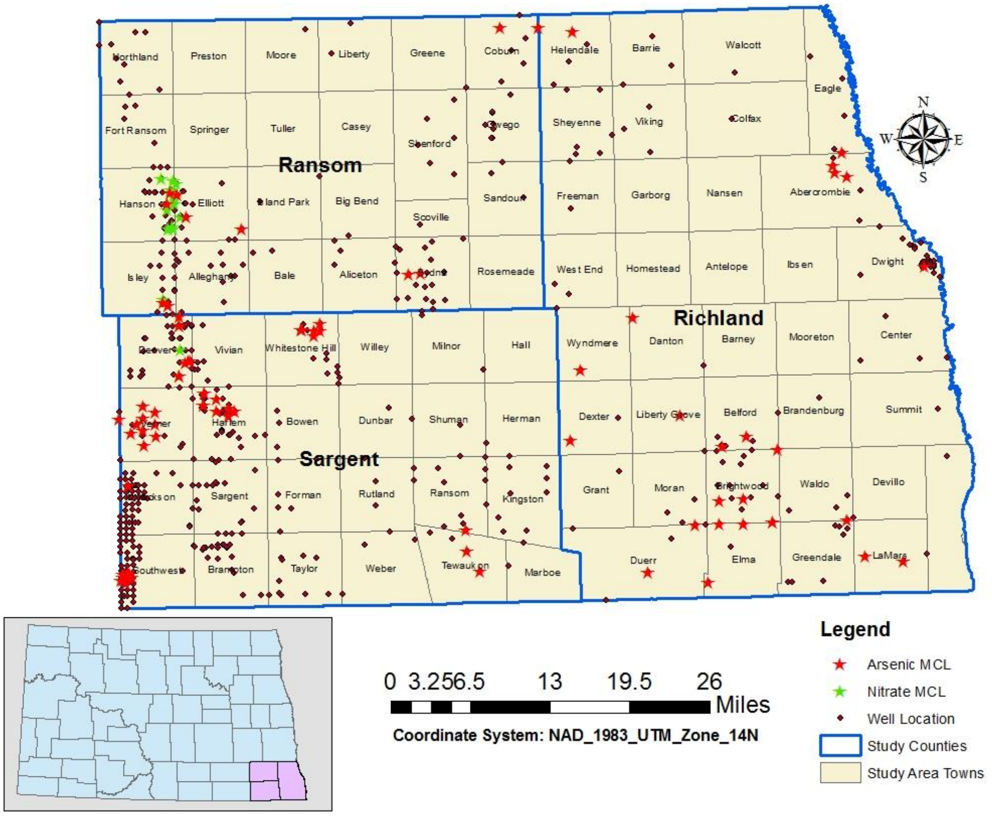

Figure 3.1. Study area showing well locations and wells with maximum concentration level (MCL) of arsenic and nitrate.

3.3. Data Sources and Preprocessing

3.3.1. Data Sources

GIS data for soil, topography and land use land cover were collected from NRCS geospatial data gateway (https://gdg.sc.egov.usda.gov). Aquifer, groundwater recharge, groundwater level and groundwater quality data were collected from various USGS websites. Geology data for the study area were collected from ND GIS hub (https://apps.nd.gov/hubdataportal/srv/en/main.home). Data for impact of vadose zone and hydraulic conductivity were not readily available. These data were estimated based on the SWAT SSUGRO soils lockup table. Links for the data are listed below:

NRCS Geospatial Data gateway: https://gdg.sc.egov.usda.gov/

ND GIS Hub: https://apps.nd.gov/hubdataportal/srv/en/main.home

Aquifer Data: http://water.usgs.gov/ogw/aquifer/map.html

Groundwater recharge: http://water.usgs.gov/GIS/metadata/usgswrd/XML/rech48grd.xml

GW levels and quality:

http://nwis.waterdata.usgs.gov/nwis/gwlevels?search_criteria=state_cd&submitted_form=introduction

3.3.2. Creation of Map Layers

3.3.2.1. Depth of Water

Depth of water level data collected were linked with the well locations in ArcGIS, and a point shapefile was created. The point shapefile was then converted to raster file (30 m resolution) using Krigging interpolation method and clipped for the study area. The raster file was then reclassified using the NDDoH rating guidelines (NDDoH, 2015) for modified DRASTIC and Stigter et al. (2006) for susceptibility index. A list of the ratings for the modified DRASTIC and SI are given in table 3.1 corresponding rating maps for DRASTIC-G and SI are shown in Figure 3.2.

Table 3.1. Ratings for depth of water.

Depth of water (ft)	Ratings for DRASTIC (NDDoH, 2015)	Ratings for SI (Stigter et al., 2006)
0-5	10	100
5-15	9	90
15-30	7	70
30-50	5	50
50-75	3	30
75-90	2	20
> 90	1	10

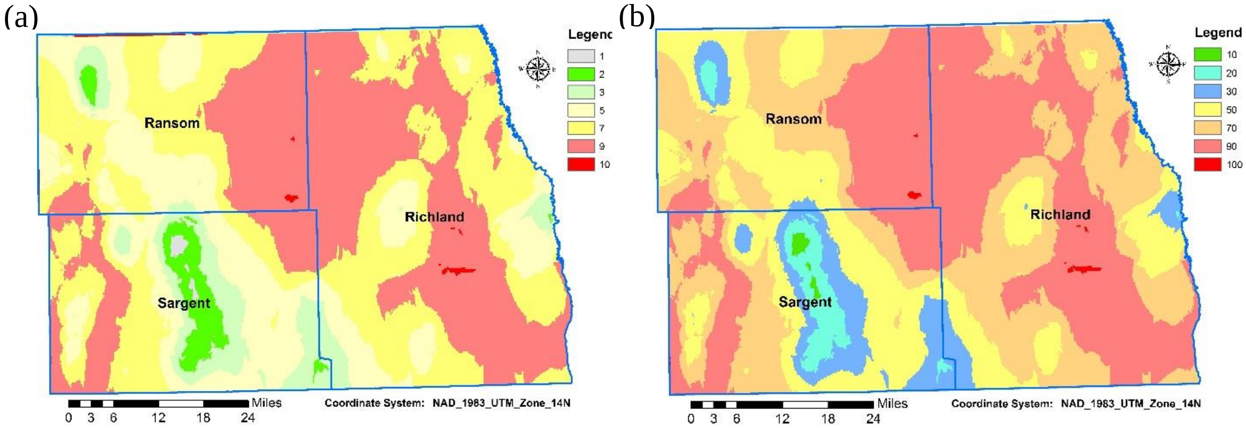

Figure 3.2. Depth of water rating maps for (a) DRASTIC-G, (b) SI for the study area.

3.3.2.2. Net Recharge

Net recharge data was collected from USGS study on estimated mean annual natural ground-water recharge in the conterminous United States. Net recharge for the study area was clipped for the study area and reclassified based on NDDoH rating guidelines (NDDoH, 2015) for modified DRASTIC and Stigter et al. (2006) for susceptibility index. A list of ratings used for modified DRASTIC and SI are listed in table 3.2 and corresponding rating maps for DRASTIC-G and SI are shown in Figure 3.3.

