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ASSESSMENT OF DRINKING WATER/ AQUIFER VULNERABILITY TO CONTAMINATION BY NATURAL MANGANESE AND ANTHROPOGENIC CHEMICALS IN THE U.S.

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ASSESSMENT OF DRINKING WATER/AQUIFER VULNERABILITY TO CONTAMINATION BY NATURAL MANGANESE AND ANTHROPOGENIC CHEMICALS IN THE U.S.

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And accepted on the recommendation of

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ABSTRACT

ASSESSMENT OF DRINKING WATER/AQUIFER VULNERABILITY TO CONTAMINATION BY NATURAL MANGANESE AND ANTHROPOGENIC CHEMICALS IN THE U.S.

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Aquifers in the U.S. store groundwater used by many Americans every day for drinking eating, bathing and cleaning. These underground sources of water are vital to life and may be subject to contamination from both natural and anthropogenic pollution, including manganese (Mn) – especially shallow aquifers (<100 feet to bedrock). Natural sources of Mn are found in soils, surficial deposits, and bedrock, while anthropogenic contamination derives from landfills, waste facilities, or industries that use toxic materials. Pollutants like Mn raise concern because there is no policy in place to enforce regulation of Mn levels in water supplies based on limited information about health effects. Yet studies have shown elevated levels of Mn intake can lead to adverse human health effects. This study uses ArcMap to identify potential sources of Mn and/or toxics contamination in *shallow U.S. aquifers* based on geologic characteristics of a given aquifer source and proximity to waste sites. The results show approximately 2 million Americans may be at risk of consuming water with natural Mn contamination, and of those 2 million, close to 1.7 million are also vulnerable to additional toxics from anthropogenic waste. These data are alarming since they are based on populations directly within aquifer boundaries for natural contamination and because only a small fraction of anthropogenic waste sites were considered based on Trichloroethylene (TCE) release sites, Mn release sites, and CIRCLA (Superfund) sites. This study provides useful information to identify potential areas of oral Mn exposure, but there are still many unknowns. A more comprehensive assessment of aquifer vulnerability as well as continued research into human health effects from oral exposure are recommended.

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1.0 Introduction

Every day, people are exposed to potentially hazardous substances that come from the food and water they consume, air they breathe, and things they come into contact with. It is of utmost importance for scientists, policy makers, and citizens to make a concerted effort to understand the sources and dangers of potentially harmful toxins entering their bodies that may come from basic necessities such as drinking water. Purchasing bottled water or installing home filtration systems can be one way to avoid the risk of ingesting unknown harmful substances from public drinking water supplies, but many people do not have the means or ability to buy enough water or install expensive filtration systems to support their families, especially when considering the uptake of water from showers and bathing. No one should have to worry about ingesting toxic substances from their water supplies that could potentially harm them or their families, yet this may be the case in many parts of the U.S. If risks of groundwater contamination from natural and anthropogenic sources exist, then measures need to be taken to identify where areas at risk are in the U.S. Manganese (Mn) is one of many potentially harmful elements found in public drinking water supplies that may be of concern. The problems with Mn contamination in drinking water are: 1) it comes primarily from natural sources (aquifers) that are abundant in the U.S., meaning risks tend to be undervalued; and 2) although new studies are coming to the fore, there are still too few data surrounding human health effects from oral exposure to Mn (WHO 2011, USEPA 2004), meaning Mn is not regulated based on health concerns. Therefore, current USEPA regulations may not be adequately protecting public health.

Manganese is a very common, natural contaminant, being found in rocks/bedrock, loose sediment, stable soil, and surficial deposits, with many different mineral forms at varying concentrations. Manganese can also be mixed with many other elements in rock formations and exist in several elemental states based on environmental factors. Manganese is also a relatively abundant element found in waste sites and landfills because of its role in the production of iron and steel, as well as in products that include dry cell batteries, glass, aluminum cans, and more. This is concerning because there are so many landfills, waste sites, and businesses that either contain or use heavy metals like Mn in most parts of the U.S. Although most landfills are required to have protective measures in place to prevent pollution from seepage, leachate (liquid waste by-product from dumps and landfills) can penetrate deeply into soils and transport to groundwater via rainwater infiltration and groundwater movement if these barriers break down or were never constructed in the first place.

There is currently no enforceable policy or regulation regarding Mn in drinking water (USEPA, 2004), which is a problem for a number of reasons. One problem is there are little data on what the health effects are, arguably still insufficient for regulation – although the growing number of studies that do show associations between Mn exposure and adverse outcomes have led USEPA to consider Mn an "emerging contaminant" of interest (ibid). The U.S. Congress enacted the *Safe Drinking Water Act* (SDWA) in 1974 to regulate public drinking water standards and protect Americans from drinking water contamination from natural and anthropogenic sources, and the U.S. Environmental Protection Agency (USEPA) helps at state and local levels to carry out these standards (USEPA, 2018a). However, the current regulation regarding Mn in drinking water uses a Secondary Maximum Containment Level (SMCL) of 0.05 mg/L and is based on the color and taste of the water being a nuisance to consumers, not from health risks (USEPA, 2004). Although the EPA claims there are little data regarding ingestion of drinking water, several studies indicate otherwise (Mora et al., 2018; Warner & Ayotte, 2014; Hafeman et al., 2007; Ljung & Vahter, 2007; Sahni et al., 2007; Yokel, 2006; Woolf et al., 2002; Iwami et al., 1994; Kilburn, 1987). These studies range from symptoms of hyperactivity in children, to infant mortality from consumption of Mn in drinking water by the pregnant mother. In light of emerging data, a policy update may be needed in the future.

This study attempts to address the issue of potential Mn contamination in drinking water by exploring the questions: *1) What shallow aquifers in the continental U.S. are most vulnerable to natural*

Mn contamination, 2) Which areas at risk of natural Mn contamination are at increased vulnerability from anthropogenic toxics, and 3) How many people are potentially affected? A review of studies relating to natural Mn and anthropogenic sources of toxic contamination in drinking water were combined with a geographic information systems (GIS) approach to answer these questions. This paper begins with background information on Mn in relation to groundwater, sources of contamination, and health and policy, then describes in detail the methods used to identify vulnerable aquifers, and finishes with a discussion of results that conclude with recommendations and future research.

2.0 Background on drinking water contamination

2.1 Groundwater and manganese

Life on Earth depends on drinking water for survival. Groundwater used for public and private drinking water sources comes from aquifers below the Earth's surface in saturated surficial deposits with water holding characteristics based on the sediment structure and geology. In the U.S., 50% of the drinking water supply comes from these aquifers (Stackelberg, 2017). Soil and rock formations in and around aquifers are comprised of a variety of different elements across landscapes that can contaminate drinking water supplies by releasing dissolved trace elements such as Mn. This is important to consider when using or consuming water because many elements and minerals can be toxic when excess amounts are ingested (WHO, 2011; USEPA, 2004). Trace elements such as Mn found in groundwater can vary over several orders of magnitude across local well networks and across regions of the U.S. (Groschen et al., 2008), which is why constant monitoring of water quality and continued research into health effects from excessive human consumption of Mn is important to ensure public safety.

Groundwater can also be contaminated by Mn from human activities, and other toxics. Manganese is primarily used in the production of steel and iron, but is also found in aluminum alloys, dry cell batteries, glass, roofing materials, and automobiles (Corathers, 2014). When considering how abundant Mn is in both natural and anthropogenic environments, questions and concerns should arise regarding where Mn or other elements could be accumulating in higher concentrations regionally and what human health risks exist. Current policy regarding exposure does not enforce a [primary] Maximum Containment Level (MCL) of Mn in groundwater (USEPA, 2004), and may require a reassessment (Bouchard et al., 2007; Ljung & Vahter, 2007) and caution should be taken when considering the accuracy of health guidelines and the purposes of their set limits.

