Geospatial and statistical analysis of anthropogenic ground-water contamination

Jessica Warrack

Department of Civil Engineering

McGill University, Montreal

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Contributions of Authors

Chapter 3 and 4 of this report are based on two separate papers. Chapter 3 is a paper called *Groundwater phosphorus concentrations: global trends and links with agricultural and oil and gas activities* that was submitted to Environmental Research Letters (ERL) in August 2021 and is currently under review. This paper is co-authored by my supervisors, Dr. Mary Kang in the Civil Engineering department at McGill University, and Dr. Christian von Sperber from the Geography department at McGill University. The research contained within this article is my own and I am the corresponding author. Dr. Kang and Dr. von Sperber provided guidance on project conception, methodology development, and writing. Chapter 4, titled *Estimating the base of fresh water in California*, was submitted to an article collection titled *Management of Unconventional Water Resources* in the journal *Frontiers of Water* in June 2021 and is currently under review. I am the corresponding author on this paper, and Dr. Mary Kang is a co-author. Again, the research completed within this section and the subsequent writing is my own. Dr. Kang assisted in project conception, methodology development, and writing.

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Abstract

We use geospatial and statistical analysis to identify areas where there may be gaps in current legislation that protects aquifers and to identify anthropogenic contamination sources and pathways. Specifically, we focus on phosphorus (P) concentrations in groundwater and total dissolved solids (TDS) concentrations in groundwater in California. The results obtained from the analysis of these datasets can be used to guide sustainable water and ecosystem management policies and inform future groundwater monitoring efforts.

Excess P in surface waters is a main driver of eutrophication, but P monitoring in groundwater is often overlooked because it was historically assumed that P is immobile in groundwater. To examine the risk P in groundwater poses to surface waters and ecosystems, we compile and analyze 161,321 groundwater P measurements from 12 different countries. We find that all 12 countries report groundwater P concentrations high enough to potentially cause ongoing or continued eutrophication in surface waters. Additionally, in Canada and the United States, we find that 93% of total P (TP) samples are found within 50 km of crop/pastureland. We also find a correlation between distance from the closest oil and gas well and elevated TP concentrations in the Canadian provinces of Alberta and Ontario. We focus on these provinces because there is a high density of oil and gas wells and of TP concentrations >0.1 mg P/L. These case studies indicate the need to further investigate the role of agriculture and oil and gas wells on groundwater impacts by P and other contaminants. The global data synthesis shows that there are many data gaps limiting our ability to assess groundwater P contamination, including their sources and pathways. Understanding the sources and pathways for groundwater contamination is important for sustainable groundwater management practices and protection.

Total dissolved solids (TDS) concentrations represent minerals, salts, metals cations, or anions dissolved in water and is often taken as an indicator for overall

groundwater quality. We use 216,754 total dissolved solids (TDS) concentration measurements in groundwater in California, United States, to examine the effectiveness of current groundwater legislation with respect to the base of fresh water (BFW), which is commonly used to identify the vertical extent to which aquifers are subject to groundwater management in the state. The definition for “fresh” water varies between regulating bodies but is generally taken to range from 1,000 to 3,000 mg/L. We analyze trends in the TDS dataset and find that we cannot estimate the BFW in 73% of California. We are able to estimate the BFW in 22% of the Central Valley, a key agricultural region with large groundwater demands and many critically overdrafted groundwater basins. Using a TDS limit of 3,000 mg/L, we estimate the shallowest BFW to be 155 m below ground surface in Kern County and the deepest BFW to be 589 m below ground surface in Stanislaus County.

Our analysis demonstrates that geospatial and statistical analysis are useful for managing and analyzing groundwater contamination data. Specifically, there are opportunities for enhanced and strategic management and monitoring of groundwater, focusing on P and TDS. Currently, limitations in the availability of groundwater quality data make the delineation of usable groundwater and the extent of groundwater contamination challenging to identify. Moreover, implementing groundwater management that simultaneously considers and balances impacts of agricultural and oil and gas activities is needed. The results from this thesis can be used to design data-driven groundwater management programs and strategies that protect groundwater resources around the world.

Abstract in French

On utilise des analyses géospatiales et statistiques pour identifier les zones où il y a des lacunes dans la législation actuelle qui protège les aquifères et pour identifier les sources et les voies de contamination anthropique. On étudie les concentrations de phosphore (P) dans les eaux souterraines et les concentrations de solides dissous totaux (SDT) dans les eaux souterraines en Californie. Nos résultats guideront les politiques de gestion de durabilité de l'eau et des écosystèmes et informerons futurs efforts de surveillance des eaux souterraines.

L'excès de P dans les eaux de surface est l'un des principaux responsables de l'eutrophisation, mais la surveillance du P dans les eaux souterraines est négligée car historiquement le P était censé d'être immobile dans les eaux souterraines. On examine le risque que pose le P dans les eaux souterraines pour les eaux de surface et les écosystèmes, on compile et analyse 61 321 mesures de P dans les eaux souterraines de 12 pays. Ces pays ont des concentrations de P dans ces eaux suffisamment élevées pour potentiellement provoquer l'eutrophisation continue des eaux de surface. De plus, on constate qu'au Canada et aux USA, 93% des échantillons de P total (PT) se trouvent à moins de 50 km de cultures/pâturages et qu'il y a une corrélation entre la distance des puits de pétrole et de gaz les plus proche et les concentrations élevées de PT en Alberta et Ontario (provinces avec une forte densité de puits de pétrole et gaz et de concentrations de PT >0,1 mg P/L). On doit donc étudier le rôle de l'agriculture et des puits de pétrole et gaz sur les impacts du P et d'autres contaminants sur les eaux souterraines. La synthèse mondiale des données montre l'existence de nombreuses lacunes qui limitent la capacité à évaluer la contamination par le P des eaux souterraines, y compris leurs sources et leurs voies d'accès. Comprendre les sources et les voies de contamination des eaux souterraines aidera à de meilleurs pratiques de gestion et de protection durables de ces eaux.

Les concentrations SDT indiquent la qualité des eaux souterraines. On utilise 216 754 mesures de concentration de SDT des eaux souterraines Californiennes pour examiner l'efficacité de la législation actuelle sur les eaux souterraines en ce qui concerne la base d'eau douce (BDD), couramment utilisée pour identifier l'étendue verticale dans laquelle les aquifères sont soumis à la gestion des eaux souterraines. La définition d'eau douce varie mais est généralement comprise entre 1 000 et 3 000 mg/L. Nos analyses des tendances dans l'ensemble de données TDS indiquent que nous ne pouvons pas estimer le BDD dans 73% de la Californie. On peut cependant estimer la BDD dans 22% de la vallée centrale, une région agricole clé avec de grandes demandes en eau souterraine et de nombreux bassins d'eau souterraine gravement surexploités. Utilisant une limite SDT de 3 000 mg/L, on estime que le BDD la moins profonde se trouve à 155 m sous la surface du sol dans le comté de Kern et la plus profonde à 589 m sous la surface du sol dans le comté de Stanislaus.

On démontre que l'analyse géospatiale et statistique sont utiles pour gérer et analyser les données de contamination des eaux souterraines et qu'il y a des opportunités pour améliorer stratégiquement la gestion et surveillance des eaux souterraines, en se concentrant sur le P et le SDT. Les limites de la disponibilité des données sur la qualité des eaux souterraines rendent la délimitation des eaux souterraines utilisables et l'étendue de la contamination des eaux souterraines difficiles à identifier. De plus, l'établissement d'une gestion des eaux souterraines qui considère et équilibre simultanément les impacts des activités agricoles et pétrolières et gazières est nécessaire. Nos résultats aideront à concevoir des programmes et stratégies de gestion des eaux souterraines basés sur les données qui protègent les ressources en eaux souterraines mondiales.

Table of Contents

1. Introduction

1.1. Groundwater quality, contamination sources, and geospatial analysis

Groundwater is a widely used resource, supplying more than two billion people globally with water for agricultural, industrial and residential needs [1]. However, because groundwater is not currently as well monitored as other resources, it is often underregulated or poorly characterized [2-6]. Groundwater research is particularly valuable as growing populations, climate change and pollution will place even greater stress on groundwater resources in the future [7]. Therefore, understanding the potential risks of anthropogenic activities, such as agriculture and oil and gas development, and characterizing groundwater quality are useful for the implementation of groundwater management, preventing the exploitation and pollution of this valuable resource.

Data and data analysis are key components for identifying and solving environmental problems. Utilizing geospatial analysis with large datasets is an important tool for researchers in many fields including environmental conservation and water resource management [8, 9]. Governments worldwide including Canada [10], the United States [11], and Poland [12] are using results obtained from geospatial analysis to develop effective management practices for groundwater that address economic, social, and environmental challenges [13].

In this thesis, we conduct geospatial and statistical analysis on phosphorus (P) and total dissolved solids (TDS) concentrations in groundwater to identify potential sources and pathways for contamination and discuss the sustainability of current groundwater management strategies.

1.1.1. Phosphorus concentrations in groundwater

Nutrient enrichment from excess nitrogen and P, is a primary cause of surface water quality degradation, specifically eutrophication [14-16]. Eutrophication is defined as excessive plant growth in water bodies as a result of excess nutrients and is one of the most pressing environmental concerns for surface water systems around the world [15, 17-22]. Phosphorus has often been overlooked as a concern in groundwater aquifers for two main reasons: (1) it was historically assumed that P in groundwater is largely immobile [18] and anthropogenic P could not reach groundwater due to the high affinity of P to adsorb to soil particles [15], and (2) concentrations of P in groundwater are often compared to drinking water standards, rather than guidelines for ecological maintenance [23] or human health. Recent research has shown that anthropogenic phosphorus applications at the ground surface can reach groundwater [23, 24], that it is possible for phosphorus to be mobile in groundwater [24-28], and that high concentrations of P in groundwater can contribute to eutrophication of surface waters [18, 22, 28]. Moreover, P limits on drinking water are not set in many countries, including Canada and the United States [29-31]. Countries where there is a limit on phosphorus in drinking water have chosen concentrations that are significantly higher than limits set for phosphorus based on the preservation of surface water quality [23, 32]. To protect the quality of surface waters and prevent eutrophication, it is important to determine where contamination has already occurred and to understand the pathways through which P contamination of groundwater could occur in the future.

To date several studies have been conducted that analyze groundwater P contamination at specific sites [15, 24, 25, 28] or within certain countries [23, 33], but there has been no effort to gather groundwater P concentrations globally thus far. Identifying areas where there is limited groundwater data could present opportunities for localized sampling campaigns or gaps in government groundwater monitoring networks. Amalgamating global P data would help to identify which countries, if any, have relatively low concentrations of groundwater compared to the rest of the world. Countries with lower concentrations of P in groundwater could provide valuable insight into policies and strategies for effectively reducing or preventing groundwater P pollution.

Although agricultural runoff has been identified as one of the leading contributors to surface water eutrophication, limited research has been conducted on agriculture as a non-point source of phosphorus in groundwater aquifers [23]. To meet the needs of a growing population, cultivated land area and P fertilizer use are increasing; from 1970 to 2005 the cultivated area worldwide increased by 21.3% [34] and P fertilizer use increased over 300% in the period from 1961 to 2015 [35]. By 2050, it is estimated that agricultural land area could begin to decrease [34], but P fertilizer use will have to increase in order to maintain crop productivity [35]. As the prevalence of agricultural land and P fertilizer use increase in the coming years, it will be increasingly important to understand how agricultural activities impact the quality of groundwater so that effective mitigation techniques can be implemented.

Researchers have identified leaky oil and gas wells as a source of subsurface contamination and a potential pathway for surface contaminants to migrate to the subsurface [36-38]. Although previously unexplored, it is possible that runoff high in P from agricultural fields or urban areas could contaminate groundwater through improperly abandoned or otherwise leaky oil and gas wells. There are more than four million oil and gas wells in Canada and the United States alone [39], many of which are located on or near agricultural land. It is possible that leaking oil and gas wells could be a significant and overlooked contributor to groundwater P contamination and eventual surface eutrophication. For governments and other agencies to effectively monitor and minimize contamination of groundwater resources, it is necessary to identify all possible pathways through which contamination can occur.