Table 3.2. Ratings for net recharge.

Net recharge	Ratings for DRASTIC (NDDoH, 2015)	Ratings for SI (Stigter et al., 2006)
4-7	6	60
7-10	8	80
≥ 10	9	90

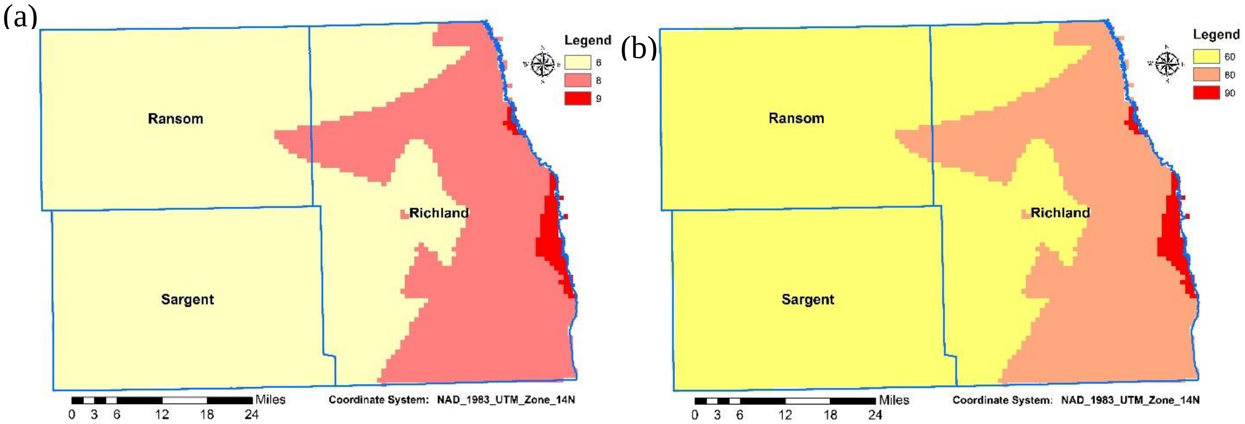

Figure 3.3. Net recharge rating maps for (a) DRASTIC-G, (b) SI for the study area.

3.3.2.3. Aquifer

Aquifer data were classified into two groups, glacial or non-glacial origins. Highest rating was provided for the glacial origin aquifer because it is considered to be responsible for arsenic and other major contaminants in groundwater in the upper Midwest (Erickson and Barnes, 2005). A list for aquifer ratings are listed in table 3.3 and corresponding rating maps for DRASTIC-G and SI are shown in Figure 3.4.

Table 3.3. Ratings for aquifer.

Net recharge	Ratings for DRASTIC	Ratings for SI
Glacial aquifer	10	100
Non-glacial	5	50

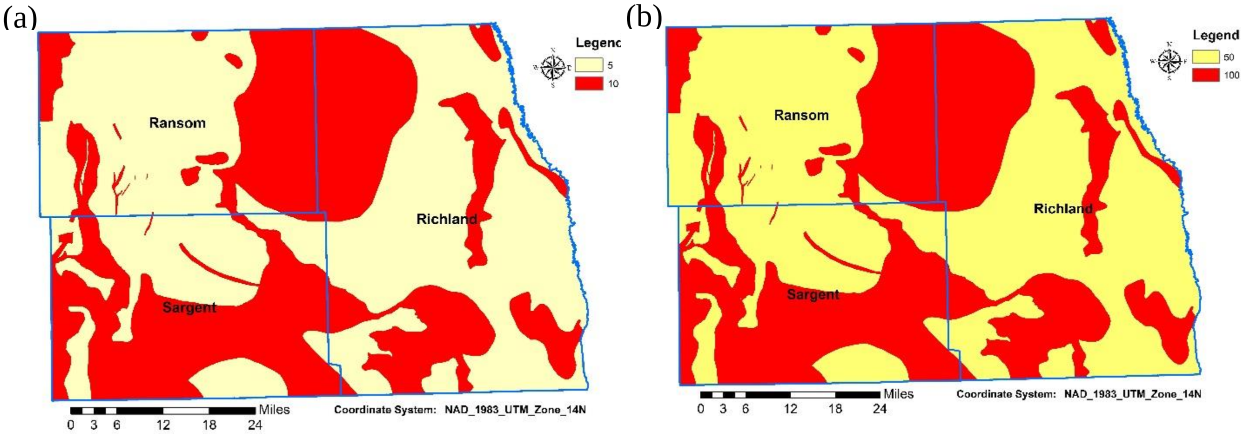

Figure 3.4. Aquifer rating maps for (a) DRASTIC-G, (b) SI for the study area.

3.3.2.4. Soil Media

Soil type data were reclassified based on hydrologic soil group (Table 3.4). There are 4 soil hydrologic groups; A, B, C and D. Among these soil groups, Group A soils have low runoff potential and high infiltration rates and group D soils have very low infiltration and high runoff potential. Group B soils have moderate infiltration rate and group C soils have low infiltration rates. There are some points where the soil type varied between two groups and ratings were provided accordingly. The corresponding soil rating map for DRASTIC-G is shown in Figure 3.5.

Table 3.4. Ratings for soil media.

Soil hydrologic groups	Ratings for DRASTIC
A	10
A/D	5
B	7
B/D	4
C	4
C/D	2
D	1

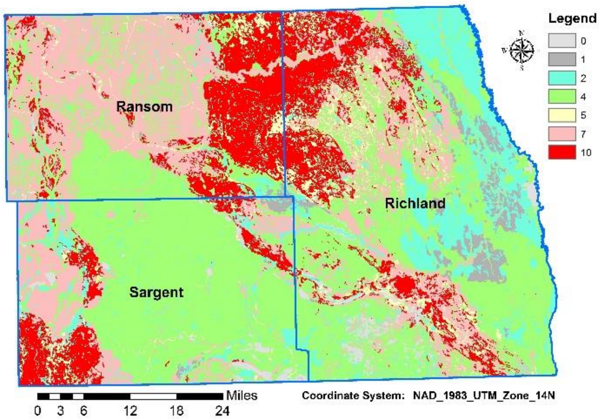

Figure 3.5. Soil rating maps for DRASTIC-G for the study area.

3.3.2.5. Topography

Slopes for the study area were estimated from the DEM raster file of the study area using slope feature of the spatial analyst tools and ratings were provided using NDDoH rating guidelines (NDDoH, 2015) for modified DRASTIC and Stigter et al. (2006) for SI index (Table 3.5). The corresponding rating maps for DRASTIC-G and SI are shown in Figure 3.6.

Table 3.5. Ratings for depth of water.