2.2 Drinking water contamination from natural sources of manganese

Manganese is one of the most abundant elements in rocks and soils, most commonly found in igneous and metamorphic rocks (Moore, 2004). It comprises about 1% of the Earth's crust, which makes it the 12th most abundant element in the crust (Cannon et al., 2017), and is a naturally occurring element that rarely exists in its pure, elemental state, but instead combines with other elements in nearly 300 different minerals (Webb, 2008). It is highly abundant in bedrock, soils, and surficial deposits, (Taylor & McLennan, 1995) which can lead to groundwater contamination based on the geology and mineral composition of deposits near or within aquifers.

It is important to consider areas of the U.S. that were covered by two miles of ice 12,000 years ago because of the likelihood of bedrock fractures caused by stresses from the erosion of overlying rock, melting of ice sheets, tectonic activity, and cooling stresses associated with igneous intrusion (Robinson et al., 2004; Hansen & Simcox, 1994). These fractures allow potentially Mn-rich fluids to migrate through bedrock, change in temperature and pressure, and precipitate out as manganese oxide (MnO) (Webb, 2008). These reactions occur often due to the susceptibility of Mn to oxidation-reduction (redox) processes, which are based on factors such as pH and temperature (Schäffner et al., 2015; Warner & Ayotte, 2014). Past glacial activity has also yielded glacial deposit/over-burden aquifers that are *very shallow* (less than 50 feet from surface to bedrock). These may be more at risk of having fractures in bedrock due to the proximity of the bedrock to the surface (Schmidt, 1987), putting the aquifer at greater risk of Mn contamination.

In addition to bedrock, surficial deposits (soil material below the first five feet of Earth and beyond) are also an important consideration of natural Mn contamination to drinking water. Manganese is abundant in layers of Earth's upper, bulk, and lower continental crust, at concentrations of 600ppm, 1400ppm, and 1700ppm, respectively (Taylor & McLennan, 1995), which illustrates the importance of how soil and surficial deposits can influence groundwater based on their elemental compositions. Manganese detection in water sources is high in the U.S. because of the ubiquity of Mn in soil and rock (WHO, 2011; USEPA, 2004), and concentrations of Mn in the glacial aquifer system in particular are among the highest in the nation because glacial deposits contain little to no dissolved oxygen, i.e., they are highly anoxic (Warner & Ayotte, 2014). Anoxic conditions allow metal oxide minerals that coat aquifer sediments to dissolve and release Mn into the groundwater (Warner & Ayotte, 2014). This raises concern since the glacial aquifer system in the northern contiguous U.S. ranks first in the Nation as a source of groundwater, with over 2.6 billion gallons of water being pumped each day for public and domestic supply to 98 million residents in these areas (Stackelberg, 2017). The continental glaciers created a heterogeneous geologic landscape by leaving behind permeable, unconsolidated sediments that vary in size, shape, texture, and elemental characteristics (Stackelberg, 2017; Warner & Ayotte, 2014). Permeability, structure, composition, conductivity, and pH are just some of the characteristics of soil/surficial deposits that can influence groundwater chemistry; they deserve inclusion in a more comprehensive evaluation of groundwater vulnerability.

2.3 Drinking water contamination from anthropogenic sources

As previously mentioned, Mn is a naturally occurring element found in groundwater sources as well as in soils that can affect groundwater, but human activities are also responsible for contamination in many drinking water sources. In fact, 91% of 'environmental' Mn comes from land disposal of manganese-containing waste sites (USEPA, 2004). This is of particular concern because landfills, waste sites, and industries that use hazardous materials are found in most cities and towns across the U.S., posing risks to groundwater contamination.

In this study, waste site locations were limited to 1) sites designated under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA): "Superfund" sites, 2) anthropogenic Mn release sites, and 3) anthropogenic TCE release sites. Superfund site locations were retrieved from the USEPA website (USEPA, 2018b). The Superfund program began in 1980 to establish prohibitions and requirements for waste sites, enforce liability to companies or agencies at fault for a contamination site, and to set up a trust fund to clean up areas of concern that constitute an emergency (USEPA, 2018b). The list of sites contain National Priorities List (NPL) sites, which are polluted areas that require a long-term cleanup effort, deleted NPL sites, and proposed NPL sites (USEPA, 2018b). Currently there are 1181 sites on the NPL and 50 on the proposed NPL list throughout the U.S. (USEPA, 2018b). Over half of NPL waste sites contain Mn, and Mn detection was reported in 692 out of 869 groundwater samples near NPL sites (ATSDR, 2012). Many of the sites represent industries or businesses that involve mining, utilities, manufacturing, and hazardous waste that use chemicals with significant adverse effects to human health or the environment. Superfund sites do not include all waste sites in the U.S., so the results of this study are a *limited, preliminary estimate* of aquifer vulnerability; there are tens of thousands of non-NPL waste sites not yet included in the analysis.

Surficial or shallow aquifers such as those of glacial origin make matters worse by increasing the risk of anthropogenic contamination from waste sites (Claus Henn et al., 2017; Wang et al., 2016; Groschen et al., 2008). Aquifer contamination from waste sites often occurs via waste site leachate that contains many organic and inorganic compounds that contaminate water sources (Mor et al., 2006).

One study from Gazipur, India discovered increased concentrations of several hazardous chemical compounds found in groundwater samples taken from up to a kilometer and a half from a waste site with no natural or other reason for the presence of the chemicals (Mor et al., 2006). One study found elevated Mn concentrations of 1.21 mg/L in drinking water from a home near a toxic waste site that may be responsible for memory loss and other adverse neurological effects in a 10-year-old boy (Woolf et al., 2002). Another study found average Mn concentrations of 0.859 mg/L from samples taken near a landfill in Alexandria, Egypt (Abd El Salam & Abu-Zuid, 2015).

It is understandable why Mn is commonly found in groundwater near waste sites. In 2009 alone, 50 million pounds of waste containing Mn was deposited in landfills (ATSDR, 2012). Waste materials containing Mn primarily come from steel, iron, aluminum alloy, construction materials, and dry cell batteries (Cannon et al., 2017; ATSDR, 2012; Yokel, 2006). Some landfills have barriers in place to prevent contamination of groundwater using materials such as limestone and crushed concrete, but these barriers can break down over time and become less effective after only three years of implementation (Wang et al., 2016). Similar to factors of natural sources of Mn to become mobilized in groundwater systems, pH can mobilize anthropogenic sources of Mn and other toxics, allowing transfer from waste sites into other systems via redox reactions (Cannon et al., 2017; Wang et al., 2016). Furthermore, newer waste sites have younger leachate, which is more acidic and therefore increases the risk of mobilizing Mn and other toxics to contaminate groundwater (Warner & Ayotte, 2014; Bashir et al., 2009).