1.1.2. Total dissolved solids concentrations in groundwater

To ensure usable groundwater is effectively protected from contamination, agencies around the world develop policies that limit the risk subsurface activities, such as oil and gas development, pose on groundwater quality. Some agencies utilize water quality to identify usable groundwater and subsequently restrict activities that may cause contamination in these areas [2, 40, 41]. This thesis will focus on groundwater quality and management in California, where groundwater is a critical resource with high demand. In California, total dissolved solids (TDS) concentrations are used to determine the base of fresh water, which stipulates depths where subsurface activities can occur [2, 41]. The “base of fresh water” is defined as “the depth in a well where the water in overlying aquifers has less than or equal to 3,000 mg per liter (mg/L or parts per million) of total dissolved solids” (quoting ref [42]). There are several assumptions embedded in the use of the base of fresh water concept to delineate protected zones in aquifers and these assumptions have not been sufficiently evaluated across the state, meaning they may not be valid in many locations. Moreover, the lack of current data further reduces the validity of the base of fresh water method [41].

Total dissolved solids (TDS) concentrations represent the presence of inorganic and organic matter dissolved in water. Primarily this includes cations such as calcium, magnesium, sodium, potassium, and silica and the anions bicarbonate, sulphate, and nitrate [43, 44]. Because combinations of these ions form salts, salinity is a related term used to describe TDS concentrations in water [43]. Total dissolved solids concentrations do not directly determine the quality of water, and the World Health Organization currently has no health-based guidelines for TDS concentrations [45]. Instead, several countries, including Canada, use TDS concentrations to classify water as fresh, brackish or saline. Water samples with higher TDS concentrations may not be suitable for all purposes because elevated TDS concentrations influence the taste of water and can cause corrosion in pipes and other equipment or salt build up in soils if used in agriculture [43, 44].

Although TDS limits for drinking water vary nationally and internationally depending on the agency [46-51], the upper limit for "fresh" human drinking water is highly variable depending on the authority [31, 41, 52], but is taken to be 1,000 mg/L by the United States Geological Survey (USGS) [53]. Water with TDS concentrations above that of fresh water but <10,000 mg/L is considered brackish [54]. It is possible to use brackish instead of fresh water directly in some applications [55-57], but desalination is becoming more economically feasible and treating brackish groundwater could reduce stress on fresh groundwater resources [48, 54]. Beyond TDS concentrations of 10,000 mg/L, the United States Geological Survey (USGS) classifies water as "highly saline" and water with TDS concentrations >35,000 mg/L is considered seawater or brine [53]. Groundwater contamination has become a growing concern over the last 50 years, and governments around the world, including Canada and the United States, are beginning to design and implement policies that will ensure sustainable groundwater use.

The invisible nature of groundwater makes it inherently difficult to monitor and manage. However, as the largest freshwater store on Earth and an essential part of many of Earth's systems, it is essential that groundwater is governed sustainably. Around the world, groundwater governance is highly diverse, but several reports have found that existing groundwater management is not sustainable [3, 58]. Identification of novel sources through which groundwater contamination is occurring and assessing the current state of groundwater quality will allow for updated groundwater management initiatives that protect usable groundwater and identification of areas where remediation efforts could be valuable.

1.2. Objectives and approach

To effectively manage groundwater, it is important to increase the understanding of groundwater resources in terms of how and where contamination is occurring and better estimating the quality and quantity of groundwater aquifers. These concerns imply the need to study three important but distinct issues:

1. Global assessment of phosphorus concentrations in groundwater
    i. Determine the availability of phosphorus data in groundwater worldwide and identify gaps in current monitoring systems globally.
    ii. Identify countries with concerning levels of phosphorus in groundwater with regards to surface water eutrophication.
2. Identify potential sources of anthropogenic contamination
    i. Identify land use linked to enhanced phosphorus concentrations in groundwater in Canada and the United States.
    ii. In areas with a high density of oil and gas wells (Canadian provinces of Alberta and Ontario), determine if high concentrations of phosphorus in groundwater are more prevalent.
3. Characterization of groundwater in California using available total dissolved solids concentration data
    i. Evaluate TDS concentration profiles.
    ii. Estimate the base of fresh water where possible in the Central Valley and compare them to current BFW estimates.
    iii. Discuss whether the base of fresh water is an acceptable method for developing sustainable groundwater management plans and protect usable groundwater resources, and consider alternatives (i.e., base of brackish water).

1.3. Organization of the thesis

Following the first chapter, which is the introduction, there are four subsequent chapters. Chapter two is a literature review that examines the current understanding of the movement of P in subsurface environments and the dynamics, discusses agricultural systems as a source of P in the environment, summarizes current efforts to characterize groundwater in California, and identifies current knowledge gaps with regards to BFW estimations and groundwater management policies. Chapter three discusses the results of a global data collection campaign for groundwater P data, an analysis of agricultural land use on P concentrations in groundwater, and the identification of oil and gas wells as a potential pathway for surface P to reach groundwater. subsurface contamination of P. Chapter four explains the results achieved from analysis of a large dataset (216,754 TDS concentrations) of groundwater total dissolved solids concentration data and the estimation of the base of fresh water throughout California. Chapter five concludes the thesis by discussing the significance of the research conducted within and giving recommendations for future work.

2. Literature review

2.1. Groundwater contamination sources and pathways

For groundwater contamination to occur, it is necessary to have both a source and a pathway. The source is the origin of pollution, and the pathway is "a means through which the pollutant can reach and affect" groundwater [59]. We focus on agriculture as a primary source through which excess P is introduced to the environment. **Figure 1** shows potential pathways which include P infiltration into soils, P runoff into surface waters, or P runoff into oil and gas wells where contamination could reach groundwater aquifers.

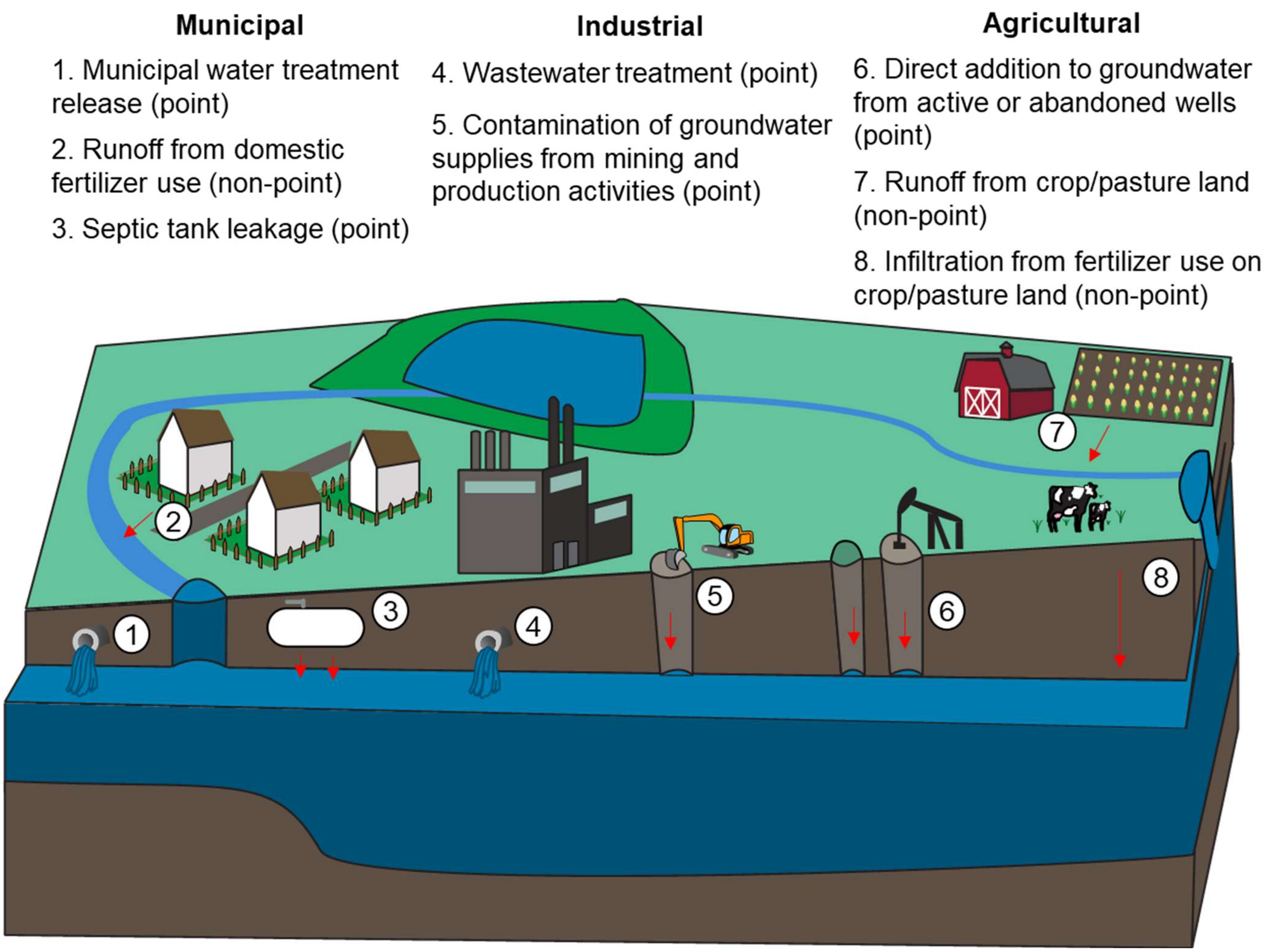


Figure 1. Potential sources and pathways through which anthropogenic contamination can reach groundwater aquifers.

2.1.1. Anthropogenic sources of phosphorus

As a critical nutrient for all life forms, phosphorus (P) is naturally occurring in all aquatic and terrestrial ecosystems. Because the phosphorus cycle has a significantly longer timescale than other nutrients and phosphorus has a relatively low solubility when compared to nitrogen [60], and transform rapidly to insoluble forms, phosphorus is commonly a limiting nutrient, especially in aquatic ecosystems [61]. However, excess P is known to reduce biodiversity, and in aquatic ecosystems, excess P is a leading contributor to eutrophication [62]. Anthropogenic impacts to the phosphorus cycle that are well studied and known are: (i) increased run off and erosion as a result of land use conversion, (ii) use of organic waste in agricultural systems, (iii) application of inorganic fertilizers, and (iv) release of sewage containing human waste and detergents with phosphorus [61, 63].

Eutrophication resulting from anthropogenic phosphorus pollution has been a significant environmental concern since the 1960's. Initially, point source pollution from wastewater release or septic tank leakage was identified as a main concern for regulators to address and numerous researchers have focused on the impact and movement of P in groundwater from point sources [18, 24, 25, 28]. New research has shown that the portion of P contributions to freshwater from diffuse sources, specifically fertilizer and manure use in agricultural settings through runoff, erosion and leaching, has grown from 37% in 2002 to 41% in 2010 and is now a main driver of eutrophication [64-66].

2.1.2. Oil and gas wells as a pathway from the surface to the subsurface

Environmental damage caused by oil and gas wells is a widely studied issue. Currently, the two major environmental concerns regarding leaking oil and gas wells are the risk of groundwater contamination and increased greenhouse gas emissions to the atmosphere. Numerous studies have documented that the amount of leaking oil and gas wells and the atmospheric emissions from these wells are grossly under-reported [37-

39, 67] and there have been several studies that identify groundwater contamination to be a result of oil and gas development, specifically leakage of injected fluids such as in hydraulic fracturing [68-70]. Although studies have shown that subsurface contamination of groundwater with methane can be caused by leaking oil and gas wells [71, 72], the extent of the contamination has not been quantified. This thesis examines the leakage of excess P in agricultural runoff from the surface through leaking oil and gas wells to the subsurface. There has been no research conducted on this possible pathway for P contamination to reach groundwater.