Slope	Ratings for DRASTIC (NDDoH, 2015)	Ratings for SI (Stigter et al., 2006)
0-2	10	100
2-6	9	90
6-12	5	50
12-18	3	30
≥ 18	1	10

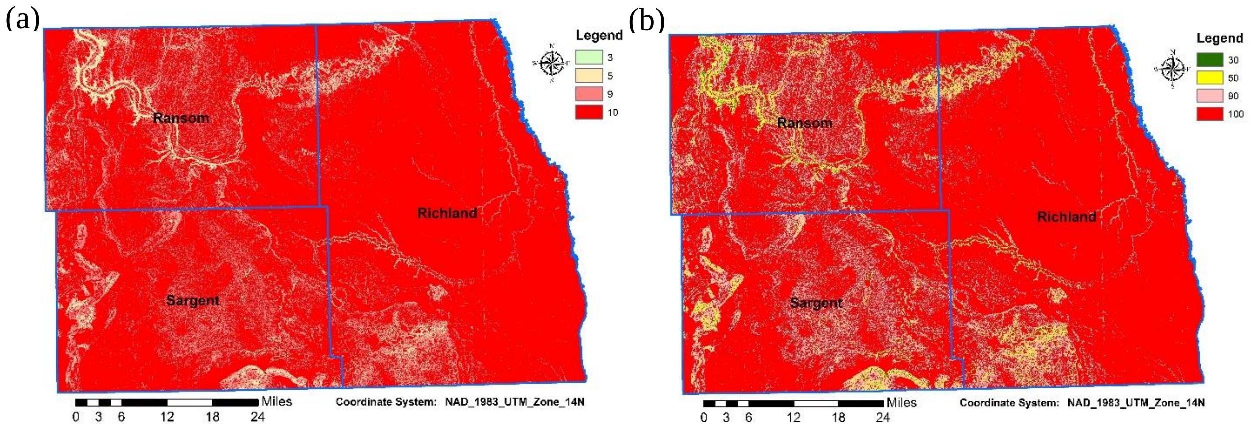

Figure 3.6. Topography rating maps for (a) DRASTIC-G, (b) SI for the study area.

3.3.2.6. Impact of Vadose Zone

Impact of vadose zone data were not readily available for the study area. SWAT SSURGRO soil lock up table was used for estimating the impacts of vadose zone (Table 3.6). Average soil texture type was estimated from the soil profile data and rating was provided based on the soil type provided in NDDoH rating guidelines (NDDoH, 2015). The corresponding impact of vadose zone rating map for modified DRASTIC is shown in Figure 3.7.

Table 3.6. Ratings for impact of vadose zone.

Average profile texture	Ratings for DRASTIC
Sand	9
Sandy loam	6
Loam	5
Silt/silty loam	4
Silty clay loam	3
Silty clay	2
Clay	1

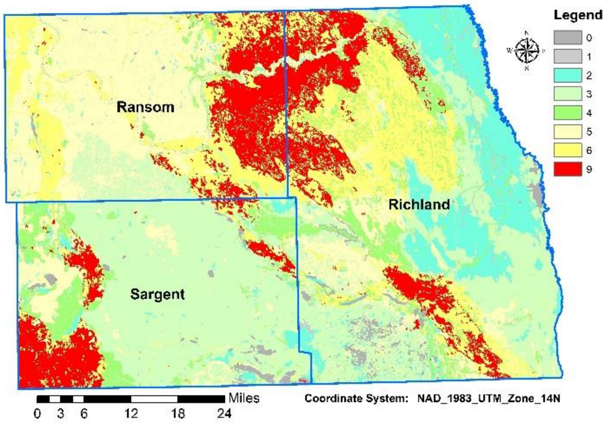

Figure 3.7. Impact of vadose zone rating maps for DRASTIC-G for the study area.

3.3.2.7. Hydraulic Conductivity

Hydraulic conductivity data for the study area were collected from GeoNet, 2014 (an Esri community) as geodatabase and linked with soil map unit IDs. Ratings for hydraulic conductivity was then provided for modified DRASTIC model (Table 3.7). The corresponding conductivity rating map for DRASTIC-G is shown in Figure 3.8.

Table 3.7. Ratings for hydraulic conductivity.

Hydraulic conductivity	Ratings for DRASTIC
1-50	1
50-100	3
100-200	5
200-300	7
> 300	9

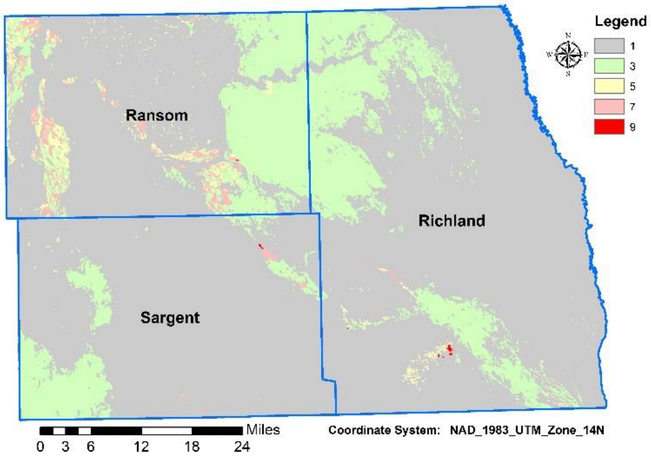

Figure 3.8. Conductivity rating maps for DRASTIC-G for the study area.

3.3.2.8. Geology

Geology rating was provided based on their formation type (Table 3.8). Geology from glacial formation was provided the maximum rating since geology from glacial origin is considered to be major arsenic and other major contaminants source in groundwater of the upper Midwest regions (Erickson and Barnes, 2005). The corresponding geology rating map for modified DRASTIC is shown in Figure 3.9.

Table 3.8. Ratings for geology.

Geology formation	Ratings for DRASTIC
Glacial	5
River sediment	3
Coleharbor	3
Water	3
Ohae formation	2
Pierre formation	2
Niobrara formation	1

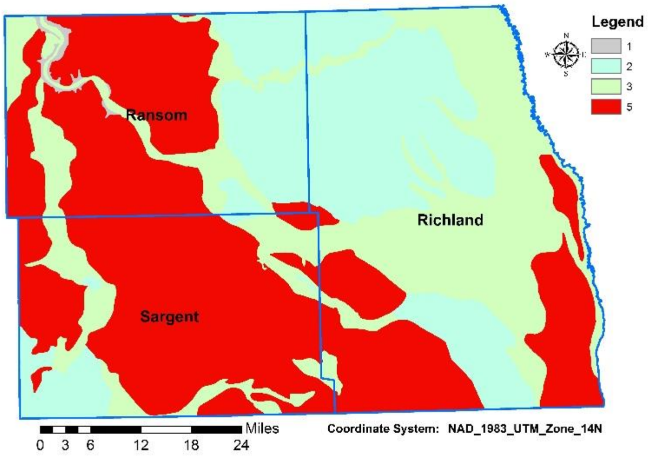

Figure 3.9. Geology rating maps for DRASTIC-G for the study area.

3.3.2.9. Land Use

Land use data for the study area was reclassified and ratings were provided following CAFO DRASTIC model (Dickerson, 2007) (Table 2.4 in the literature review section). The corresponding land use land cover rating map for SI Index is shown in Figure 3.10.