2.4 Health and policy concerns

There are limited data regarding the toxic effects of Mn through oral exposure, yet the EPA sets drinking water standards for allowable levels of Mn in drinking water (USEPA, 2018a). The standard is currently set based on the inconvenience of color and undesirable taste of water to consumers (WHO

2011; USEPA, 2004). Manganese is found in many foods including leafy vegetables and nuts, and is an essential element to the proper functioning of both animals and humans, yet it is recognized that Mn can cause adverse effects to people when consumed in higher concentrations (WHO, 2011; USEPA, 2004). Knowledge relating to the toxic effects on humans from Mn has grown significantly over the years (Frisbie et al., 2012), and several studies have reported human health effects from Mn that include neurotoxic conditions such as manganism, Amyotrophic Lateral Sclerosis (ALS), and Parkinsonism, as well as birth defects and brain impairment (Mora et al., 2018; Warner & Ayotte, 2014; Hafeman et al., 2007; Ljung & Vahter, 2007; Sahni et al., 2007; Yokel, 2006; Woolf et al., 2002; Iwami et al., 1994; Kilburn, 1987). In addition to EPA health benchmarks like MCL, there are several other terms and acronyms correlated with human exposure to Mn, including Secondary MCL (SMCL), Life Health Advisory (LHA), Health Based Screening Level (HBSL), Human Health Benchmark (HHB), or Health Based Value (HBV) to name a few (Warner & Ayotte, 2014; WHO, 2011; Groschen et al., 2008; USEPA, 2004), which make the data difficult to interpret across governments and public associations. The current EPA policy regarding Mn in drinking water is a SMCL of 0.05 mg/L based on the color of the water and staining of clothes or fixtures (WHO, 2011; USEPA, 2004). The variety of acronyms listed above come from agencies like the WHO, which has changed their safety guidelines regarding Mn in drinking water several times over the past 60 years (WHO, 2011; Ljung & Vahter, 2007). While this project is not focused on the health effects associated with Mn, these relevant studies highlight the importance of identifying aquifers at risk of contamination.

3.0 Methods

3.1 Study area

Claus Henn et al. (2017) conducted an integrated assessment of shallow-aquifer vulnerability to multiple contaminants and drinking-water exposure pathways in Holliston, Massachusetts based on numerous reports of metals and solvents in groundwater. The study revealed that Holliston has a highly vulnerable aquifer system and it is likely that multiple chemicals enter the drinking water supply, putting residents at risk of exposure. The assessment also suggests the qualitative analysis of aquifer vulnerability used in their study may be applied to other aquifer systems. Based on the assessment and the call for further research by Claus Henn et al. (2017), this project seeks to reveal similar geologic conditions to those in Holliston, Massachusetts, (specifically the bedrock and aquifer types), and to identify aquifers in the U.S. that are: 1) vulnerable to natural sources of Mn contamination, and 2) at additional risk of contamination from natural Mn and anthropogenic toxics from waste sites. The Town of Holliston, like the rest of New England and northern parts of the contiguous U.S., represents area once covered by the Laurentide Ice Sheet during the last ice age (Warner and Ayotte, 2014). The pressure from the ice and the deposits of till left behind created a landscape full of unsorted and unstratified geologic material that formed aquifers with similar characteristics to each other, which include being shallow (Groschen et al., 2008). This is indicative of the of the study area since the glacial aquifer system has the most shallow aquifers in the U.S. (Warner and Ayotte, 2014), which describes Holliston's surficial aquifers (Claus Henn et al., 2017).

The ArcGIS program ArcMap 10.5.1 (ESRI, 2017) was used to conduct this analysis. To create the study area, a polygon shapefile of glacial aquifers was downloaded from the United States Geological Survey (USGS) website (USGS, 2002) and layered over a U.S. States layer downloaded from ArcGIS online to create a map of glacial aquifers across the U.S. that are similar to Holliston in regards to both shallow characteristics and composition of glacial surficial deposits. For these reasons, the glacial aquifers shapefile was the most appropriate choice to represent aquifer areas similar to Holliston. Next, a U.S. bedrock lithology layer was downloaded from the USGS website (Horton, 2017) and used in the "intersect" tool with a Holliston Town boundary layer downloaded from the Massachusetts Geographic Information Systems (MassGIS) website (MassGIS, 2018). This identified the specific bedrock types from the lithology layer that fell within the Holliston Town boundary. The “select by attributes” tool was used to create a new layer from the bedrock lithology layer that included bedrock types in the U.S. that were the same as those within the Holliston Town boundary. The output layer with bedrock similar to Holliston and the glacial aquifer layer were then used with the “intersect” tool to create a polygon layer with both characteristics, and was used as the study area for this project.

3.2 Vulnerability maps

Since the study area shapefile consisted of many polygons based on bedrock and aquifer type, the “dissolve” tool was used to combine the entire aquifer area into one polygon feature. The output resulted in a single polygon in terms of attribute data, yet consisted of several polygons not connected with each other. Next, a U.S. Counties layer was used in the “clip” tool with the study area polygon, which created a layer of study area counties. This provided a means to later calculate populations by county above the study area and exclude all areas outside the study area for a more accurate population count rather than using the entire county.

A raster map of population data from 2015 in 1km x 1km pixels was download from the National Aeronautics and Space Administration (NASA) Socioeconomic Data and Applications Center (SEDAC) website (CIESIN, 2017) and used in the “zonal statistics to table” tool with the study area county layer. This created a table that combined the raster population data with the study area counties layer. The table was then joined with the study area county layer using the “join” feature, which identified the number of people at risk of consuming contaminated water in each county within the study area from natural sources of Mn based on geologic characteristics of their aquifers.

Since Holliston’s water contamination may also be caused by inputs from anthropogenic sources of contamination (Claus Henn et al., 2017), waste sites were added to identify potential areas of increased risk. TCE and Mn release sites were retrieved from the USEPA’s Toxic Release Inventory (TRI) explorer Release Reports list generating tool (USEPA, 2018c). The dataset generator gives the option to select a chemical or element of interest and identify all facility release reports across the U.S., with results from a 2017 dataset released in October 2018. The online tool allows the user to select latitude and longitude data for each site, which was then used in the "excel to table" tool in ArcMAP. Using the table data, point shapefiles were then created with the "add x, y data" tool. Superfund sites were retrieved from the USEPA Superfund website using the "*Superfund National Priorities List (NPL) Where You Live Map*" tool (USEPA, 2018b). Using the EPA's Superfund webpage, a map of current Superfund sites was created and the corresponding attribute table with latitude and longitude data was then exported to an excel document and converted to a table in ArcMap using the "excel to table" tool. The "add x, y data" tool was used again to convert the table into a point shapefile in ArcMap.

These processes created shapefiles for TCE release sites, Mn release sites, and Superfund sites. The various waste site shape files were then used with the "intersect" tool to identify the study site counties either containing or within 1km of waste sites. The "intersect" tool was used with study area counties and 1) TCE sites, 2) combined TCE and Mn release sites created by using the "merge" tool, and 3) combined TCE release sites, Mn release sites, and Superfund sites that were created using the "merge" tool. The ArcMap "summarize" and "statistics" tools were used to identify population data for: 1) areas vulnerable to natural Mn contamination, 2) areas of natural Mn contamination that are also vulnerable to anthropogenic toxics from TCE release sites, 3) areas of natural Mn contamination that are also vulnerable to anthropogenic toxics from TCE release sites and Mn release sites, and 4) areas of natural Mn contamination that are also vulnerable to anthropogenic toxics from TCE release sites, Mn release sites, and Superfund sites.

One problem encountered during this study was the inconsistency or lack of local waste site data across states. An example additional map of waste facilities was created to show just how many waste sites can be found in a state at more local scales: a layer for the state of Vermont was created by selecting the state from the U.S. States layer and using the "create layer from selected features" tool. A layer containing waste facilities and both open and closed landfills was added to the state map from the ArgGIS online database. GIS data used in this study are listed below in Table 1.

Data Layer	Source	File Type	Description
U.S. States	Esri	Shapefile – Polygon	Represents U.S. States
U.S. Counties	Esri	Shapefile – Polygon	Represents U.S. Counties
Town of Holliston	MassGIS	Shapefile – Polygon	Represents border around area of Town of Holliston
U.S. Bedrock lithology	USGS	Shapefile – Polygon	Represents bedrock types across the U.S.
Glacial Aquifers	USGS	Shapefile – Polygon	Represents glacial aquifer area across Northern U.S.
Superfund sites (created)	USEPA	Shapefile – Point	Created from lat/long attribute table data from the USEPA Superfund webpage
TCE and Mn sites (created)	USEPA	Shapefile – Point	Created from lat/long data retrieved from the USEPA TRI explorer Release Reports webpage
Population count 2015 30 sec	CIESIN	GeoTIFF – Raster	Provided population data in 1km x 1km pixels over study area
Vermont landfills and waste facilities	Vermont AEC	Shapefile – Points	Provides locations of waste facilities and open/closed landfills

Table 1: Data layers used or created using ArcGIS software ArcMap 10.5.1.