Research conducted on leaking oil and gas wells in Canada has found that a small portion of wells are responsible for leaking both gases and liquids to the environment from the subsurface. One study conducted in Alberta found that a minimum of 4.6% of wells are responsible for leaking gases but did not provide data for the percentage of wells that will leak liquids, hypothesizing the value would be so low as to be negligible [73]. A subsequent study conducted in British Columbia calculated the proportion of wells that leak gases and found it to be 11% and determined that 0.002% of wells were leaking liquids as well [67]. Liquids are less likely to migrate upwards because larger pressure increases that overcome the weight of the liquid is needed for subsurface liquids to leak to shallower formations and the ground surface. In contrast, liquids at the ground surface will migrated downward given a sufficiently permeable pathway driven by gravity. Additionally, researchers find that the properties of the sedimentary basin can impact the likelihood of the well to leak, implying that unique regulations may be necessary for specific basins [74]. Factors such as changes in the tectonic stresses in the formation, pressure change or land subsidence after well abandonment [75] that may be challenging to regulate can also instigate well leakage after abandonment.

2.2. Phosphorus in groundwater

2.2.1. Phosphorus movement in the subsurface

Historically, phosphorus transport from the surface to the subsurface through leaching was dismissed as negligible, and the primary focus was on P losses to surface waters from erosion and runoff. Leaching is the transport of dissolved P with vertical downward water flow [76]. Because P has a high adsorption affinity to soil particles and environmental P concentrations are naturally low, it was assumed that subsurface movement of P would also be minimal provided P concentrations were not elevated. However, new research has shown that subsurface movement of P can be substantial from both point and non-point sources [16, 25, 26]. Moreover, it has since been identified that subsurface transport of P from agricultural areas is of specific concern where there are high levels of P in the soil, soils with low sorption capabilities, and artificial or tile drainage systems in place [66, 77].

Anthropogenic activities in the subsurface, such as leaking septic tanks, can result in point source pollution, which subsequently increases P concentrations in groundwater [24, 28]. In contrast, non-point sources, such as agriculture, have proven more difficult to isolate and quantify than point sources. However, it has been proposed that statistical differences in groundwater concentrations under agricultural land can indicate P accumulation in soils. Elevated P concentrations in soils result in a higher risk of leaching and can cause P contamination in groundwater [22]. Another study found that long term, heavy loading of P in soils can increase leaching to groundwater [16]. Agricultural land where fertilizers and manures were applied to soils was one of the most significant contributors to P pollution in groundwater and leaching, especially in areas with shallow water tables or coarse textured soils [16].

2.2.2. Movement of phosphorus from ground to surface waters

Groundwater P concentrations have largely been overlooked when considering P inflows to lakes and other freshwaters. Mobile P, typically orthophosphate, has a high affinity to adsorb to soil particles meaning that natural P concentrations in groundwater are typically well below concentrations that would be of concern for eutrophication [18]. However, anthropogenic P is increasingly reaching groundwater aquifers. Although P can be mobile in groundwater, the mobility of P is quite low when compared to nitrogen [78] and correlations between nitrogen and P have been challenging to identify [79, 80]. An international assessment of groundwater in the United Kingdom and Ireland found that there were several groundwater samples that reported elevated P concentrations and that P concentrations in groundwater could induce or sustain surface water eutrophication [22, 23]. A site-specific study focused on Lake Arendsee in Northern Germany found that groundwater discharge to the lake accounted for 50% of overall P loads and was a leading contributor to lake eutrophication [18].

2.2.3. Global groundwater quality guidelines for phosphorus

Although the European Union suggests a limit of 2.2 mg P/L for drinking water, a limit most groundwater P concentrations are compared to [23], Canada and the United States have no limits on P in drinking water [81, 82]. Moreover, most countries have no limits on P for human or livestock consumption.

Federal governments in Canada and the United States are not responsible for setting phosphorus limits for surface water. In Canada, the Canadian Council for Ministers of the Environment (CCME), which is composed of the Canadian environment ministers, has set forth a guidance framework that details “trigger ranges” for Canadian lakes and rivers [30]. According to the CCME, these trigger ranges represent a desired concentration range for P. If the upper limit of a range is exceeded, further investigation is required to identify potential environmental problems. The CCME upper limit for eutrophic waters is 0.1 mg P/L, this is in general agreement with lake quality models that have found TP concentrations above 0.1 mg/L to be a consistent cause of eutrophication [83]. The CCME also recommends further investigation if P concentrations increase by more than 50% above baseline values although determining background levels for P in water bodies is a difficult task as many water bodies were polluted by anthropogenic sources before being sampled [23]. On a provincial level, British Columbia, Alberta, Manitoba, Ontario and Quebec have recommended concentrations for P in surface waters ranging from 0.01 mg P/L for recreational lakes in British Columbia to 0.05 mg P/L for all surface waters in Alberta [84].

Although the United States Environmental Protection Agency (USEPA) assists states in developing individual P criteria for surface waters. The USEPA implements criteria based on three main types of surface water bodies: lakes/reservoirs, rivers/streams, and estuaries. Because each state is responsible for assessing the quality of water, P criteria varies widely among types of water bodies and states. California's Lake Tahoe has the lowest P criteria with a recommended range of 0.005 – 0.30 mg P/L, while Salt River in Arizona has the highest P criteria with a recommended value of 1 mg/L [85]. Hawaii is currently the only state with a complete P criterion for all surface waterbodies [32]. 27 states including Washington, Idaho, North Dakota, Michigan, Ohio, Pennsylvania, New York, New Hampshire, and Maine do not have any P concentration criterion [32].

2.3. Base of freshwater estimations in California

2.3.1. Groundwater in California

The state of California has a population of 39.5 million and an area of 424,000 km^2, of which 43% is dedicated to agriculture [86]. It is also the 8^{th} highest oil producing state [87]. Climate change, population growth and reoccurring drought conditions have significantly increased stress on groundwater resources in the state [88]. Today, 85% of the state’s population uses groundwater daily and 40% of the annual water use in the state comes from groundwater abstractions [89]. In order to preserve the quantity and quality of groundwater in California, Governor Jerry Brown enacted the Sustainable Groundwater Management Act (SGMA) in September 2014. As a requirement of SGMA, groundwater sustainability agencies are required to develop and adopt groundwater sustainability plans for “high and medium priority” groundwater basins to limit adverse impacts [90, 91]. Groundwater sustainability agencies use groundwater quality metrics such as total dissolved solids (TDS) concentrations to classify the bottom of groundwater basins or the depths at which water is protected from activities that could result in the contamination of groundwater [41, 92].

2.3.2. Current base of fresh water estimations

Several Groundwater Sustainability Agencies in California use the “base of fresh water” to identify volumes that are protected from anthropogenic activities such as oil and gas development [40-42]. Although current estimations define the base of fresh water (BFW) using TDS concentrations, a geochemical property of the water, it is also possible to define the BFW using physical properties of the basin. In California, the largest current BFW estimation was completed in the Central Valley and classified “fresh” water as having a TDS concentration <2,000 mg/L [52, 93]. Additional base of fresh water estimates are available for oil and gas fields or field areas by the California Geologic Energy Management Division (CalGEM; formerly the Division of Oil, Gas, and Geothermal Resources (DOGGR)) and these BFW estimations define “fresh” water has having TDS concentrations <3,000 mg/L [42]. The validity of using the current BFW data for effective groundwater management has been questioned because large portions of the base of fresh water estimates used today have not been updated since 1973 [52, 93], and there are inconsistencies in the definitions of “fresh” water between BFW estimates within the state. Moreover, a recent study shows that fresh water (TDS<2,000 mg/L) exists below the currently defined BFW [41].

The two main assumptions inherent in the base of fresh water concept for groundwater management are: (1) groundwater with TDS concentrations >2,000 mg/L is not usable and (2) TDS concentrations are monotonically increasing with depth [41]. Although the nature of the relationship between TDS concentrations and depth has been examined at local levels in California [2], a state-wide assessment has not yet been conducted. In addition, groundwater with TDS concentrations between 3,000 and 10,000 mg/L, or brackish water, is increasingly being used to satisfy growing demands as water treatment technologies improve and become more economic [54-56, 94, 95]. Given that brackish water may be the most viable alternative to fresh groundwater resources, there is a need to better characterize, protect, and manage brackish groundwater resources, in addition to fresh groundwater resources [2].

3. Groundwater phosphorus concentrations: global trends and links with agricultural and oil and gas activities

3.1. Introduction

Excess phosphorus (P) in surface water systems can lead to ecological effects such as eutrophication, which is one of the most prevalent causes of water quality impairment, and eventual death of aquatic ecosystems [22, 65, 96]. To sustain health of lakes, rivers, estuaries, and other surface water systems, government agencies are actively working to monitor and control anthropogenic sources of P. The current extent of P contamination in groundwater worldwide and the full range of pathways through which this contamination is occurring are unknown. Historically, it has been assumed that groundwater concentrations of P are negligible due to high rates of adsorption of mobile P, typically orthophosphate, to the soil and sediment matrix [97]. However, recent studies indicate that P concentrations in groundwater may not be negligible and that characterizing the extent of P contamination in groundwater is important due to interactions between groundwater and surface water [18, 22, 25, 26, 28, 97-104].

Although there have been site-specific studies on local or “point” sources of P in groundwater, such as wastewater releases and residential underground septic tank systems [24-26, 28, 103, 105-107], there have been limited studies conducted on nonpoint sources, such as agriculture. However, agricultural activities account for more than 60% of anthropogenic P additions to the environment through the use of commercial fertilizers as well as manure from livestock [108]. Globally, 38% of anthropogenic P loads to freshwater ecosystems are contributed by agriculture [64]. Therefore, we evaluate P concentrations with respect to land cover/use types, encompassing all P sources from wastewater to agriculture to evaluate their relative effects.

A potential pathway through which anthropogenic P, including those from fertilizer, may enter groundwater is oil and gas wells, particularly those that are unplugged and leaky. Numerous studies have documented leakage of hydrocarbons and water through oil and gas wells from deep formations to shallow groundwater aquifers and the atmosphere [37, 67]. Studies so far have found that the risk of upward migration of brines and produced water from oil and gas production is relatively small, especially compared to surface spills [70, 72, 109-111]. Groundwater samples are typically collected within 200 m of the surface [112], which is shallow relative to depths of most oil and gas activities, which generally occur at depths greater than 1,000 m [113]. Based on available studies detailing oil and gas well leakage and the abundance of oil and gas wells in Canada and the United States [114], oil and gas wells can potentially act as a pathway through which surface P enters the subsurface. To characterize the potential effects of oil and gas wells on P concentrations in groundwater, we analyze oil and gas well distributions and available concentrations of P in groundwater.

In this paper, we: (i) compile available global groundwater P data, (ii) analyze the extent of elevated P concentrations in groundwater and the spatial distribution of available data globally, (iii) examine the relationship between dissolved oxygen (DO) and P concentrations in groundwater, (iv) identify spatial relationships between anthropogenic sources (crop/pastureland, oil and gas wells) and elevated total P concentrations in groundwater in Canada and the United States using land use/cover data, and (iv) compare oil and gas well locations to elevated groundwater P concentrations in regions with high densities of oil and gas wells and P data (British Columbia, Ontario and Alberta, Canada). These results can be used to guide agricultural and energy policy development and inform plans for monitoring of P in groundwater.

3.2. Materials and methods

3.2.1. Global data

We compile 161,321 P measurements using data from 15 government agencies and eight peer-reviewed studies conducted in 12 different countries (Appendix A: Table S1).

Data is categorized by country/region and P concentration type. Where available, we provide the groundwater depth ranges at which samples have been collected, the range of sampling dates, and the phosphorus concentration detection limits (Appendix A: Table S2). Samples that report concentrations less than the detection limit are assumed to have a concentration of 0 mg/L (Appendix A Table S3, Treatment of phosphorus data). We categorize the measurements based on five different analysis methods: (1) total phosphorus using molybdate blue and ultraviolet-visible absorption spectroscopy (20%, TP ICP-OES), (2) total phosphorus as determined by inductively coupled argon plasma emission spectroscopy (<1%, TP ICP-MS), (3) dissolved orthophosphate as P (78%, DP), (4) total dissolved P (2%, TDP), and (5) particulate P (<1%) [115] (Appendix A, Table S4, Treatment of phosphorus data).