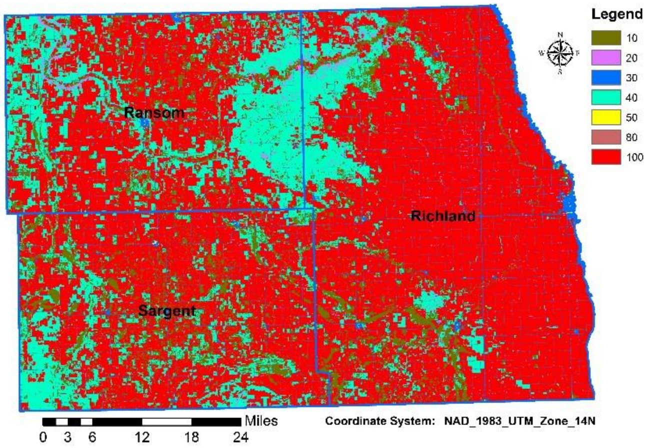

Figure 3.10. Land use land cover rating maps for SI Index for the study area.

3.4. Groundwater Quality Vulnerability Index

3.4.1. Modified DRASTIC-G for Arsenic Vulnerability

In our study, DRASTIC model were modified incorporating geology for arsenic vulnerability in the study area. Within the study area, geological formation of the glacial drift deposit is considered to be the primary source of arsenic in the groundwater (Erickson and Barnes, 2005). For this reason, we have decided to include geology parameter in the current DRASTIC model and modify it for contaminants like arsenic whose primary source is considered to be natural geologic formations.

The modified DRASTIC-G Index will be calculated using the following equation:

$$DRASTICG = D_r D_w + R_r R_w + A_r A_w + S_r S_w + T_r T_w + I_r I_w + C_r C_w + G_r G_c \qquad (3.1)$$

where, D is the depth of water, R is recharge, A is the aquifer, S is soil, T is topography, I is the Impact of vadose zone, C is the conductivity and G is the geology. In the equation, r denotes the rating for the particular property and w is the weight for that property.

Weight for the parameters used for calculating the modified DRASTIC-G index for groundwater arsenic vulnerability is given in table 3.9.

Table 3.9. Parameters and weights for modified DRASTIC-G index.

Parameter	Acronym	Modified DRASTIC-G Weight
Depth of water	D	5
Net recharge	R	4
Aquifer media	A	3
Soil media	S	2
Topography	T	1
Impact of vadose zone	I	5
Hydraulic conductivity	C	3
Geology	G	3

Modified DRASTIC-G index were calculated using the weighted sum overlay method in a 30 m resolution raster format. The index was then reclassified into three categories, high vulnerable/risk area (160-208), medium vulnerable/risk areas (130-160) and low vulnerable/risk areas (58-130). Groundwater quality data for arsenic was also classified into three categories, low risk (0-5 μg/l), medium risk (5 to < 10 μg/l), and high risk (≥ 10 μg/l) arsenic. These areas with different risk levels were then compared against the arsenic observations recorded by the groundwater monitoring wells.

3.4.2. Susceptibility Index (SI) for Nitrate Vulnerability

The primary source for groundwater nitrate is agricultural chemicals. So susceptibility index model was used to analyze groundwater nitrate vulnerability for the study area. For the index calculation, equation 2.2 and table 2.3 (for the weights) in the literature review section were used. Susceptibility index were calculated using weighted sum overlay method in a 30m resolution raster format. The index was reclassified into three categories, high vulnerable/risk area (80-100), medium vulnerable/risk areas (60-80) and low vulnerable/risk areas (32-60). Groundwater quality data for nitrate was classified into three categories, low risk (0-5 mg/l), medium risk (5 to < 10 mg/l), and high risk (≥ 10 mg/l). These areas with difference level of risk were then compared against the nitrate observations recorded in the groundwater monitoring wells.

3.5. Model Evaluation

Performance of the modified DRASTIC-G and SI model were evaluated using Cohen's kappa coefficient, a statistic that measures inter-categorical agreement for qualitative items (Ahmed et al., 2013). It is usually thought to be a more robust measure than simple percent agreement calculation, because Cohen’s Kappa takes into account the possibility of the agreement occurring by chance. Cohen’s Kappa coefficient is calculated using the formula below:

$$Cohen'sKappa\ (\kappa) = \frac{(TP+TN)-(\widehat{TP}+\widehat{TN})}{m-(\widehat{TP}+\widehat{TN})} \qquad (3.2)$$

where, $(TP + TN)$ is the actual agreement, $\left(\widehat{TP} + \widehat{TN}\right)$ is the expected agreement, TP is the true positive, TN is the true negative and m is the total number of observations. The value of Cohen's Kappa ranges between less than zero to 1. A negative value indicates no agreement and a value of 1 indicates perfect agreement. For the modified DRASTIC-G and SI, Cohen's Kappa values were calculated for the three vulnerable areas using three categories of arsenic/nitrate.

4. RESULTS AND DISCUSSION

4.1. Groundwater Quality Vulnerability Indices

4.1.1. Groundwater Vulnerability Index for Arsenic

The DRASTIC-G map for arsenic vulnerability for the study area is presented in Figure 4.1. Vulnerability indices were classified into three categories; low (58-130), medium (130-160) and high (160-208). The area for each of the categories are listed in Table 4.1. The highest indices are calculated in those areas where the soil hydrological class type is A (Figure 3.5), and aquifer (Figure 3.4 (a)) and geologic formations (Figure 3.9) are of glacial types. Type A soil hydrologic class indicates that, there is less surface runoff and more infiltration in those areas. Glacial aquifer and geologic formation is known to be the major primary source of groundwater arsenic in the upper Midwest regions (Erickson and Barnes, 2005). The main properties of the vadose zone (Figure 3.7) in these high vulnerability indices areas are sandy, indicating easy water flow. Depth of water tables were also low in these area (Figure 3.2(a)).

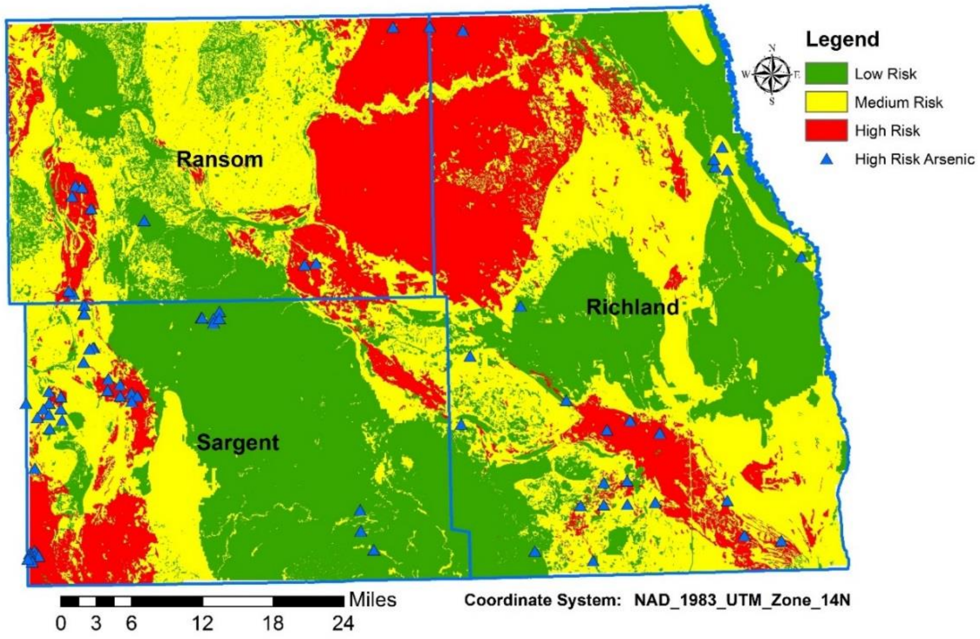

Figure 4.1. Groundwater quality vulnerability map for arsenic using DRASTIC-G index.