4.0 Results

The study area map was created based on the intersecting features of glacial aquifers (Figure 1) and bedrock lithology similar to the Holliston area (Figure 2), which included granite, gabbro, quartzite, and metavolcanic rock. The resulting study area included 14 states across the Northern U.S. from Maine to Minnesota (Figure 3). A map of the study areas with population by county is shown in Figure 4. These data were used to help provide an understanding of how many people may be at risk to *natural Mn contamination* in their drinking water. Table 2 summarizes the population and county data by state with aquifers vulnerable to contamination. The results identified a population of 2,019,509 million across 14 states at risk of natural sources of Mn contamination when considering only those who reside above the study area. The state of Massachusetts had the greatest population affected with approximately 1.17 million people potentially at risk. Waste sites were added to the study area map to

Study Area: U.S. Aquifers Vulnerable to Natural Manganese Contamination

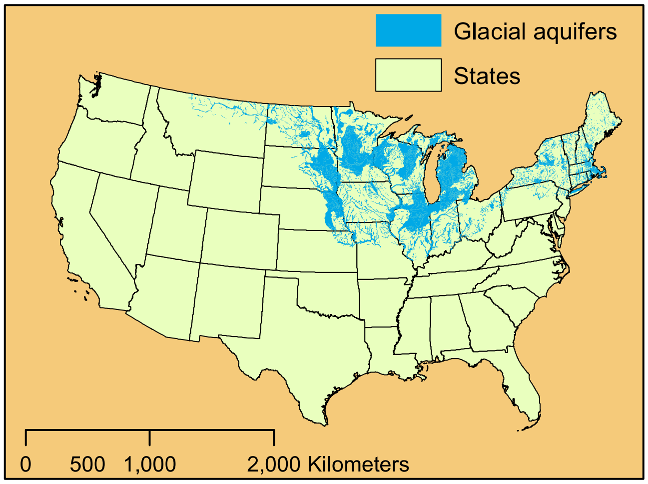


Figure 1: Glacial aquifers in the United States.

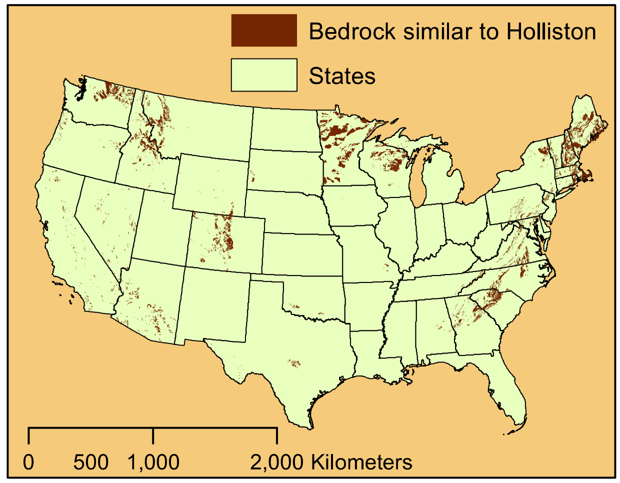


Figure 2: Bedrock similar to Holliston.

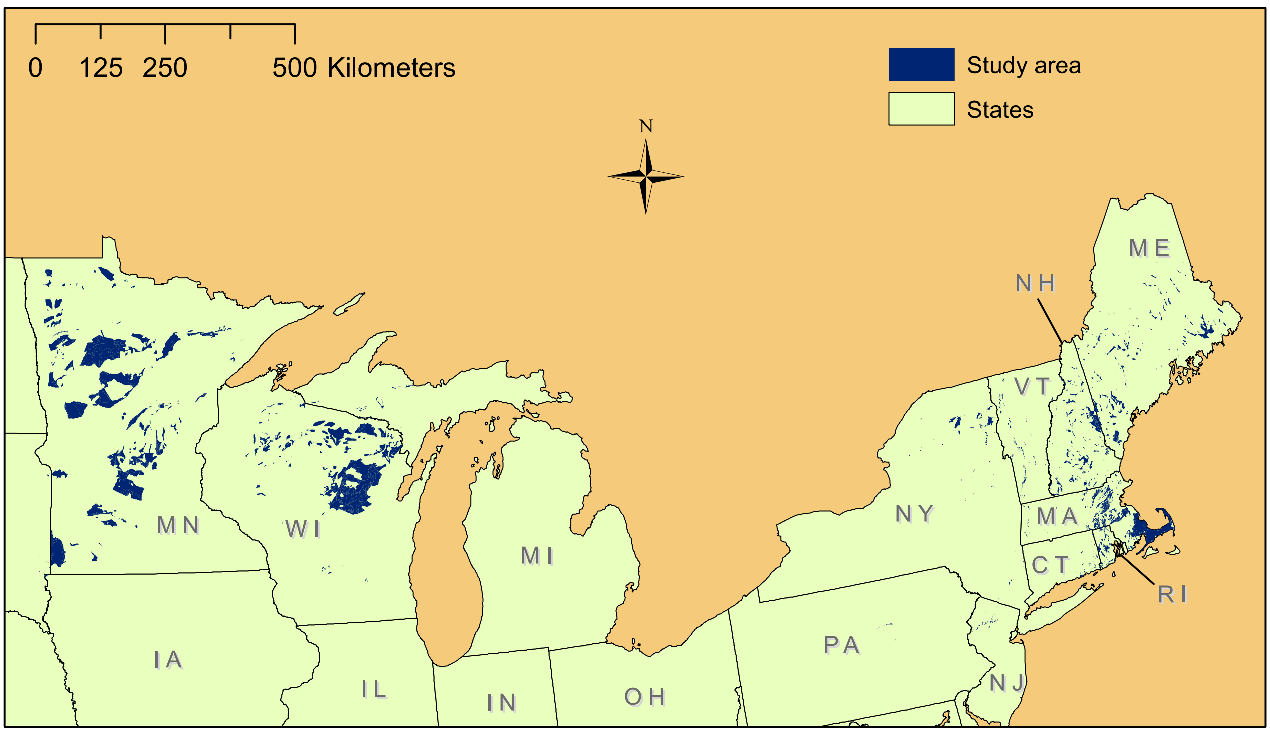


Figure 3: Study area created from intersection of glacial aquifer systems (Figure 1) and bedrock similar to Holliston (Figure 2).

Sources: Esri Data and Maps 2011;USGS
Projection: NAD 1983 (2011) Contiguous USA Albers.