3.2.2. Geospatial analysis

We geospatially analyze land use data, TP concentrations in groundwater, and oil and gas well locations in ArcGIS to determine anthropogenic causes of increased TP concentrations in groundwater. To identify relationships between anthropogenic sources and enhanced P concentrations, we use all P concentration types. We analyze land use types throughout the United States and Canada to evaluate the effects of anthropogenic activities such as agriculture and oil and gas on P concentrations in groundwater (Appendix A: Geospatial analysis). We conduct an analysis of oil and gas well proximity and P concentrations in groundwater in the Canadian provinces of British Columbia (Appendix A: Analysis of oil and gas well proximity impact on phosphorus concentrations in British Columbia**),** Alberta, and Ontario.

3.2.3. Statistical analysis

Due to the non-normality of the P and DO measurements, we use nonparametric methods to conduct statistical analysis on the data. We use Spearman rank correlation to measure the degree of association between DO and P measurements, and we use a chi-square (Chi^2) test to compare the distribution of P measurements found at distances closer to oil and gas wells to P measurements found farther away from oil and gas wells [116, 117]. For the oil and gas analysis, we analyze the top 30th percentile of P measurements because research has shown that a small percentage, approximately 10%, of oil and gas wells have reported leakage [67].

3.3. Results

3.3.1. Global distribution of P in groundwater data

Of the 12 countries with P in groundwater data, we find that all countries have groundwater samples with concentrations >0.1 mg P/L. **Figure 2** represents the sampling type and location of the wells used in this paper as well as the overall distribution of all samples within each country. China and Brazil have the largest percentage of measurements with concentrations >0.1 mg P/L with 78% and 66%, respectively. Although these percentages are subject to bias in the sampling design, the high percentages clearly show that groundwater P contamination is a problem in some parts of China and Brazil. Wales, Mexico and the United States are also found to have more than 20% of samples with concentrations >0.1 mg P/L. We find that South Africa and Ireland are the only countries with less than 10% of samples reporting concentrations >0.1 mg P/L.

The maximum concentration is recorded in Sweden, with a dissolved P concentration of 793 mg P/L. The maximum reported concentration in the United States is 72.1 mg P/L in Michigan (land use is water) and the maximum reported concentration in Canada is 250 mg P/L in Ontario (land use is settlement). The United States is found to have the highest sample mean of 0.66 mg P/L, followed by Brazil with 0.64 mg P/L. Brazil is also found to have the largest sample median with a value of 0.18 mg P/L, followed by China with a value of 0.16 mg P/L. The Canadian provinces of Quebec (0.09 mg P/L), Alberta (0.09 mg P/L), British Columbia (0.07 mg P/L) and Manitoba (0.02 mg P/L), as well as South Africa (0.06 mg P/L), New Zealand (0.03 mg P/L) and Ireland (0.02 mg P/L), all report mean values less than 0.1 mg P/L.

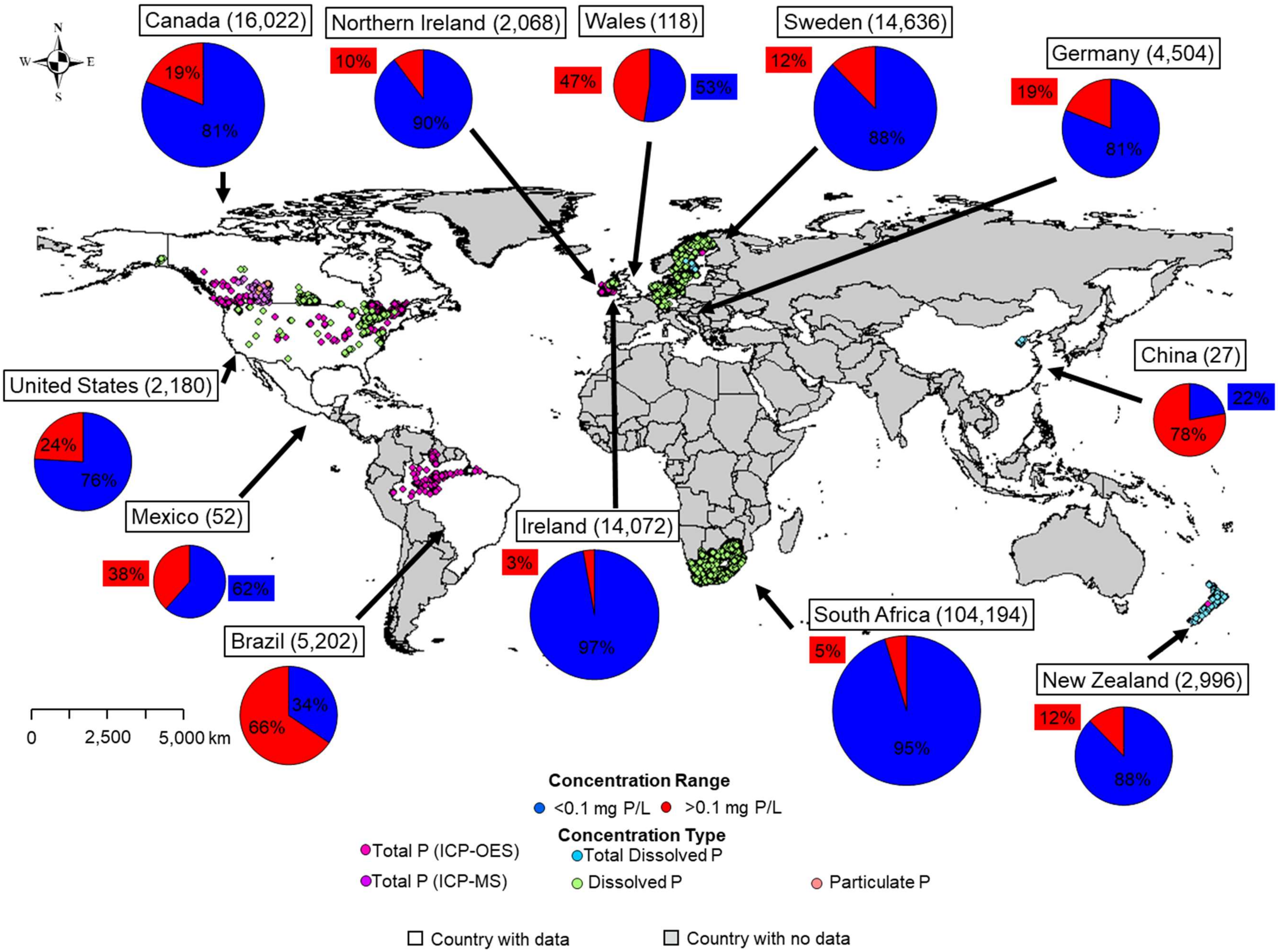


Figure 2. Global distribution of P samples by type and country. Numbers in brackets represent total number of samples collected in that country. The pie charts show the distribution of samples with concentrations greater than (red) and less than (blue) 0.1 mg P/L.

3.3.2. Association of dissolved oxygen and phosphorus concentrations in groundwater

Elevated P concentrations in groundwater have been attributed to anthropogenic sources [17, 18, 24, 25, 118] and natural processes that govern the movement of P in the subsurface [119]. Several natural factors including temperature and pH can impact P concentrations in groundwater, but dissolved oxygen (DO), which affects the ability of iron oxides to adsorb and retain P [100], has been identified as a primary natural control on P concentrations in water [100, 120-122]. High DO concentrations in the subsurface allow for iron oxides to remain stable, but in low oxygen environments, iron oxides can dissolve, releasing adsorbed P back into the water and increasing P concentrations [100]. An inverse correlation between DO and P concentrations would therefore indicate a natural explanation for elevated P concentrations in groundwater.

Using Spearman's Rank Correlation to judge the degree of association between DO concentrations and P concentrations, we find that the inverse correlation between DO and P is weaker for P concentrations >0.1 mg P/L. For the 1,529 available locations with DO and P concentration data available in Canada and the United States, we find that the overall correlation between DO and P is -0.61, suggesting a strong inverse relationship as expected. When looking at sites that report P concentrations <0.1 mg P/L only, we again find a strong inverse relationship between DO and P with a Spearman rank correlation equal to -0.54. However, for sites that report >0.1 mg P/L, the correlation between DO concentrations and P concentrations is -0.16, suggesting a very weak inverse relationship. Moreover, decreasing the distance from P monitoring sites to cropland results in an even weaker correlation between DO and P (Spearman rank correlation of -0.11 if there is cropland within 50 m of the P monitoring site), supporting the notion that enhanced P concentrations in groundwater near cropland is likely linked to agricultural activities (Appendix A: Table S9).

3.3.3. Land use types linked with higher phosphorus concentrations in groundwater

There are significant spatial gaps in the current location of P monitoring sites; only 4% of land area in Canada and 0.9% of land area in the United States have at least one P monitoring site within a 30 km by 30 km area. In Canada, P monitoring sites are relatively dense in British Columbia, Alberta, Manitoba, Quebec, and Ontario with 5%, 14%, 11%, 6%, and 9% of the provinces respectively having at least one monitoring site within a 30 km by 30 km search area. The maximum P monitoring site density in the United States is 0.5 P sites/km^2 in Idaho and the largest in Canada is 1.3 P sites/km^2 in Alberta (white circled area in **Figure 3**).

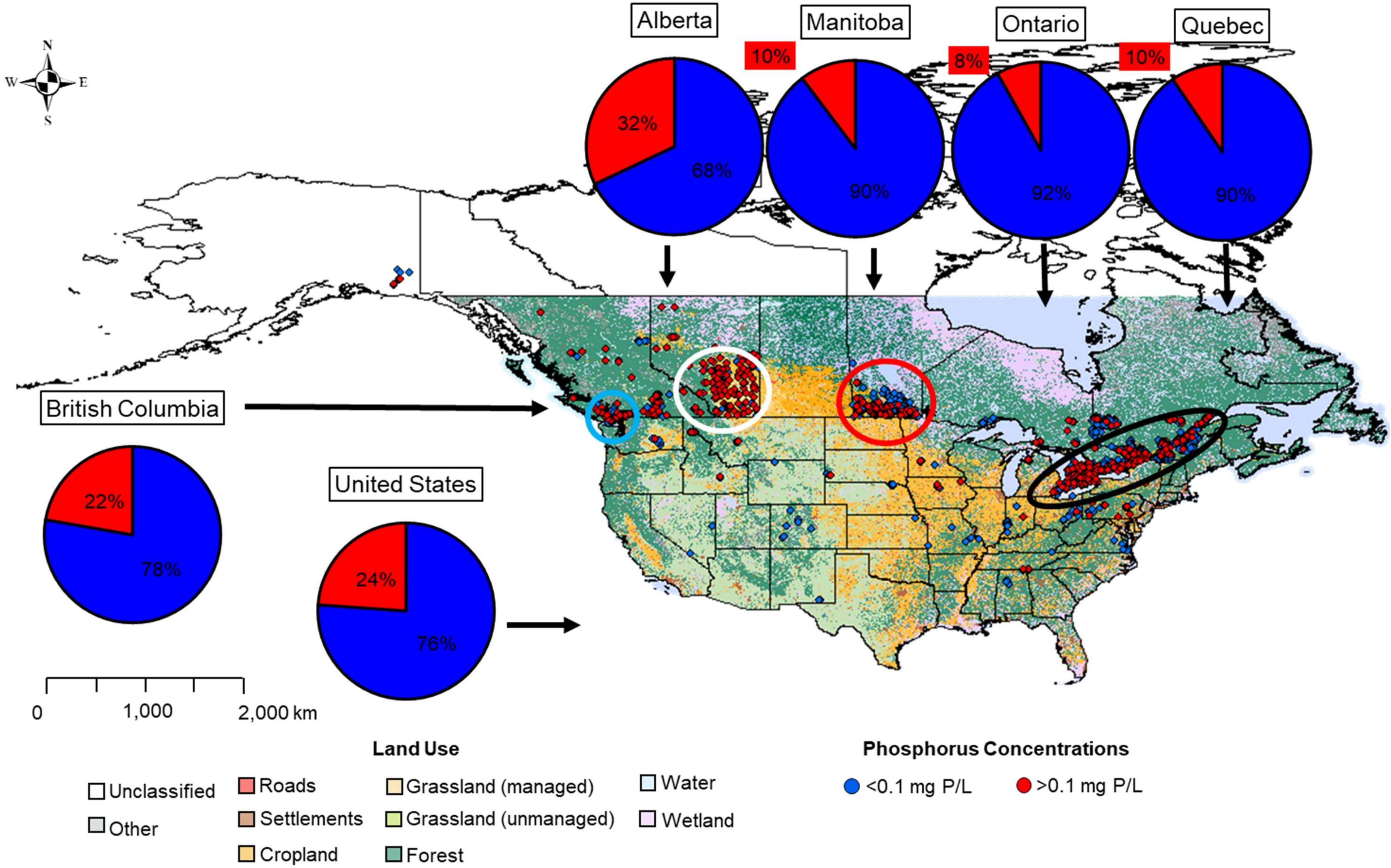


Figure 3. Land use map of Canada and the United States overlaid by TP in groundwater sample locations. Circled areas represent regions with high density of TP concentrations >0.1 mg P/L in the samples collected according to a point density analysis using ArcGIS. The pie charts represent the distribution of sample concentrations greater than (red) or less than (blue) 0.1 mg P/L.