Total arsenic concentrations in the study site groundwater wells were classified into three categories; low, medium and high risk wells. A total of 33 out of 84 wells with arsenic concentration higher than 10 μg/l fall within the high risk arsenic vulnerable areas, 34 wells fall in the medium risk areas. But, there are also 17 wells with arsenic concentration higher than 10 μg/l fall in the low risk vulnerable areas (Table 4.2). For the medium risk wells, 10 out of 29 falls within the medium risk vulnerable areas and for low risk arsenic wells, 288 out of 736 falls within the low risk vulnerable areas. The Cohen's Kappa values for the three categories of arsenic were 0.02, 0.056 and 0.072 for high, medium and low risk arsenic respectively (Table 4.2). The Cohen's Kappa values indicate a low agreement with respect to well distribution within the risk vulnerable areas. The observation wells are not well distributed within the study areas and aggregated in some regions.

Table 4.1. Vulnerability areas for arsenic and nitrate.

Vulnerability level	Area for arsenic (sq miles)	Area for nitrate (sq miles)
Low	1253.10	407.76
Medium	1241.36	1875.17
High	676.53	888.06

Table 4.2. Groundwater observation wells distribution within the DRASTIC-G map vulnerability area.

Arsenic risk	DRASTIC-G map vulnerability area			Total	Cohen's Kappa
	High	Medium	Low		
High	33	34	17	84	0.02
Medium	13	10	6	29	0.056
Low	339	109	288	736	0.072

4.1.2. Groundwater Vulnerability Index for Nitrate

Susceptibility index map for nitrate vulnerability for the study area is presented in Figure 4.2. Vulnerability indices were classified into three categories; low (32-60), medium (60-80) and high (80-100). The area for each of the categories are listed in Table 4.1. The highest indices are calculated in those areas where there is more cultivated crop lands (Figure 3.10) with shallow water table depths (Figure 3.2(b)). Applications of nitrogenous fertilizers in the cultivated crop lands are major sources of groundwater contamination of nitrate (Stigter et al., 2006; Neshat et al., 2014). Topography of the high index areas are flat (with slope of 0-2) indicating more infiltration and less surface runoff.

Total nitrate concentrations within the study site groundwater wells were also classified into three categories; low, medium and high risk wells. A total of 16 out of 28 wells with nitrate concentration higher than 10 mg/l fall within high risk nitrate vulnerable areas and rest falls in the medium risk areas (Table 4.3). For the medium risk wells, 5 out of 7 falls within the medium risk areas and for low risk nitrate wells, 58 out of 814 observation wells fall within the low risk areas. The Cohen's Kappa value for the three categories of nitrate were 0.04, 0.004 and 0.006 for high, medium and low risk nitrate respectively (Table 4.3). The Cohen's Kappa values were again low indicating a low agreement with respect to well distribution within the risk vulnerable areas. The reason is again the non-uniform distribution of the observation wells within the study areas.

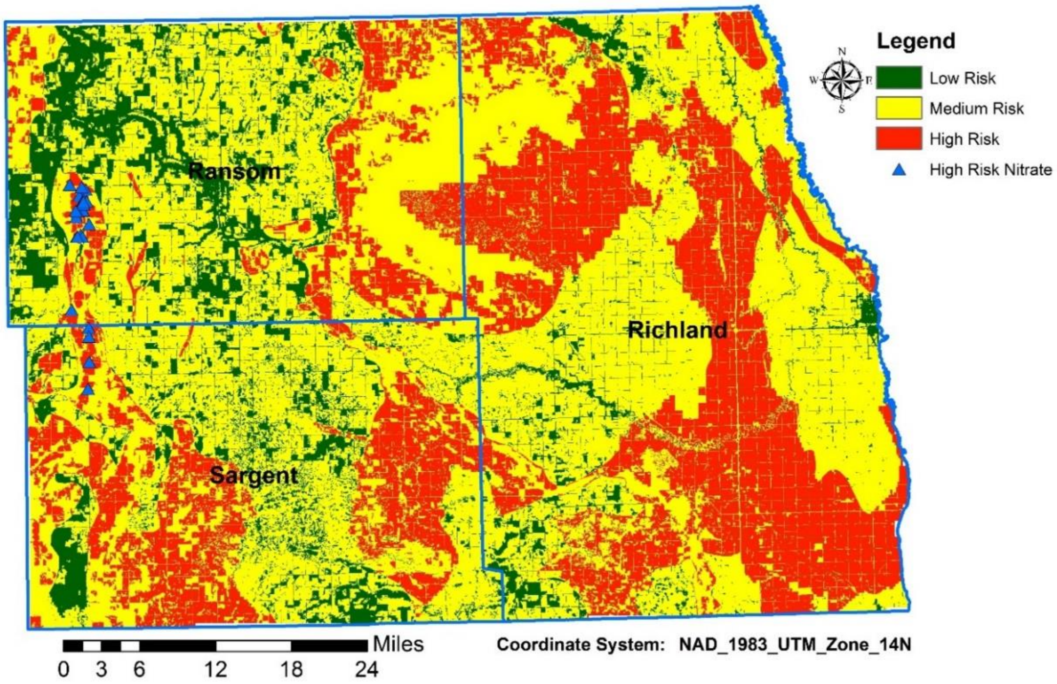

Figure 4.2. Study area groundwater quality vulnerability map for nitrate using susceptibility indexes.

Table 4.3. Groundwater observation wells distribution within the susceptibility index map vulnerability area.

Nitrate risk	Susceptibility Index map Vulnerability area			Total well	Cohen's Kappa value
	High	Medium	Low		
High	16	12	0	28	0.04
Medium	2	5	0	7	0.004
Low	283	473	58	814	0.006

4.1.3. Groundwater Vulnerability of the Cities

There are 26 cities and towns within our study area. The city map was overlaid with the groundwater arsenic and nitrate vulnerability maps. A list of the cities with their arsenic and nitrate vulnerability along with city populations are given in Table 4.4. Among the cities, Wahpeton has the highest population of 7766 and it falls in low risk vulnerable area for both arsenic and nitrate vulnerability (Table 4.4 and Figure 4.3 (a) and (b)). Out of the 26 cities, 11 cities fall within low and 10 falls within medium arsenic vulnerability areas. Only Hankinson falls within the high risk arsenic vulnerable areas that has a total population of 919. For groundwater nitrate vulnerability, most of the cities are within the low to medium or medium to high vulnerability areas and only four (Elliot, Fort Ransom, Wahpeton and Wyndmere) fall within the low risk vulnerable areas.