U.S. Population Above Aquifers Vulnerable to Natural Sources of Mn Contamination

Total population at risk: 2,019,509

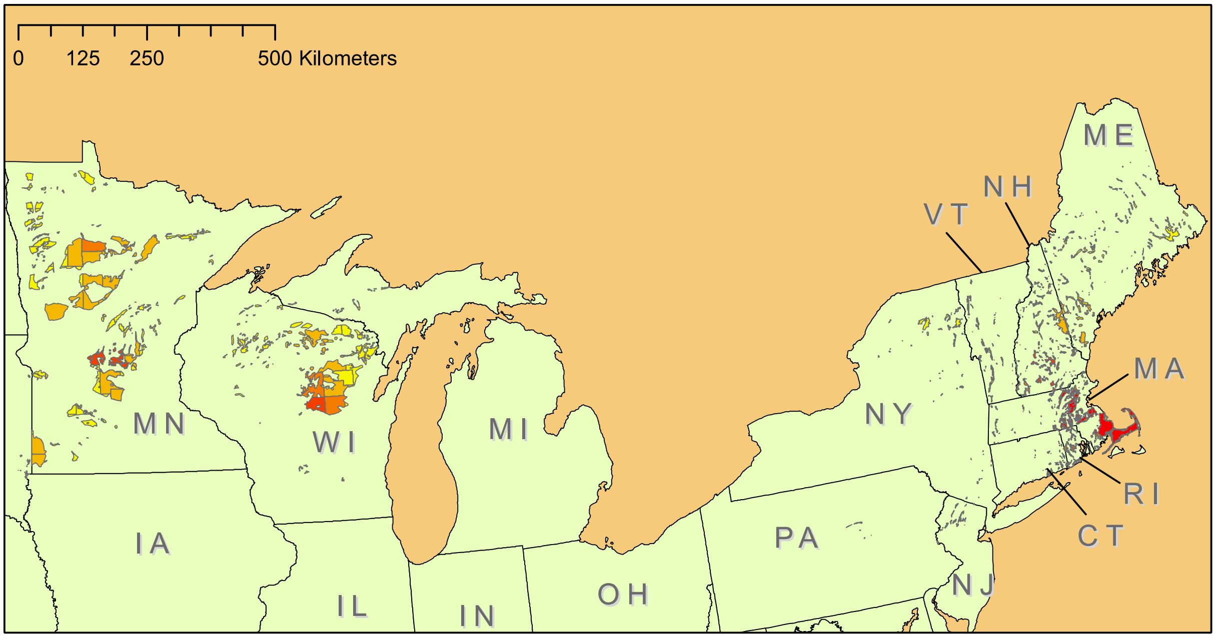
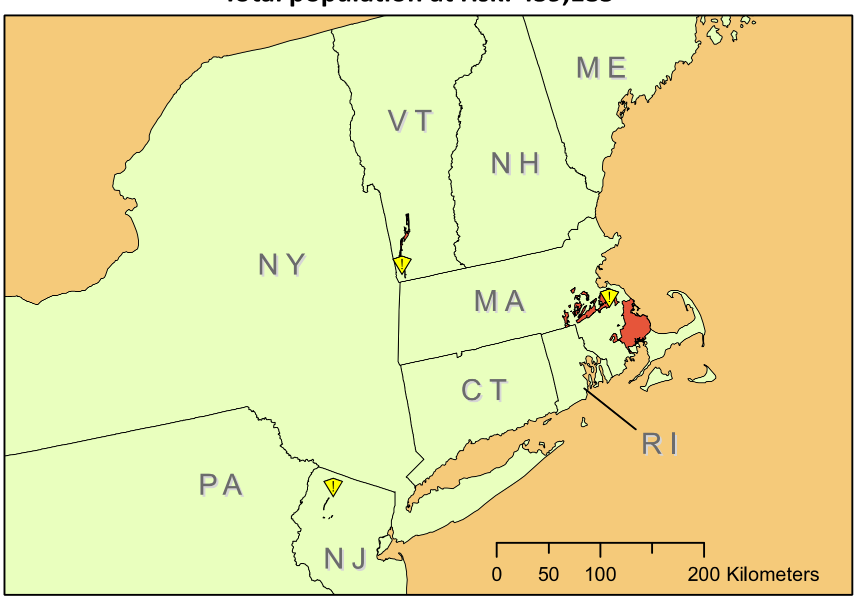


Figure 4: U.S. population above aquifers vulnerable to natural Mn contamination

U.S. Population Above Aquifers Vulnerable to Natural Sources of Mn Contamination and Anthropogenic Toxics From TCE Release Sites

Total population at risk: 439,183



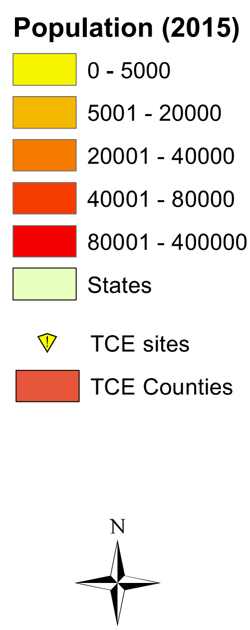


Figure 5: U.S. aquifers vulnerable to natural Mn contamination that are also at riskof anthropogenic toxics from TCE release sites

Sources: Esri Data and Maps 2011; USGS; CEISIN; USEPA. Projection: NAD 1983 (2011) Contiguous USA Albers.

U.S. Population Above Aquifers Vulnerable to Natural Sources of Mn Contamination and Anthropogenic Toxics From TCE and Mn Release Sites

Total population at risk: 1,173,712

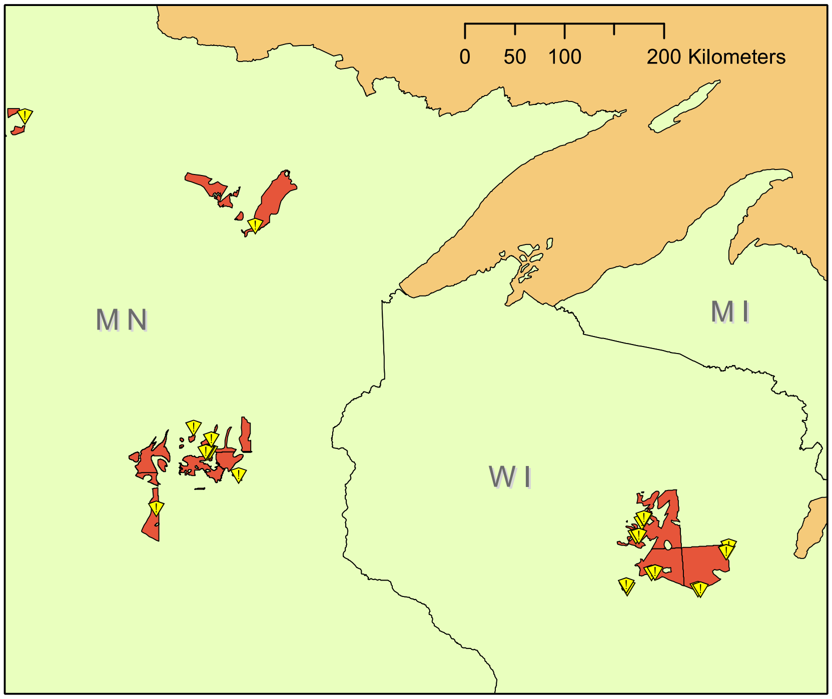


Figure 6: Western section of U.S. aquifers vulnerable to natural Mn contamination that are also at risk of anthropogenic toxics from Mn and TCE release sites.