Correlations between land use types and areas with high P concentrations in groundwater may help identify the source of P contamination. **Figure 3** shows the land use map for Canada and the United States and P data collected in these regions separated into the CCME TP concentration ranges. According to a point density analysis on ArcGIS using a search area of 900 km^2, we find a high density of elevated P concentrations in Alberta (white circle), Manitoba (red circle), the Southern Ontario/Great Lakes region and Southern Quebec (black circle) and the urban areas, Vancouver and Victoria, in British Columbia (blue circle) (Appendix A: Figure S2).

We analyze 24,146 P concentrations located in Canada and the United States to determine the relationship between land use. We find that 12% (2,899) of all P concentrations are >0.1 mg P/L. For the P samples located directly on managed grasslands, we find that 33% of samples report concentrations >0.1 mg P/L and the “other” category reports 21% of samples to have >0.1 mg P/L, which are significantly higher percentages than the total number of samples with >0.1 mg P/L. The remaining land use categories report having between 11% and 15% of samples >0.1 mg P/L. (Appendix A: Table S12, Representativeness of land use surrounding P monitoring sites in Canada and the United States**)**. In other words, P concentrations in groundwater are more elevated than expected on managed grasslands and “other” (including rocks, ice, and beaches) category lands.

3.3.4. Relationship between oil and gas wells and phosphorus concentrations in groundwater

Based on **Figure 2** and Appendix A: Figure S4, we select Alberta and Ontario as regions of focus to identify the potential effects of oil and gas wells on P concentrations in groundwater. Both Alberta and Ontario have high densities of TP monitoring sites in addition to high densities of oil and gas wells. Although regions with elevated P concentrations in British Columbia do not have oil and gas wells, we evaluate the correlations between P concentrations and proximity to oil and gas wells in British Columbia as a basis for comparison to the Ontario and Alberta correlations (Appendix A: Analysis of oil and gas well proximity impact on phosphorus concentrations in British Columbia).

There are 609,877 oil and gas wells in the province of Alberta, with all 306 TP monitoring sites located within a 10 km radius of at least one oil and gas well as shown in **Figure 4**. The maximum distance from a TP monitoring site to an oil and gas well occurs at 8.16 km with a TP concentration of 0.001 mg P/L. The maximum TP concentration in Alberta is found to be 1.67 mg P/L, more than 10 times the required TP concentration for surface water eutrophication, and this is found at a distance of 0.41 km from an oil and gas well. In Ontario, there are 26,968 oil and gas wells, the majority (98%) of which are in the southwestern region of the province (**Figure 4**). The maximum TP concentration is more than 600 times the CCME recommendation of 68 mg P/L, and the monitoring site is located 10.8 km from the nearest oil and gas well. One of the lowest P concentrations (0.005 mg P/L) is found at the monitoring site located 428 km, the farthest distance from an oil and gas well. Based on proximity of high P concentrations to oil and gas wells, we conduct a Chi^2 analysis to determine if there are statistical differences between P concentrations located closer to oil and gas wells.

Conducting a Chi^2 analysis on the top 30^{th} percentile of TP concentrations using a 90% confidence interval, $\alpha = 0.1$, we find differences in populations of TP samples collected closer to oil and gas wells in Alberta and Ontario. We use the median distance in both provinces to select the cutoff distances at which TP monitoring sites are considered to be located closer to oil and gas wells. For Alberta, the cutoff distance is 0.3 km, and for Ontario, it is 15 km. In Alberta, 97% of TP monitoring sites within 0.3 km of an oil and gas well reported TP concentrations >0.1 mg P/L. At distances greater than 0.3 km, only 61% of TP monitoring sites report concentrations >0.1 mg P/L (Appendix A: Table S13). A similar trend is seen in Ontario where we find 50% of TP concentrations at TP monitoring sites within 15 km of an oil and gas well are >0.1 mg P/L. At monitoring sites located farther than 15 km from an oil and gas well, 33% of TP concentrations are >0.1 mg P/L (Appendix A: Table S14). The increased percentage of TP monitoring sites with

>0.1 mg P/L found at P monitoring sites that are closer to oil and gas wells in Alberta and Ontario indicates that oil and gas wells may be acting as a pathway through which anthropogenic P reaches groundwater.

In both Alberta and Ontario, TP monitoring sites located close to oil and gas wells are typically also close to crop/pastureland. In Alberta, 91% (278) of all TP monitoring sites are found within 1 km of any oil and gas wells, and of these 278 TP monitoring sites, 269 (97%) are found within 1 km of crop/pastureland. In Ontario, oil and gas wells are found at greater distances from TP monitoring wells than in Alberta. Only 12% (47) of all TP monitoring sites are found within 1 km of an oil and gas well, while 49% (196) of all TP monitoring sites are found within 5 km from any oil and gas wells. Of the 47 TP monitoring sites within 1 km of an oil and gas well in Ontario, 98% (46) are located within 1 km of crop/pastureland. In both provinces, the proximity of oil and gas wells to crop/pastureland increases the likelihood that agricultural runoff could reach groundwater through leaking oil and gas wells.

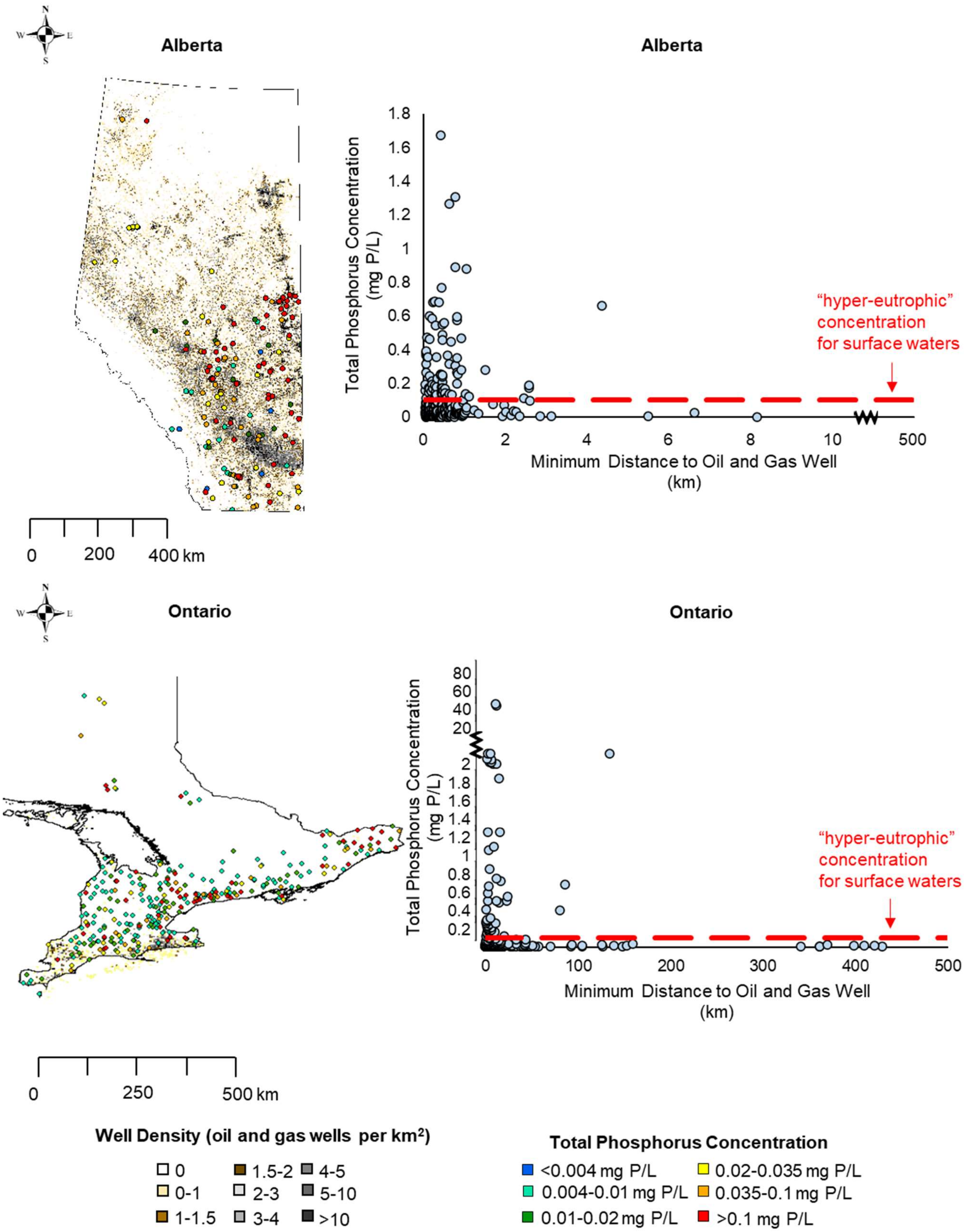


Figure 4. Well density map of all oil and gas wells in Alberta and Ontario with TP concentration values separated by CCME concentration range. The dotted red lines on the scatter plots represent the CCME “hyper-eutrophic” TP concentration of 0.1 mg P/L.

3.4. Discussion

3.4.1. Limitations of global samples

Even in tropical regions, such as Brazil and Mexico, where P concentrations in groundwater are expected to be quite low due to the strong adsorption of P to soil particles, we find P concentrations >0.1 mg P/L. Although we do not have the detection limits from the Geological Survey of Brazil, Brazil has been responsible for the largest amount of deforestation in the Amazon [123]. 66 Mha (8% of Brazil's land area [124]) of land has been converted for agricultural use in the decades between 1985 and 2017 [125]. Currently 28% of land in Brazil is used for pasture or agricultural purposes [125]. Moreover, multiple studies in recent years have focused on the degradation of soil and groundwater quality as a result of excess P application from fertilizers [126-128]. In Mexico, we could not obtain a government database of P concentrations in groundwater, and the P data we collected was from site-specific peer reviewed studies. These studies are primarily conducted in areas of concern from P contamination, specifically from wastewater irrigation, which is suspected to be responsible for increased concentrations of nutrients in soils [129-132]. In other words, because P contamination from anthropogenic sources can be significant, relying on our understanding of natural P controls may lead to overlooking important anthropogenic groundwater P contamination.

Our database of P in groundwater samples lack data in the majority of South America, Europe and Asia. These regions have significant portions of land use designated to agricultural activities, a major source of P; 38% in South America [133], 39% in Europe [134] and 69% in Asia [135], meaning P contamination of groundwater supplies could be a significant problem. Moreover, there are many regions where high oil and gas well density coincides with intense agricultural areas such as the Middle East, Europe and several South American countries including Venezuela [136, 137]. Additional data collection and sampling campaigns in these regions could identify areas with potentially high P concentrations in groundwater.