Table 4.4. Arsenic and Nitrate vulnerability for the study area cities.

City Name	Population	Arsenic Vulnerability	Nitrate Vulnerability
Abercrombie	263	Low	Medium
Barney	52	Low	Low to Medium
Cayuga	27	Medium	Medium to High
Christine	150	Medium	Medium to High
Cogswell	99	Medium to High	Medium to High
Colfax	121	Medium	Medium to High
Dwight	82	Low	Low to Medium
Elliott	25	Low	Low
Enderlin	886	Medium	Medium
Fairmount	367	Medium	Medium
Forman	504	Low	Low to Medium
Fort Ransom	77	Low	Low
Great Bend	60	Medium	Medium to High
Gwinner	753	Low	Low to Medium
Hankinson	919	High	Medium to High
Havana	71	Low	Medium
Lidgerwood	652	Low to Medium	Low to Medium
Lisbon	2154	Medium to High	Low to Medium
Mantador	64	Medium	Low to Medium
Milnor	653	Medium to High	Medium to High
Mooreton	197	Medium	Medium
Rutland	163	Low	Low to Medium
Sheldon	116	Medium	Low to Medium
Wahpeton	7766	Low	Low
Walcott	235	Medium	Medium
Wyndmere	429	Low	Low

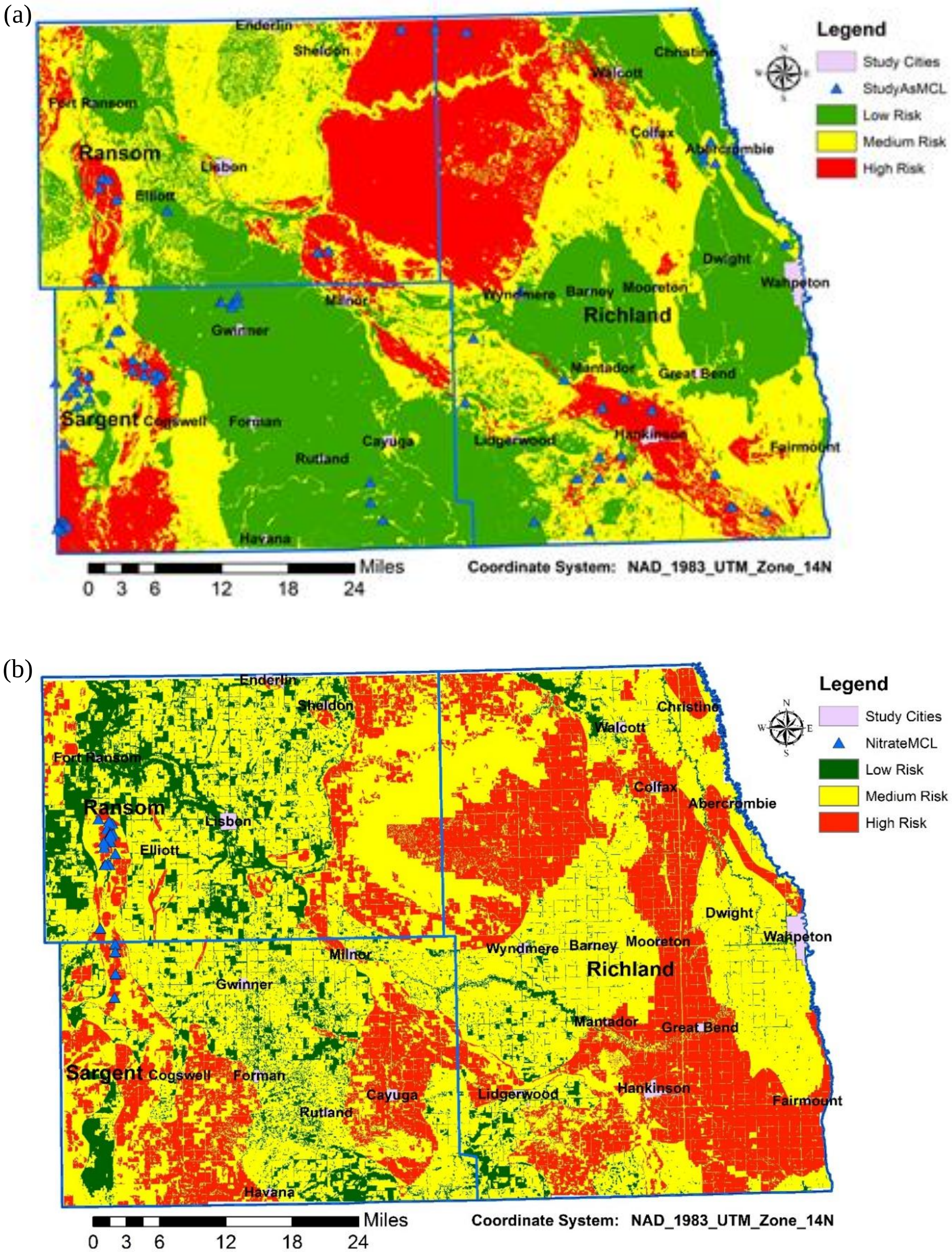

Figure 4.3. Groundwater vulnerability of (a) arsenic and (b) nitrate for the cities and towns located in the study area.

4.1.4. Livestock within Study Area

Based on 2009 livestock data for North Dakota (Collected from Dr. Shafiqur Rahman, Associate Professor, ABEN, North Dakota State University), there were 70 ranges and livestock operations. Of these 70 ranges, 16 falls within high risk arsenic vulnerable areas and for the rest of the locations, 28 falls within medium risk and 26 falls within the low risk arsenic vulnerable areas (Table 4.5 and Figure 4.4 (a)). On the other hand, 10 out of 70 livestock locations fall within high risk nitrate vulnerable areas. Of the rest livestock locations, 42 falls within medium risk and 18 falls within the low risk nitrate vulnerable areas (Table 4.5 and Figure 4.4 (b)).

Table 4.5. Livestock location distribution within the study area.