TCE and Mn sites

TCE and Mn Counties

States

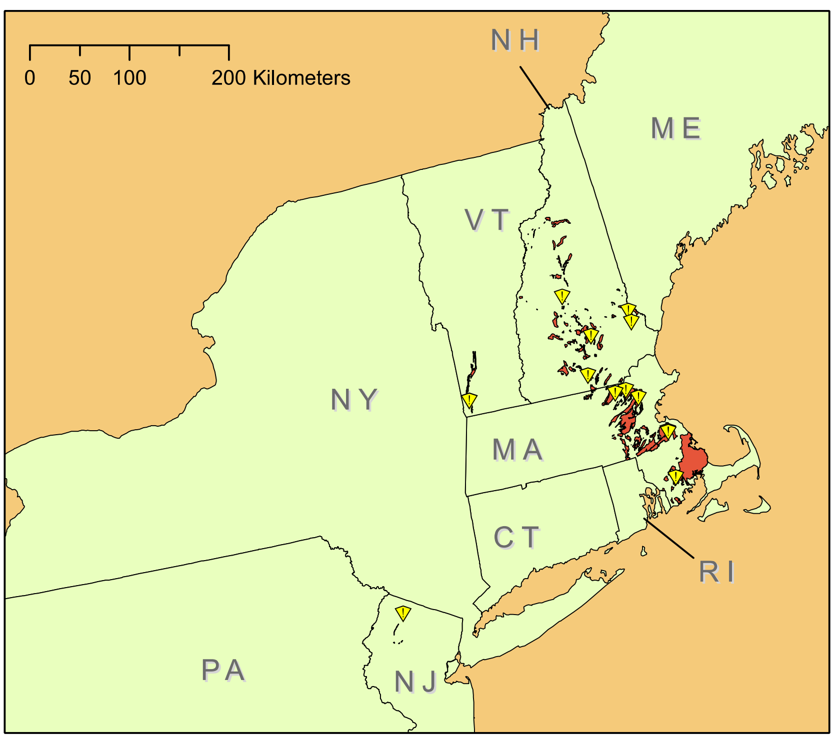
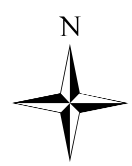


Figure 7: Eastern section of U.S. aquifers vulnerable to natural Mn contamination that are also at risk of anthropogenic toxics from Mn and TCE release sites.



Sources: Esri Data and Maps 2011; USGS; CEISIN; USEPA. Projection: NAD 1983 (2011) Contiguous USA Albers.

U.S. Population Above Aquifers Vulnerable to Natural Sources of Mn Contamination and Anthropogenic Toxics From TCE Release Sites, Mn Release Sites, and Superfund Sites

Total population at risk: 1,693,683

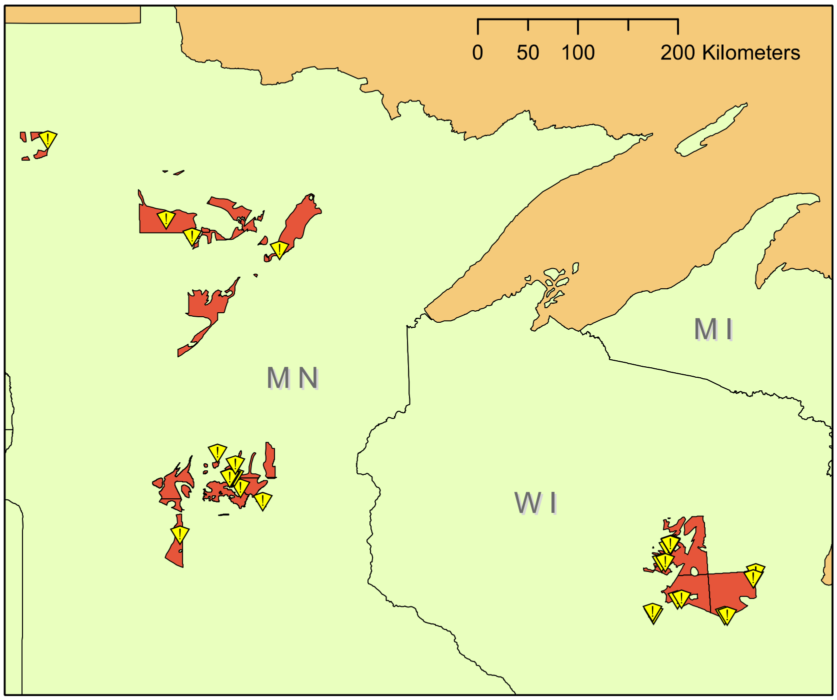


Figure 8: Western section of U.S. aquifers vulnerable to natural Mn contamination that are also at risk of anthropogenic toxics from Mn release sites, Superfund sites, and TCE release sites.

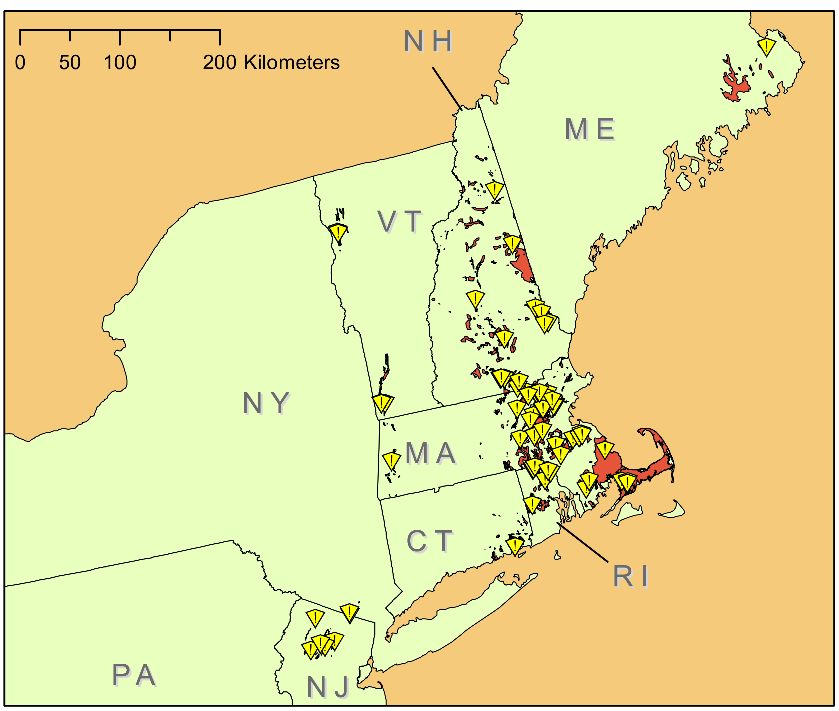
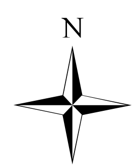


Figure 9: Eastern section of U.S. aquifers vulnerable to natural Mn contamination that are also at risk of anthropogenic toxics from Mn release sites, Superfund sites, and TCE release sites.



Sources: Esri Data and Maps 2011; USGS; CEISIN; USEPA. Projection: NAD 1983 (2011) Contiguous USA Albers.