Because the processes that govern N and P movement in the environment differ considerably, it is challenging to develop a suitable correlation between N and P to infer P concentrations in groundwater. Nitrogen is soluble in groundwater meaning that its respective forms, particularly nitrate (NO_{3-}), are highly mobile in the vadose zone and groundwater aquifers. In contrast, P is not highly soluble in groundwater and due to its high adsorption affinity in soils, it is difficult for P transport to occur through leaching through soils [138]. In future studies, with the collection of additional data such as soil properties, physically-based modeling of water flow and P and N transport through soils and groundwater aquifers can be used to relate N and P.

3.4.2. High P concentrations in groundwater linked to agricultural areas

The reduction in the strength of the inverse Spearman correlation between DO and P at P concentrations >0.1 mg P/L indicates that an anthropogenic factor is likely responsible for the elevated P concentrations. Based on the reduction of the strength of the Spearman correlation between DO and P with decreased proximity to crop/pastureland and the proximity of a majority of samples with P concentrations >0.1 mg P/L to crop/pastureland, agricultural areas appear to be linked with elevated P concentrations in groundwater. Beyond DO concentrations, several other natural factors can impact P concentrations in water. The weathering of rocks releases P into terrestrial and aquatic ecosystems. Because common rocks can have P concentrations that range from 120 ppm to 3,000 ppm [139], geology can significantly influence the concentration of P in water. Therefore, geological information of the aquifers from which groundwater P samples are collected is needed to further clarify the impact of anthropogenic activities on P concentrations in groundwater.

3.4.3. Isolating the effects of oil and gas wells on P concentrations in groundwater

Two of the regions with elevated P concentrations in groundwater are also regions with extensive oil and gas development. In Alberta and Ontario, where enhanced P concentrations in groundwater are likely a result of agricultural activity, oil and gas wells may be exacerbating the problem by acting as an open pathway for P to easily enter groundwater systems. However, it is difficult to identify relationships because most TP monitoring sites in Alberta and Ontario coincide with regions with oil and gas development. Moreover, in regions with a high density of oil and gas wells, potential contamination pathways may not necessarily be the nearest oil and gas wells but could be any one of a set of neighboring wells, some of which may not be documented. To better understand this relationship, additional sampling is needed, especially in areas located far from oil and gas wells. Moreover, analysis conjunctively exploring the relationship between other geochemical parameters such as total dissolved solids (TDS) concentrations and P concentrations can help identify the mechanisms behind the relationship between oil and gas wells and elevated P concentrations in groundwater.

3.4.4. Policy implications

The identification of agricultural land as areas likely to have high P concentrations in groundwater in Canada suggests there may be policy-based and commercial mitigation opportunities [15]. Examples of mitigative action include limits on phosphorus application to the soil [22, 140] or the use of more advanced fertilizer formulations [141] to prevent phosphorus overfertilization in agricultural areas which may result in P loss to runoff and leaching to groundwater.

Currently, there are no legally imposed limits in Canada or the United States to regulate the amount of phosphorus in drinking water, groundwater or water for use in agricultural industries, such as irrigation [31, 82, 142]. Phosphorus limits imposed on surface water bodies are implemented on a provincial basis in Canada, meaning that some provinces such as British Columbia and Manitoba have limits, while others, such as Saskatchewan, do not [143-145]. In Alberta, previously published numerical TP limits were redacted in 2018 and narrative statements have been developed for lakes, rivers and other water bodies [146]. The Ontario government has general numeric guidelines for TP concentrations, which state that TP concentrations should not exceed 0.02 mg P/L in lakes and 0.03 mg P/L in rivers and streams [147]. TP limits in the United States are proposed by individual states and approved by the Environmental Protection Agency (EPA). Currently, 27 states have no criteria for any types of surface waters. Three states (Minnesota, Wisconsin and New Jersey) have statewide TP criterion for lakes/reservoirs and rivers/streams but lack TP criteria for estuaries. Florida has a statewide TP criterion for lakes/reservoirs and estuaries, but only partial TP criteria for rivers/streams, and Hawaii is the only state to have a complete numeric TP criterion for all waterbodies. The US EPA thresholds are generally lower than the CCME recommended range of 0.1 mg P/L, although some regions and water body types have limits as high as 0.14 mg P/L [32]. Overall, establishing TP criteria for groundwater would be helpful for maintaining surface ecological systems and will be an important aspect of establishing robust phosphorus monitoring programs.

3.5. Conclusion

In all studied regions (12 countries) around the world, groundwater P concentrations can be high enough to pose a eutrophication risk to surface waters, which is increasingly important as ecosystems face stresses from climate change and other anthropogenic activities. Data from Canada and the United States show weak correlations between DO concentrations and groundwater P concentrations that indicate external factors are influencing groundwater TP concentrations. We show there is a positive correlation between distance to crop/pastureland and elevated groundwater TP concentrations. In addition, based on the higher TP concentrations we find at monitoring sites located closer to oil and gas wells in Alberta and Ontario, we identify the possibility of oil and gas wells acting as a pathway for anthropogenic phosphorus from the surface to reach groundwater. Moving forward, strategic data collection and an understanding of the mechanisms through which anthropogenic sources of P can contaminate groundwater will be useful to establish effective monitoring programs and implement mitigation efforts that preserve water quality and ecosystem health.

3.6. References

15. Mackie, C., et al., *Groundwater-surface water interactions and agricultural nutrient transport in a Great Lakes clay plain system.* Journal of Great Lakes Research, 2021. **47**(1): p. 145-159.
17. Oenema, O., L. van Liere, and O. Schoumans, *Effects of lowering nitrogen and phosphorus surpluses in agriculture on the quality of groundwater and surface water in the Netherlands.* Journal of Hydrology, 2005. **304**(1): p. 289-301.
18. Meinikmann, K., M. Hupfer, and J. Lewandowski, *Phosphorus in groundwater discharge – A potential source for lake eutrophication.* Journal of Hydrology, 2015. **524**: p. 214-226.
22. Holman, I.P., et al., *Phosphorus in groundwater—an overlooked contributor to eutrophication?* Hydrological Processes, 2008. **22**(26): p. 5121-5127.
24. McCobb T.D., et al., *Phosphorus in a Ground-Water Contaminant Plume Discharging to Ashumet Pond, Cape Cod, Massachusetts*. 2003, 1999: U.S. Geological Survey Water Resources Investigations. p. 70 p.
25. Stollenwerk, K.G., *Simulation of phosphate transport in sewage-contaminated groundwater, Cape Cod, Massachusetts.* Applied Geochemistry, 1996. **11**(1): p. 317-324.
26. Domagalski, J.L. and H.M. Johnson, *Subsurface transport of orthophosphate in five agricultural watersheds, USA.* Journal of Hydrology, 2011. **409**(1): p. 157-171.
28. Roy, J.W., et al., *Contribution of phosphorus to Georgian Bay from groundwater of a coastal beach town with decommissioned septic systems.* Journal of Great Lakes Research, 2017. **43**(6): p. 1016-1029.
31. Government of Canada, *Guidelines for Canadian Drinking Water Quality - Summary Table*. 2017.
32. EPA. *State Progress Toward Developing Numeric Nutrient Water Quality Criteria for Nitrogen and Phosphorus*. 2019; Available from: https://www.epa.gov/nutrient-policy-data/state-progress-toward-developing-numeric-nutrient-water-quality-criteria.

37. Kang, M., et al., *Identification and characterization of high methane-emitting abandoned oil and gas wells.* Proceedings of the National Academy of Sciences of the United States of America, 2016. **113**(48): p. 13636-13641.

64. Mekonnen, M.M. and A.Y. Hoekstra, *Global Anthropogenic Phosphorus Loads to Freshwater and Associated Grey Water Footprints and Water Pollution Levels: A High-Resolution Global Study.* Water Resources Research, 2018. **54**(1): p. 345-358.

65. Le Moal, M., et al., *Eutrophication: A new wine in an old bottle?* Science of The Total Environment, 2019. **651**: p. 1-11.

67. Wisen, J., et al., *A portrait of wellbore leakage in northeastern British Columbia, Canada.* Proceedings of the National Academy of Sciences of the United States of America, 2020. **117**(2): p. 913-922.

70. Osborn, S.G., et al., *Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing.* Proceedings of the National Academy of Sciences, 2011. **108**(20): p. 8172.

72. Vengosh, A., et al., *A Critical Review of the Risks to Water Resources from Unconventional Shale Gas Development and Hydraulic Fracturing in the United States.* Environmental Science & Technology, 2014. **48**(15): p. 8334-8348.

82. EPA, U.S., *2018 Edition of the Drinking Water Standards and Health Advisories Table*, in *Drinking Water Standards and Health Advisories*. 2018.

96. Kröger, R., et al., *Downstream approaches to phosphorus management in agricultural landscapes: Regional applicability and use.* Science of The Total Environment, 2013. **442**: p. 263-274.

97. USGS. *Phosphorus Doesn't Migrate in Ground Water? Better Think Again!* 2002; Available from: https://toxics.usgs.gov/highlights/phosphorous_migration.html.

98. Demirel, Z., Z. Özer, and O. gülçiçek, *Nitrogen and phosphate contamination stress of groundwater in an internationally protected area of the göksu delta, Turkey.* Fresenius Environmental Bulletin, 2010. **19**: p. 2509-2517.

99. Izbicki, J.A., *Fate of Nutrients in Shallow Groundwater Receiving Treated Septage, Malibu, CA.* Groundwater, 2014. **52**(S1): p. 218-233.

100. Johnson, J.L.D.a.H., *Phosphorus and Groundwater: Establishing Links Between Agricultural Use and Transport to Streams.* U.S. Geological Survey Fact Sheet 2012-3004, 2012.
101. Lewandowski, J., et al., *Groundwater – The disregarded component in lake water and nutrient budgets. Part 2: effects of groundwater on nutrients.* Hydrological Processes, 2015. **29**(13): p. 2922-2955.
102. Robertson, W.D., S.L. Schiff, and C.J. Ptacek, *Review of Phosphate Mobility and Persistence in 10 Septic System Plumes.* Groundwater, 1998. **36**(6): p. 1000-1010.
103. Robertson, W.D., D.R. Van Stempvoort, and S.L. Schiff, *Review of phosphorus attenuation in groundwater plumes from 24 septic systems.* Science of The Total Environment, 2019.
104. Weihrauch, C. and C.J. Weber, *Phosphorus enrichment in floodplain subsoils as a potential source of freshwater eutrophication.* Science of The Total Environment, 2020. **747**: p. 141213.
105. Waller, D.H., et al., *Estimation of the contribution of phosphorus from on-site sewage disposal systems to lakes*. Research report. 1996, [Ottawa]: CMHC.
106. Spiteri, C., et al., *Modelling the geochemical fate and transport of wastewater-derived phosphorus in contrasting groundwater systems.* Journal of Contaminant Hydrology, 2007. **92**(1): p. 87-108.
107. Chen, X., et al., *Seasonal changes in the concentrations of nitrogen and phosphorus in farmland drainage and groundwater of the Taihu Lake region of China.* Environmental Monitoring and Assessment, 2010. **169**(1): p. 159-168.
108. Chambers, P.A., A. Canada, and C. Agri-Food, *Nutrients and their impact on the Canadian environment*. 2001, [Ottawa]: [Environment Canada].
109. Darrah, T.H., et al., *Noble gases identify the mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus and Barnett Shales.* Proceedings of the National Academy of Sciences, 2014. **111**(39): p. 14076.
110. Warner, N.R., et al., *Geochemical and isotopic variations in shallow groundwater in areas of the Fayetteville Shale development, north-central Arkansas.* Applied Geochemistry, 2013. **35**: p. 207-220.