Contaminant	Vulnerability			Total
	High	Medium	Low	
Arsenic	16	28	26	70
Nitrate	10	42	18	70

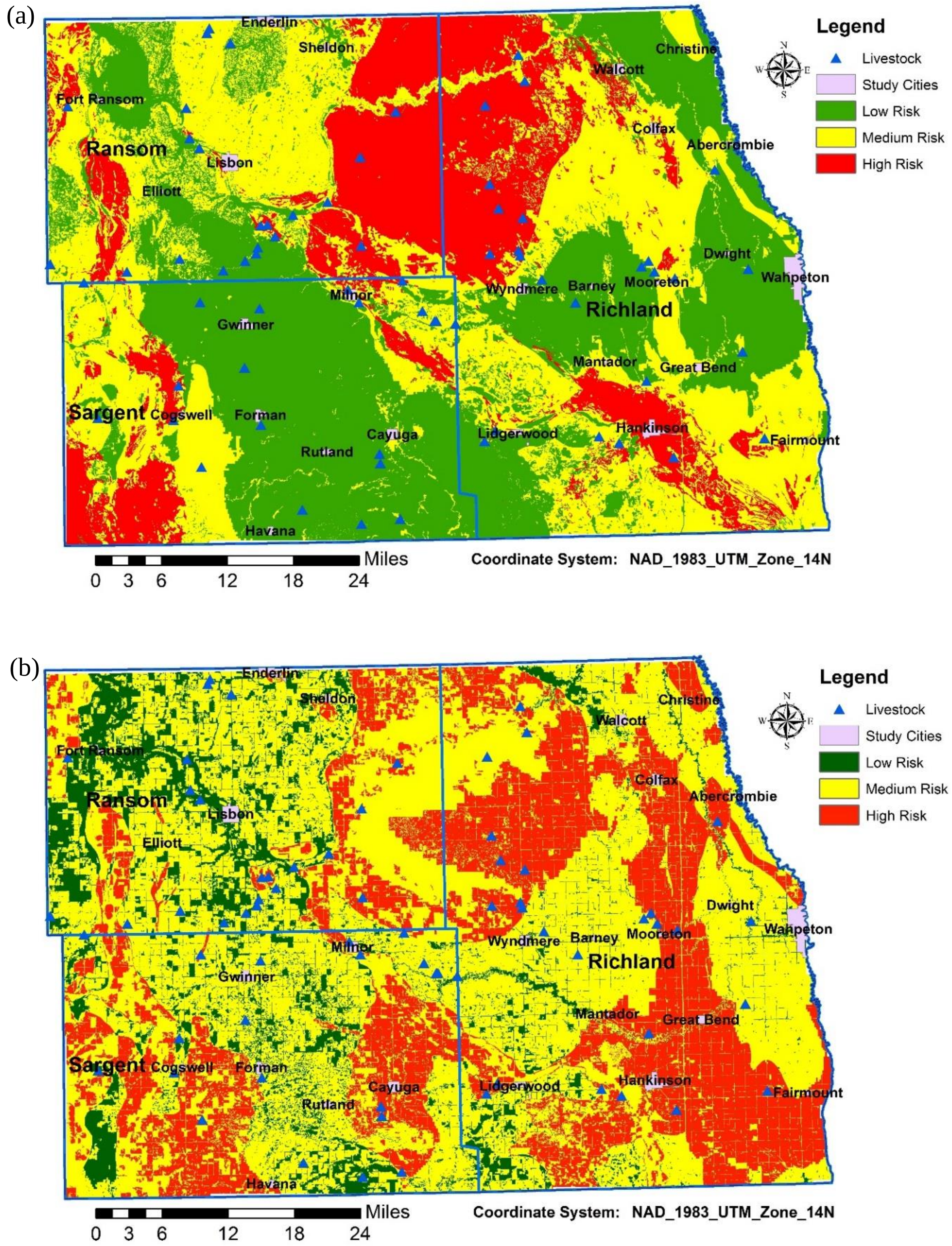

Figure 4.4. Groundwater vulnerability of (a) arsenic and (b) nitrate for livestock operations in the study area.

4.2. Discussion and Recommendations

In our study area, approximately 22% wells (191 wells out of 849) had detectable arsenic concentrations and 15% wells (130) had detectable nitrate concentrations. Among these arsenic and nitrate containing groundwater wells, 44% wells (84 wells) had arsenic concentration greater than maximum concentration limit of 10 μg/l and 21% (28 wells) wells had nitrate concentrations greater than maximum concentration level of 10 mg/l.

Most of the groundwater arsenic vulnerable regions of our study area have glacial geologic and aquifer formations with soil hydrological class type of A. Glacial aquifer and geologic formation have already been identified as the major primary source of groundwater arsenic in the upper Midwest regions (Erickson and Barnes, 2005). The primary source of groundwater nitrate is anthropogenic and comes mostly from agricultural activities.

Our study indicated that out of 26 cities within the study area, 11 cities fall within low and 10 falls within medium arsenic vulnerability areas. For groundwater nitrate vulnerability, most of the cities fall within the low to medium or medium to high vulnerability areas and only 4 cities (Elliot, Fort Ransom, Wahpeton and Wyndmere) fall within the low risk vulnerable areas. Among the cities, most densely populated Wahpeton (total population of 7766) falls within low risk area for both arsenic and nitrate vulnerability and only Hankinson falls within the high risk arsenic vulnerable areas that has a total population of 919. The livestock locations within the study area also falls mostly within low to medium vulnerable areas.

4.2.1. Groundwater Arsenic and Nitrate Monitoring Strategies

Monitoring of groundwater arsenic or nitrate should be planned nationally, starting with random testing of public and private wells throughout the state to determine the extent of the problem (UNICEF, 2010). Subsequently, comprehensive testing of all wells in selected vulnerable regions should follow, to identify each and every contaminated well (Adams et al., 2016). Comprehensive testing programs should also include other activities that are essential for additional monitoring and management operations, such as the location of each well using a Geographic Information System (GIS), the diagnosis of affected population in the affected area surveyed, and the introduction of various water treatment measures in that district (UNICEF, 2010). A comprehensive research group with geologists, hydrologists, geo-chemists, water supply and environmental engineers, and public health experts can be formed to conduct in-depth investigation on the sources and causes of arsenic and nitrate contamination in groundwater. The population exposed to the arsenic and nitrate contamination should be informed about the contamination in groundwater and drinking water, the sources of contamination-free water, and the importance of compliance with treatment programs including the nutrition.

Strategies for preventing groundwater contamination protection actions can be of two broad levels. First set of strategies are directed at individual contaminant control regulations. Second set of strategies are to advance our understanding of complex and varied hydrogeology, and actions that continue building both governmental and private sector capability to protect groundwater (Adams et al., 2016). Minnesota Environmental Quality Board (EQB) in a report proposed a number of recommendations to minimize and prevent the impacts of contaminants on groundwater quality (Adams et al., 2016), which can also be adopted and used for North Dakota. These recommendation are listed below:

1) For human-caused contaminants like nitrate, pollution prevention activities, remediation programs, permit regulations, monitoring, and numerous best management practices (BMPs) can be utilized at both state and local levels to prevent and minimize groundwater contamination.

2) For groundwater nitrate contaminations, targeted alternative management tools can be used to reduce nitrogen inputs, which include: increasing the adoption of cover crops, growing perennial crops such as alfalfa, retiring land from production, conservation easement practices, grazing, alternative cropping varieties that require less nitrogen, and other new technologies.
3) For naturally occurring contaminants like arsenic, monitoring and identification of the aquifers and information on conditions where these contaminants occur can be used to guide future well drilling, away from these sources of contaminants. Groundwater testing can also be provided to decide if water treatment or blending is necessary to reduce contaminant concentrations below their health based drinking water standards.
4) State Department of Health can take initiatives to provide guidance to well drillers to minimize arsenic contamination in water supply wells.
5) State Department of Health should continue to provide information on: 1) laboratories that private citizens can use to test water samples for arsenic and 2) water treatment systems that remove arsenic from water.