State of Vermont Landfills and Waste Facilities

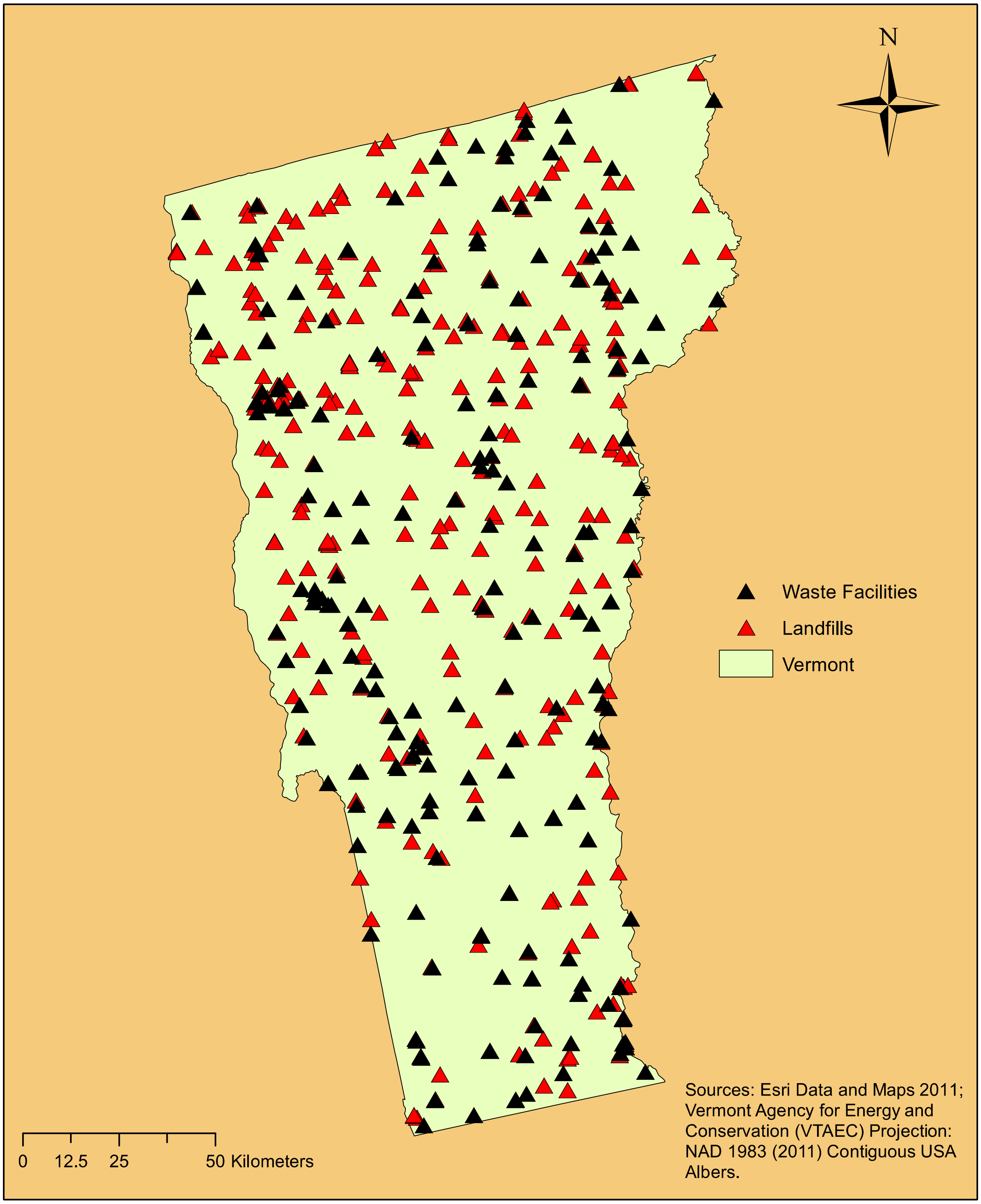


Figure 10: State of Vermont landfills and waste facilities - displaying a total of 196 waste facilities and 334 landfills throughout the State

identify areas vulnerable to drinking water contamination by both natural Mn and anthropogenic toxics from, posing an even greater risk of contamination.

Superfund sites consist of sites that are either currently on, proposed for, or deleted from the NPL and consist of landfills, oil industries, recycling centers, toxic facilities, and several other sites associated with the use of hazardous materials. Although some sites have been deleted from the NPL, understanding locations of former areas of contamination or closed landfills remains important when considering sources of contamination due to the uncertainty of mobilization and transport patterns of previously reported contaminants.

The USEPA TRI tool identified 151 TCE release sites across the U.S., and of those 151, three out TCE release sites fell within 1km of the study area counties (Figure 5 and Table 2). These three sites affect four counties across three states with a population of 439,181 . Thirty-eight out of 3,839

	Nat: Mn		***Nat: Mn / Anthro: TCE, Mn, Superfund***		***Nat: Mn / Anthro: TCE, Mn***		***Nat: Mn / Anthro: TCE***	
State	**Counties**	**Population**	**Counties**	**Population**	**Counties**	**Population**	**Counties**	**Population**
Connecticut	7	10,511	1	8,344				
Iowa	1	89						
Maine	14	47,853	1	672				
Massachusetts	13	1,168,594	8	1,157,566	4	837,621	2	434,488
Michigan	6	1,890						
Minnesota	50	272,273	8	144,654	6	105,372		
New Hampshire	10	168,458	6	138,780	4	118,871		
New Jersey	6	35,537	3	34,769	1	1,214	1	1,214
New York	16	8,951	1	1,509				
Pennsylvania	5	681						
Rhode Island	5	72,560	2	60,802				
South Dakota	3	3,438						
Vermont	12	44,199	2	39,434	1	3,481	1	3,481
Wisconsin	30	184,476	4	107,153	4	107,153		
Total	**178**	**2,019,509**	**36**	**1,693,683**	**20**	**1,173,712**	**4**	**439,183**

Table 2: County and population data by State for areas at risk of 1) Natural ("Nat" in header) Mn contamination, 2) Natural Mn contamination and anthropogenic ("Anthro" in header) toxics from TCE release, Mn release, and Superfund sites, 3) Natural Mn contamination and anthropogenic toxics from TCE and Mn release sites, and 4) Natural Mn contamination and anthropogenic toxics from TCE release sites

anthropogenic Mn release sites fell within 1km of the study area, and were added with the three TCE sites to show how many people were affected by natural Mn and anthropogenic TCE and Mn (Figures 6 and 7). These sites affect 1,173,712 people in 20 counties across six states (Table 2). Finally, Figures 8 and 9 show study areas at risk of natural Mn contamination and anthropogenic toxics from TCE release sites, Mn release sites, and Superfund sites. These waste sites include 79 Superfund sites, 38 Mn release sites, and three TCE release sites within 1km of the study area, and affect 1,693,683 people in 36 counties across 10 states (Table 2).

To exemplify the need to carry out follow-on work that also includes myriad other waste sites (e.g. Massachusetts 21E Sites), the state of Vermont waste sites shown in Figure 10 consist of 334 open and close landfills and 196 waste facilities within all counties throughout the state.

5.0 Discussion

The study area results identified approximately 2.02 million people throughout 14 states who may be using water sources with a potential of Mn contamination from natural sources. Data show groundwater contamination from Mn can be correlated with factors such as bedrock type (in this study based on Holliston Massachusetts lithology represented by gabbro, granite, quartzite, and metavolcanic rock), glacial systems, and surficial aquifers. These four rock types are shown to have concentrations of Mn contained within them (Kabata-Pendias, 2001; Force & Cox, 1991; Andresen & Gabrielsen, 1979). By utilizing intersecting layers of glacial aquifers and the Town of Holliston's bedrock types, the study area is indicative of aquifers and areas susceptible to Mn contamination at a basic level. Several other factors must be taken into account for a more inclusive assessment of aquifer vulnerability to natural Mn contamination. Some of these factors include but are not limited to:

- *hydrologic factors such as watershed, ground, and surface water flows;*

- *other minerals and elements from natural sources with potentially harmful effects on humans; and*
- *soil and surficial deposit data that include pH, mineral composition, and other hydrogeologic factors.*

This information may be useful if applied to a weighted model or even a Mahalanobis Typicality Function model in mapping programs like Terrset as a starting point to determine which factors are the most influencing on groundwater. The present study is useful as a jumping-off point for continued research and reiterates the fact that many areas warrant further investigation. A question of whether the 2.02 million people at risk is a realistic figure or not can be taken into consideration based on the aforementioned factors. This number could be *decreased* by limiting the affected areas based on:

- *the number of people actually using groundwater – some may not use public water sources;*
- *identification of which domestic and public water systems have treatment facilities that can remove potentially harmful elements like Mn, and;*
- *areas where geology may have little to no effect on Mn levels in groundwater.*

On the other hand, the population of those affected could be *increased* significantly by considering:

- *hydrologic processes that enable water to move mobilized minerals and elements into groundwater based on factors such as watershed, geology, soil type, pH, and topography;*
- *bedrock, soil, and aquifer types with depths other than the Town of Holliston bedrock and glacial aquifers that can also be associated with high concentrations of Mn, such as deeper anoxic groundwater that can be high in Mn (Groschen et al., 2008); and*

- *the amount of people using aquifers within the study site – this assessment only includes population data directly above the study site, yet aquifers can be recharged from areas far beyond the actual aquifer boundary.*

Therefore, with a possible increase or decrease in either direction of the estimated number of people at risk in this study, the 2.02 million people identified at risk seems a reasonable preliminary estimate.