111. Rosecrans, C.Z., et al., *Groundwater Quality of Aquifers Overlying the Oxnard Oil Field, Ventura County, California.* Science of The Total Environment, 2021. **771**: p. 144822.
112. U.S Environmental Protection Agency, *Design and Installation of Monitoring Wells*, Science and Ecosystem Support, Editor. 2018.
113. U.S. Energy Information Administration, *Average Depth of Crude Oil and Natural Gas Wells*. 2021.
114. Kang, M., et al., *Orphaned oil and gas well stimulus—Maximizing economic and environmental benefits.* Elementa: Science of the Anthropocene, 2021. **9**(1).
115. Haygarth, P.M. and A.N. Sharpley, *Terminology for Phosphorus Transfer.* Journal of Environmental Quality, 2000. **29**(1): p. 10-15.
116. Minnesota Pollution Control Agency, *Data Analysis Protocol for the Ground Water Monitoring and Assessment Program*. 1999.
117. McHugh, M.L., *The chi-square test of independence.* Biochemia medica, 2013. **23**(2): p. 143-149.
118. S.J. Rodvang, et al., *Groundwater quality in the eastern portion of the Lethbridge Northern Irrigation District: 1995 to 2001*, Alberta Agriculture, Food and Rurual Development, Lethbridge, Alberta, Canada,, Editor. 2002.
119. Tao, Y., et al., *Sources and enrichment of phosphorus in groundwater of the Central Yangtze River Basin.* Science of The Total Environment, 2020. **737**: p. 139837.
120. Wang, S., et al., *Effects of dissolved oxygen supply level on phosphorus release from lake sediments.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2008. **316**(1): p. 245-252.
121. Kim, L.-H., et al., *Phosphorus release rates from sediments and pollutant characteristics in Han River, Seoul, Korea.* Science of The Total Environment, 2004. **321**(1): p. 115-125.
122. Kent, R., T.D. Johnson, and M.R. Rosen, *Status and trends of orthophosphate concentrations in groundwater used for public supply in California.* Environmental Monitoring and Assessment, 2020. **192**(8): p. 550.

123. Marengo, J.A., et al., *Changes in Climate and Land Use Over the Amazon Region: Current and Future Variability and Trends.* Frontiers in Earth Science, 2018. **6**(228).
124. Souza, C., *Federal Republic of Brazil.* der.), A Global Dialogue on Federalism, 2005. **1**: p. 76-102.
125. Souza, C.M., et al., *Reconstructing Three Decades of Land Use and Land Cover Changes in Brazilian Biomes with Landsat Archive and Earth Engine.* Remote Sensing, 2020. **12**(17): p. 2735.
126. Shigaki, F., A. Sharpley, and L.I. Prochnow, *Animal-based agriculture, phosphorus management and water quality in Brazil: options for the future.* Scientia Agricola, 2006. **63**: p. 194-209.
127. Campos, V., *Arsenic in groundwater affected by phosphate fertilizers at São Paulo, Brazil.* Environmental Geology, 2002. **42**(1): p. 83-87.
128. Roy, E., et al., *Soil phosphorus sorption capacity after three decades of intensive fertilization in Mato Grosso, Brazil.* Agriculture Ecosystems & Environment, 2017. **249**: p. 206-214.
129. Hanjra, M.A., et al., *Wastewater irrigation and environmental health: Implications for water governance and public policy.* International Journal of Hygiene and Environmental Health, 2012. **215**(3): p. 255-269.
130. Siebe, C. and E. Cifuentes, *Environmental impact of wastewater irrigation in central Mexico: An overview.* International Journal of Environmental Health Research, 1995. **5**(2): p. 161-173.
131. Zhang, Y. and Y. Shen, *Wastewater irrigation: past, present, and future.* WIREs Water, 2019. **6**(3): p. e1234.
132. Singh, A., *A review of wastewater irrigation: Environmental implications.* Resources, Conservation and Recycling, 2021. **168**: p. 105454.
133. Organisation for Economic Co-operation and Development (OECD) and Food and Agriculture Organization of the United Nations (FAO), *OECD-FAO Agricultural Outlook 2019-2028*. 2019. p. 70-71.

134. European Environment Agency (EEA), *Landscapes in transition an account of 25 years of land cover change in Europe*. 2017.
135. Dixon, J., et al., *Farming Systems and Poverty: Improving Farmers' Livelihoods in a Changing World*, ed. M. Hall. 2001.
136. Gale, S., G. Thomson, and F. Zarlenga, *Capter 5 - Underground geological storage*. 2005. p. 195-265.
137. Ritchie, H. and M. Roser. *Land Use*. 2013; Available from: https://ourworldindata.org/land-use.
138. Dupas, R., et al., *The role of mobilisation and delivery processes on contrasting dissolved nitrogen and phosphorus exports in groundwater fed catchments.* Sci Total Environ, 2017. **599-600**: p. 1275-1287.
139. Porder, S. and S. Ramachandran, *The phosphorus concentration of common rocks—a potential driver of ecosystem P status.* Plant and Soil, 2013. **367**(1-2): p. 41-55.
140. Geisseler, D. and G. Miyao, *Soil testing for P and K has value in nutrient management for annual crops.* California Agriculture, 2016. **70**(3): p. 152-159.
141. Sharpley, A., *Managing agricultural phosphorus to minimize water quality impacts.* Scientia agricola., 2016. **73**(1): p. 1-8.
142. Canadian Council of Ministers of the Environment, *Water Quality for the Protection of Agriculture*. 2007.
143. Government of Manitoba. *Nutrient Management Regulation*. 2020 January, 2020]; Available from: https://www.manitoba.ca/sd/pubs/water/lakes-beaches-rivers/limitsandthresholds.pdf.
144. Government of British Columbia, D. Poon, and O. Schmidt, *Phosphorus Considerations for Nutrient Management*. 2010.
145. Government of Saskatchewan, *Surface Water Quality Objectives.* Environmental and Municipal Management Services Division of Saskachewan Water Security Agency,, 2015. **EPB 356**: p. 4.

146. Government of Alberta, *Environmental Quality Guidelines for Alberta Surface Waters*, Water Policy Branch, Alberta Environment and Parks, Editor. 2018: Edmonton, Alberta.
147. Government of Ontario, *Water management: policies, guidelines, provincial water quality objectives*, Environment and energy, Editor. 2016.

4. Estimating the base of fresh water in California

4.1. Introduction

Groundwater is an essential resource in California and accounts for 40% of the total annual water supply in the state [89]. In order to develop groundwater sustainability plans, several groundwater sustainability agencies in California utilize the base of fresh water concept [41]. The base of fresh water (BFW) is defined as “the depth in a well where the water in overlying aquifers has less than or equal to 3,000 mg per liter (mg/L or parts per million) of total dissolved solids” (quoting ref [42]). In California, the BFW has not been mapped since 1973 and has only been estimated for a portion of the state, specifically the Central Valley aquifer [52, 93]. When using the BFW for groundwater management, an inherent assumption is that total dissolved solids (TDS) concentrations monotonically increase with depth and that groundwater with TDS concentrations above 3,000 mg/L does not require sustainable management (Appendix B: Figure S1). However, a state-wide assessment of the relationship between TDS concentrations and depth has not been conducted, and fresh groundwater has been observed below the BFW [41]. Moreover, brackish water, which is defined as water with TDS concentrations less than 10,000 mg/L but greater than fresh water, is increasingly becoming economical to treat and use [48, 54-56]. Therefore, there is a need to understand how TDS varies with depth and to accurately map the base of fresh and brackish water, including identifying the limitations of these bases.

In 2014, the Sustainable Groundwater Management Act (SGMA) was signed into California law. The intention of SGMA is to provide guidance for long term sustainable groundwater management across the state through the creation of Groundwater Sustainability Plans (GSP) in medium and high priority groundwater basins across California [91]. In December 2019, the SGMA Basin Prioritization was completed and classified 94 (18%) of the 515 basins as medium or high priority [148]. The basins classified as medium or high priority are primarily located in the Central Valley [148, 149], an agriculturally intensive area that accounts for approximately 75% of California's groundwater use [150]. [151] estimate that the Central Valley aquifer system is experiencing a groundwater loss of 31 mm annually. During recent droughts, parts of the valley subsided by up to 60 cm over the course of a year due to over abstraction of groundwater [90]. The creation of Groundwater Sustainability Plans (GSP) under SGMA has brought to light major data and knowledge gaps, including information need to identify groundwaters to be managed and protected.

Definitions for groundwater quality by TDS concentrations vary depending on the context of use and the regulating body [46-51]. Generally, the upper limit for "fresh" water to be used as drinking water for humans is taken to be 1,000 mg/L [53], which serves as the upper limit for human drinking water according to the California State Water Resources Control Board (SWRCB) [152]. The United States Geological Survey (USGS) assumed a definition for fresh water as having TDS concentrations <2,000 mg/L for the 1971 and 1973 BFW estimations [52, 93]. Brackish water is considered to have TDS concentrations greater than fresh water but <10,000 mg/L [54]. There are several uses for brackish water including drinking water for livestock [94], irrigation for agricultural and floricultural crops [56, 95] and thermoelectric power generation [55]. The United States Geological Survey (USGS) classifies water with a TDS concentration >10,000 mg/L as "highly saline" and water with TDS concentrations >35,000 mg/L as seawater or brine [53]. Seawater is desalinated to supply fresh water in many parts of the world, including California [153, 154]. Desalination of brackish water is considerably cheaper than seawater due to the lower concentration of impurities that must be removed [54]. Therefore, replacing the BFW concept with the base of brackish water may ensure that groundwaters usable now and in the future are sustainably managed and protected.

Bases of fresh water are widely being used in groundwater sustainability plans in California [41]. However, new research suggests there are large volumes of fresh water in groundwater aquifers not included in previous estimates [2] and that fresh groundwater exists below the currently defined BFW in California [41]. Therefore, there may be a need to consider approaches alternative to using the BFW [155]. One potential approach is the use of the base of brackish water, which is generally deeper than the BFW providing a more conservative approach and protecting additional usable groundwater resources. Therefore, we evaluate the TDS data to understand the challenges and uncertainties associated with estimating the base of brackish water.

In this paper, we: (i) develop a framework to estimate the salinity profile and the BFW water, (ii) estimate the BFW and the base of brackish water, where possible, and (iii) compare our BFW estimates with USGS-estimated BFWs. We then use our results to consider the limitations of utilizing the BFW for sustainable groundwater management. Overall, our results can be used to guide groundwater policy development that prevents contamination and ensure the sustainable use of groundwater resources in California and elsewhere.

4.2. Methodology

4.2.1. TDS Data

We analyze 216,754 groundwater TDS measurements from five different sources; (1) the USGS Produced Waters Database (PWD), (2) the Department of California's Division of Oil, Gas, and Geothermal Resources (DOGGR) (now California Geologic Energy Management (CalGEM)) Data Sheets, (3) the USGS Brackish Groundwater Assessment (BGA), (4) the Water Quality Portal (WQP), and (5) the USGS Groundwater Ambient Monitoring and Assessment (GAMA) Program. We use the total well depth as the depth associated with the TDS measurement [41, 156]. We group TDS measurements by the associated depths: 0-25 m, 25-75 m, 75-150 m, 150-305 m, 305-1,000 m, 1,000-2,000 m, and >2,000 m. Because of the disproportionately large number of TDS data closer to the surface with 60% of data located within 75 m of the surface, we divide the first depth zone (75 m) used by [41] into two distinct depth zones. We select a depth of 25 m because this splits the available data within 75 m of the surface evenly between the newly created depth zones (Appendix B: Table S1). The depth of 75 m is chosen based on the average well depth in the western United States (72 m) [41, 157]. The remaining depth zones are based on the boundaries of previously studied depths which aim to have data in the deeper depth zones [41].

4.2.2. Estimation of the base of fresh water

To examine the relationship between TDS measurements and depth, we divide the area across California into 10x10 km grid sections. To develop a BFW estimation methodology, we choose 20 grid sections across the Central Valley aquifer such that all of the Central Valley is no more than 50 km from a chosen grid section. We choose the Central Valley aquifer because of data availability and because the Central Valley aquifer is sufficiently continuous and connected hydraulically such that interpolations can reasonably be made [158]. Additionally, the Central Valley is an important agricultural region with large groundwater demands and critically overdrafted groundwater basins subject to SGMA [159, 160].