4.2.2. Groundwater Arsenic and Nitrate Remediation Techniques

Although in small quantities it is necessary, however, arsenic is known to be highly toxic if ingested in large dose. High concentrations of arsenic have been observed in groundwater in some areas of the United States due to naturally occurring arsenic containing glacial aquifer sediment (Bang et al., 2005). Thus, in order to reduce the health risk arising due to the direct consumption of arsenic contaminated water or due to the consumption of food/vegetables, grown in soil irrigated with arsenic contaminated water, there is need to develop strategies to solve the problem and identify suitable and sustainable technologies that could alleviate toxicity and availability of arsenic from soil to edible portions of food/vegetables as well as removal of arsenic from the groundwater and drinking water. Removal of arsenic highly depends on the chemistry and composition of the arsenic contaminated water. In most of the major reported incidences arsenic occurs as As (III) and oxidation of As (III) to As (V) is believed necessary to achieve the satisfactory results of arsenic removal (Singh et al., 2015). A number of arsenic removal technologies are currently available. Each of the technologies has different levels of efficiency with some advantages and disadvantages. A list of the currently available technologies with their basic mechanisms, advantages and disadvantages are listed in Table 4.6. A number of methods are also available for the removal of nitrate, another major groundwater contaminant in North Dakota. A list of the currently available methods with their advantages and disadvantages are listed in Table 4.7.

Table 4.6. Groundwater arsenic remediation techniques.

Arsenic Removal Technology	Basic Mechanisms	Efficiency	Advantages	Disadvantages
Reverse Osmosis (Schneiter and Middlebrooks, 1983)	A membrane process containing extremely small pores to selectively remove ions.	Removes about 95% As (V) and 50-60% As (III).	Requires little maintenance.	For each gallon of treated water, creates about 7-9 gallons of “reject” water.
Membrane Distillation (Manna et al., 2010)	Boils the water and cools in a separate container to leave the contaminant behind in the boiling pot in presence of a selective membrane.	Removes both As (V) and As (III).	Simple to install and operate.	Slow process; uses a lot of electricity.
Ion Exchange (Oehmen et al., 2006)	A physical/chemical process by which an ion in the solid resin phase (typically a three dimensional hydrocarbon network) is exchanged for As (V) in the feed water.	Removes only As (V).	Operation is similar to a water softener.	Without careful maintenance, an abrupt increase in arsenic in treated water could occur; Produces waste water with elevated arsenic concentration.
Adsorption (Anjum et al., 2011; Han et al, 2013; Sun et al., 2013)	Uses solids (activated carbon, alumina, iron oxides etc.) for removing substances from liquid solutions.	Remove As (III) and As (V), but capacity to remove As (III) is lower	Produces very little wastewater; spent media is non-hazardous and disposable; simple to install and operate;	The media can be expensive, especially without using additional pretreatment.
Sono filter (Hussam and Munir, 2007)	Small scale filtration system containing zero valent iron.	Remove As (III) and As (V).	Simple to install and operate.	Without careful maintenance, an abrupt increase in arsenic in treated water could occur.
Phytoremediation (Lasat, 2002)	Use plants or microbes to remediate arsenic from contaminated sites.	As (III) is effectively removed because in this form it acts as phosphate analog.	Environmental friendly and low cost.	Slower compared to other techniques; most of the hyper-accumulators are slow growers.

Table 4.7. Groundwater nitrate remediation techniques.

Arsenic Removal Technology	Basic Mechanisms	Efficiency	Advantages	Disadvantages
Reverse Osmosis (Schoeman and Steyn, 2003)	A membrane process containing extremely small pores to selectively remove ions.	Very effective in removing nitrate.	Requires little maintenance.	Costly and requires time and energy to operate efficiently.
Distillation (Dahab, 1991)	Boils the water and cools in a separate container to leave the contaminant behind in the boiling pot.	Most effective types of demineralization.	Simple to install and operate.	Low-yield systems, and storage space for treated water is required.
Ion Exchange (Samatya et al., 2006)	A physical/chemical process by which an ion in the solid resin phase is exchanged for nitrate in the feed water.	Effective	Operation is similar to a water softener.	Without careful maintenance, an abrupt increase in nitrate in treated water could occur. Produces waste water with elevated nitrate.
Electro-dialysis (Elmidaoui et al., 2001)	Anion exchange and cation exchange membranes is used in a constant electric field.	Effective in removing nitrate.	Low chemical usage; no reagent wastes.	Expensive.
Bioremediation (Jacinthe et al., 1999)	Use microbes to remediate nitrate from contaminated sites.	Nitrate is up taken by plants as nutrients.	Environmental friendly and low cost.	Slower compared to other techniques. Most of the hyper-accumulators are slow growers.

5. CONCLUSIONS

This study modified the DRASTIC model incorporating geology to assess the groundwater pollution potential for arsenic and used susceptibility index (SI) for groundwater nitrate vulnerability for Ransom, Richland and Sargent county of North Dakota. These methods used a number of hydrogeological and land use land cover parameters to create two maps that classifies areas by the potential vulnerability: low to high vulnerability for arsenic and nitrate. A variety of data are required in order to create these required layers that contribute to the final vulnerability maps. The developed maps showed that approximately 21.33 % of the study areas are highly arsenic vulnerable and 28% areas are highly nitrate vulnerable. Natural glacial geologic and aquifer formations are the major sources of arsenic and agricultural activities are the major source of nitrate within the study area.

The major cities within the study area, falls within low to medium vulnerable areas for arsenic and medium to high vulnerable areas for nitrate. Most densely populated Wahpeton fallen within low risk vulnerable area for both arsenic and nitrate pollution potential. Most of the livestock locations of the study area also fall within the low to medium arsenic and nitrate vulnerable areas.

In North Dakota, arsenic and nitrate are two major groundwater contaminants that can pose serious health concerns. But unfortunately, currently there is scant regulation of private wells in North Dakota, and residents are on their own to test not only for bacteria but also for trace elements like arsenic in their well water, with little guidance from state health officials. For sustainable and safe utilization of the groundwater resources, a continuous monitoring, and notification systems is necessary. Developed map in this study can be used as a primary starting point for the identification of the probable vulnerable areas and future decision making.

Both models were developed using the GIS techniques first described by Aller et al. (1987), but while the methodology has been standardized, data has significant effects on the production of the final vulnerability indexes. The DRASTIC method is commonly used to analyze groundwater contamination vulnerability; however, the scale and detail of data used in the model and the accuracy has yet to be analyzed. At the same time, it should be noted that the modified DRASTIC-G and SI are only preliminary screening tools, and these should not be replaced with site-specific studies. The developed maps should guide NDDoH in planning, with analysis of available well logs, well cuttings, and geologic structure maps, and determining specific site selection.

In the current study, observation well data from USGS were used to calibrate the vulnerability maps. These wells were not uniformly distributed over the study area. In the future, some field works can be done to collect water sample data from the study area uniformly for better evaluations of the vulnerability maps.

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