Waste sites were included in this analysis to identify areas where anthropogenic sources of pollution increase the susceptibility of groundwater contamination from natural Mn and other toxics together. Similar to the first step of this assessment - just natural sources of Mn contamination - this second step was not a comprehensive evaluation because all local waste sites were not included. By considering many more waste sites that likely include other toxics, the shallow-aquifer population at risk to either natural Mn plus other toxics, but also other toxics alone (without natural Mn) may increase substantially. A map of landfills and waste facilities in the state of Vermont was created to illustrate how many more sites may be considered for a further evaluation to help identify groundwater risks of contamination (Figure 10). It is also interesting to note that Vermont is second to lowest of all states in terms of population based on the data in the U.S. Counties layer attribute table, and the amount of waste sites in each state would be expected to increase with population size. These local waste facilities, landfills, and dumps are important factors for assessing potential groundwater contamination, and can be used to strengthen larger-scale integrated risk assessments to maximize public safety. Local waste sites (aside from the example of sites in Vermont) were not included in this study because of the inconsistency in data. Attempts to retrieve local waste site and landfill site data for this study were met with challenges: each state that fell within the study area had either different sets of data with different identification factors, or files were unavailable. Some states had data layers for waste sites on ArcGIS online, but they all had different formats, descriptions, and characteristics. Maine, Wisconsin, and

Vermont were among some of the states with data that could be very useful for this assessment, but they would first need to be converted to a uniform data set for analyses. Any attempt to use mismatched data sets would undermine analysis.

The waste sites included in this study provided a basic assessment of groundwater vulnerability from anthropogenic sources with information pertaining to pollution concerns at national levels. An inclusion of local waste sites in an assessment like this would most certainly increase data and expand the number of vulnerable areas warranting inspection. The shapefile of 120 combined TCE release, Mn release, and Superfund sites used for this analysis could evolve into a file containing tens of thousands of sites when local waste site data are included. This assessment also only included waste sites that fell directly onto or within 1km of the study area aquifers with Holliston-type bedrock, which means the waste sites that did not fall directly within or close to the study area were excluded even though hydrologic factors and watershed data would likely show most of the aquifers receive inputs from zones beyond the study area. For this reason, further research into hydrologic activity and watershed data is required.

Similar to the question regarding population with regards to natural sources of Mn, a question of whether the 1.69 million people at risk from anthropogenic pollution (from combined waste sites) is a realistic estimate or not can also be considered. This population in vulnerable aquifer areas could be *decreased* if limiting the affected areas based on:

- *the number of people actually using groundwater;*
- *identification of which domestic and public water systems have treatment facilities that can remove potentially harmful elements like Mn; and*
- *areas where waste sites may have little to no effect on contaminant levels in groundwater based on construction and maintenance.*

However, the population of those affected by anthropogenic pollution is likely to *increase* based on:

- *watershed and hydrologic processes that indicate all areas that contribute to aquifer recharge, which could expand the waste site inclusion zone for analysis;*
- *waste site characteristics that include age, size, or specific materials accepted rich in contaminants;*
- *waste site treatment methods, and most importantly;*
- *inclusion of local waste site data.*

The first three factors listed for both the potential increase or decrease in population at risk may balance each other out or slightly increase or decrease the estimations in this study, but the fourth factor (*inclusion of local waste sites*) would likely result in a significant increase in the number of vulnerable aquifers and, subsequently, the population at risk since there are so many local waste sites across the U.S. This is illustrated in the state of Vermont (Figure 10) with 530 total waste sites falling within every single county throughout one of the least populated states in the U.S.

This study shows there are many Americans at risk of toxic contamination in their drinking water. Specifically, 2.02 million people at risk from natural sources of Mn, and 1.69 million at risk from both natural and anthropogenic toxics together. Based on supporting literature and data from previous studies, this approach identifies areas at risk of groundwater contamination and can be used for further analyses with the inclusion of some or all of the influencing factors previously mentioned that were not used in this study. The populations identified at potential risk and the supporting literature that discusses numerous studies relating to adverse effects from Mn consumption implies the EPA's current policy for Mn in drinking water may be inadequate for protection of population health, with U.S.

population risks substantially underestimated.

6.0 Conclusion and recommendations

This assessment used the geologic characteristics of Holliston's aquifer and bedrock types to identify similar areas in the U.S. that may be at risk of drinking water contamination from natural Mn and also toxics from anthropogenic waste sites. This analysis found over 2.02 million people across 14 states in the northern contiguous U.S. have similar bedrock and aquifer type to Holliston, putting them at potential risk of having Mn contamination in their water from natural sources.

Since landfills and waste sites have outputs of toxic chemicals (e.g. TCE) from waste site leachate, they must be considered as possible sources of groundwater contamination. This study used TCE release, Mn release, and Superfund waste sites above or within 1km of shallow glacial aquifers as possible sources of anthropogenic contamination. The population potentially affected by both natural Mn and anthropogenic contamination is estimated at 1.69 million people across 10 states. These areas warrant further investigation into groundwater vulnerability, and several other factors not included in this study should be considered for a more complete risk assessment such as:

- **Local waste sites** - there are many more waste sites at local scales across the U.S. other than the ones used in this study with potentially high levels of Mn that can enter groundwater via leachate;
- **Hydrologic factors** - water is the mover and shaker of all things, and provides a vehicle for the mobilization and movement of elements like Mn into groundwater, while also including consideration of residents who use aquifers;
- **Soil and surficial deposits** - due to the abundance and variation of Mn in the layers of Earth's crust, areas should be weighted differently;
- Areas with **water treatment plants** to prevent contamination of Mn and other toxics;

- Waste sites with **barriers or waste treatments** that provide a higher level of groundwater protection from leachate;
- The number of **people actually using** groundwater – since many people may use water from the study area even though they do not live directly above it;
- **Watershed data** that could result in a more expansive inclusion of waste sites that do not fall directly on or near the aquifer boundaries.

A more complete set of factors that includes those above and others was used in the assessment of Holliston's aquifers, and could be used use in follow-on assessments in areas identified in this study (Claus Henn et al., 2017, p. 15).

It would be of great value to identify - or if none exists, create - a database with a consistent list of waste sites throughout all states at local levels with a uniform set of attribute data. A source to create such a list could perhaps derive from inputs from Source Water Assessment and Protection (SWAP) reports. Although not mandatory, SWAP programs are recommended by the EPA for all states to use. The reports are designed to provide information on local land use and groundwater recharge, and include assessments of areas susceptible to sources of contamination (Engelberg & Grumbles, 2005). These reports can help residents understand where waste sites are at local scales and help them understand where potential risks to groundwater contamination may be. Furthermore, a waste site hazard ranking system based on site construction, practices, waste materials involved, size, age, proximity to water sources, and others could be useful to gain an even better understanding of impacts associated with local anthropogenic pollution. Such results argue strongly for greater regulatory protections for shallow aquifers – both in terms of natural and anthropogenic contaminants.

Finally, the limited knowledge regarding adverse human health effects from Mn consumption and policies currently in place regarding exposure are concerning, so continued research of human health effects from oral Mn exposure should be encouraged. As the number of studies and empirical results from these studies continue to rise, the information can be used as a tool to redefine policy regarding acceptable levels of Mn in aquifer drinking water.

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