Two different methods are tested to determine the set of TDS measurements that will be used to plot the salinity profiles, determine the relationship between TDS measurements and depth, and estimate the BFW. The first method requires the selection of all TDS measurements within a specific radius from the center of the grid section using the *Buffer* [161] and *Spatial Join* [162] tools in ArcMap. Selection radii are chosen in two different manners: (1) selection radii are the same across all grid sections but differ by depth zone to account for the larger amount of data at depths closer to the surface and (2) selection radii are based on the density of data and vary with location and depth. To ensure data is available for each depth zone using the first method, as depth increases and the density of TDS measurement decreases, the selection radius increases (see Appendix B: Table S1). The second method tested to determine salinity profiles is to select TDS measurement data points that are located closest to the center of the grid section using the *Generate Near Table* function in ArcMap. We test two different values for the number of TDS measurements: 20 and 10. Additionally, we set a 50 km limit on the search radius for all depth zones except the >2,000 m zone where we set a 100 km limit to accommodate data sparsity. As the distance between the available TDS measurement location and a grid section increases, the likelihood the data describes the TDS-depth relationship of that grid section decreases. Therefore, the 50 km search radius is chosen to ensure that the selected TDS measurements accurately reflect the salinity profiles of each grid section. For all methods, after selection of the TDS measurements, we evaluate whether the BFW can be defined and estimate the range in BFW values (Appendix B: Figure S2).

We use Python to classify the relationship between TDS measurements and depth: (1) linear and monotonic, (2) nonlinear but monotonic, and (3) nonlinear and nonmonotonic (Appendix B: Figure S3). We classify a "linear" relationship as having $R^2>0.8$. To determine the BFW, we complete a linear regression with the available data and use the linear equation to estimate the BFW using a TDS limit of 2,000 mg/L to compare to the USGS-estimated BFW. We also estimate the BFW using a TDS limit of 3,000 mg/L, which is the definition of fresh water used by DOGGR (now CalGEM) and the Bureau of Land Management [42], and we estimate the base of brackish water at the specified TDS limit of 10,000 mg/L. To avoid extrapolating the available data, we only calculate the base of brackish water in areas where at least one TDS measurement within 100 km of the grid section exceeds 10,000 mg/L. We produce BFW and base of brackish water estimates in areas of the Central Valley with a linear and monotonic TDS-depth relationship. We do not determine an equation of best fit to represent TDS measurements with depth in areas with a "nonlinear" ($R^2<0.8$) but monotonic relationship. Moreover, the corresponding areas represent only 1% of the total land area in Central Valley and 0.1% of the total land area of California. Areas with no data are classified as having a total of 10 data points or less within a 50 km search area or lacking TDS concentrations associated with depths >300 m.

There are 4 different scenarios that are possible while calculating the BFW in the 20 selected grid sections: (1) BFW is undefined due to TDS concentrations >3,000 mg/L within 25 m of the surface, (2) BFW is undefined due to a nonmonotonic TDS-depth relationship that may result from outliers in the TDS measurements or too many TDS measurements being selected, (3) the BFW is undefined because the range in which the BFW may lie is >900 m, and (4) the BFW is defined.

4.2.3. Comparison of base of fresh water estimates

We use contour maps of the USGS BFW estimates created by Kang et al [41] and compare to BFW estimations made using a TDS limit of 2,000 mg/L calculated in this paper. We use the *Spatial Join* feature in ArcGIS to identify areas where there is an overlap between the BFW estimations completed by the USGS and the BFW estimations we produce in this paper.

4.3. Results

4.3.1. Estimates of the base of fresh water in the Central Valley using 20 selected grid sections

4.3.1.1. Data within a fixed radius

Using a fixed search radius, we find that some of the 20 selected grid sections have substantially more data selected than other grid sections (**Table 1**, Appendix B: Figure S4-S7 and Table S2). There is a difference of 2,556 TDS measurements between the grid section with the most (Grid Section 1) and the least (Grid Section 20) TDS measurements selected. Grid section 1 has the most TDS measurements with 2,698 selected measurements, and grid section 20 has the fewest measurements with 142 selected measurements. Only four other grid sections (14, 12, 6, and 5) out of the 20 have more than 1,000 TDS measurements selected. We find six (30%) of the 20 selected grid sections have TDS measurements >3,000 mg/L within 25 m of the surface, 8 (40%) of the 20 selected grid sections have a nonmonotonic relationship, and 3 (15%) of the 20 selected grid sections have a BFW range >900 m. Using TDS measurements selected with a fixed radius by depth only, we can calculate the BFW in three (15%) of the 20 selected grid sections.

Next, we use a radius based on the point density of TDS measurements within range of the grid section (see Appendix B: Figure S8-10 and Table S3). We find a difference of 3,812 TDS measurements between the grid section with the largest and the smallest number of selected measurements (**Table 1**). Grid section 1, the southernmost selected grid section in Kern County, has the most selected TDS measurements with 4,414, located between 10 km in the two depth zones nearest the surface to 150 km at depths >2,000 m. Grid section 17, located in Glenn County, has the fewest TDS measurements selected with 602. The search radius in the counties of Glenn, Butte, Tehama, and Shasta ranges from 10 km in the two depth zones nearest the surface to 200 km for depths >2,000 m. We find 11 (55%) of the 20 selected grid sections have TDS measurements >3,000 mg/L within 25 m of the surface, and 8 (40%) of the 20 selected grid sections have a nonmonotonic TDS-depth relationship. We are able to determine the BFW in one (5%) of the 20 selected grid sections using TDS measurements obtained within a radius that varies with depth and location.

Table 1. Number of selected TDS measurements and ability to determine BFW for each of the 20 selected grid sections using selection methods that have a variable radius. Grey highlighted grid sections represent areas where the BFW is calculable according to the method outlined in Supplementary Material Figure S2. Red highlight represents the grid section with the smallest number of TDS measurements selected and green highlight represents the grid section with the largest number of TDS measurements selected. Grid section numbers start at the southern portion of the Central Valley with Grid Section 1 representing the southernmost grid section and Grid Section 20 representing the northernmost grid section.

		Method					
		Variable radius by depth			Variable radius by depth and location		
County	Grid section	TDS measurements selected	BFW scenario	BFW depth range (m)	TDS measurements selected	BFW scenario	BFW depth range (m)
Kern (South)	1	2698	2	N/A	4414	1	N/A
Kern (North)	2	850	1	N/A	2186	1	N/A
Kings	3	444	1	N/A	2534	1	N/A
Tulare	4	666	2	N/A	2963	1	N/A
Fresno (South)	5	1290	1	N/A	2440	1	N/A
Fresno (North)	6	1389	1	N/A	2396	1	N/A
Fresno (East)	7	674	2	N/A	2940	2	N/A
Madera (West)	8	207	1	N/A	2108	1	N/A
Madera (East)	9	209	3	372-1350	1747	2	N/A
Merced	10	205	3	372-1350	1776	2	N/A
Stanislaus	11	687	2	N/A	3027	2	N/A
San Joaquin	12	1489	2	N/A	4142	1	N/A
Yolo (South)	13	643	4	648-1056	1367	2	N/A
Sacramento	14	1109	1	N/A	4368	1	N/A
Yolo (North)	15	340	4	648-1056	980	2	N/A
Sutter	16	203	2	N/A	1312	1	N/A
Glenn	17	159	2	N/A	602	2	N/A
Butte	18	478	2	N/A	1310	2	N/A
Tehama (South)	19	296	4	278-559	841	4	407-559
Tehama (North)	20	142	3	293-1235	709	1	N/A

4.3.1.1. Nearest data

To identify a method that will increase the area in which we can estimate the BFW, we select the 20 nearest TDS measurements with a 50 km radius of each grid section (Appendix B: Figure S11-S13). We find a difference of 36 TDS measurements between the grid section with the fewest and the largest number of selected measurements. The maximum number of TDS measurements selected from all depth zones using this method is 120. Grid sections 2, 6, 7, 12, 13, 14, 15, and 16 have the maximum number of data available (**Table 2**). Grid section 11, in Stanislaus County, has the fewest data points within the selected radius with 84. Grid section 11 and 20 are the only grid sections with less than 100 selected measurements. We find 8 (40%) of the 20 selected grid sections have TDS measurements >3,000 mg/L within 25 m of the surface, 4 (20%) of the 20 selected grid sections have a nonmonotonic TDS-depth relationship, and 3 (15%) of the 20 selected grid sections have a >900 m depth range in which the BFW may be. We can determine the BFW in 5 (25%) of the 20 selected grid sections.

To further increase the likelihood of being able to estimate the BFW, we evaluate the approach that selects a maximum of the 10 closest TDS measurements in each depth zone (Appendix B: Figure S14-S16). This corresponds to a maximum of 70 TDS measurements over the seven depth zones (**Table 2**). We find that every grid section reaches the maximum of 70 selected TDS measurements, given the upper limit in search areas of 50 km radius for the top six zones and 100 km radius for the deepest depth zone (>2000 km). We find that 5 (25%) of the 20 selected grid sections have TDS measurements >3,000 mg/L within 25 m of the surface, 3 (15%) of the 20 selected grid sections have a nonmonotonic TDS-depth relationship, and 1 (5%) of the 20 selected grid sections has a BFW range >900 m. We can determine the BFW in 11 (55%) of the 20 selected grid sections, which represents the largest number of selected grid sections for which a BFW can be calculated among the four methods explored here.

Table 2. Number of selected TDS measurements and ability to determine BFW for each of the 20 selected grid sections using methods that select the nearest 20 and 10 TDS measurements to the center of each grid section. Grey highlighted grid sections represent sections where the BFW is calculable according to the method outlined in Supplementary Material Figure S2. Red highlight represents the grid section with the smallest number of TDS measurements selected and green highlight represents the grid section with the largest number of TDS measurements selected. Grid section numbers start at the southern portion of the Central Valley with Grid Section 1 representing the southernmost grid section and Grid Section 20 representing the northernmost grid section.

		Method					
		Variable radius by depth			Variable radius by depth and location		
County	Grid section	TDS measurements selected	BFW scenario	BFW depth range (m)	TDS measurements selected	BFW scenario	BFW depth range (m)
Kern (South)	1	113	4	945-990	70	4	366-1066
Kern (North)	2	120	1	N/A	70	1	N/A
Kings	3	113	1	N/A	70	1	N/A
Tulare	4	109	3	458-1981	70	4	458-1082
Fresno (South)	5	107	1	N/A	70	1	N/A
Fresno (North)	6	120	1	N/A	70	1	N/A
Fresno (East)	7	120	4	1002-1350	70	4	1012-1350
Madera (West)	8	116	1	N/A	70	1	N/A
Madera (East)	9	102	2	N/A	70	4	633-1350
Merced	10	114	3	372-1350	70	3	372-1350
Stanislaus	11	84	3	976-2133	70	4	976-1078
San Joaquin	12	120	1	N/A	70	4	458-903
Yolo (South)	13	120	2	N/A	70	2	N/A
Sacramento	14	120	2	N/A	70	2	N/A
Yolo (North)	15	120	2	N/A	70	2	N/A
Sutter	16	120	1	N/A	70	4	648-1056
Glenn	17	117	4	407-537	70	4	407-926
Butte	18	117	4	407-537	70	4	407-1027
Tehama (South)	19	113	4	407-559	70	4	407-559
Tehama (North)	20	88	1	N/A	70	4	407-559

4.3.2. Relationship between TDS and depth

Because selection of the 10 nearest TDS measurements to the center of each grid section results in the largest area where a BFW can be estimated, we use this method to determine the TDS-depth relationship throughout California. To account for high TDS concentrations at the surface we determine the relationship between TDS and depth using all depth zones and depth zones deeper than 25 m. We find that excluding TDS measured at depths deeper than 25 m does not lead to substantially greater areas in which a BFW can be calculated (Appendix B: Table S4). In both cases (with and without measurements in the top 25 m), we determine the TDS-depth relationship (Appendix B: Table S4). We find that in 20% (84,850 km^2) of California, there is a linear and monotonic relationship between TDS measurements and depth. Where a linear relationship is defined as an R^2 value >0.8 for the TDS measurements selected in all depth zones. In 7% (31,506 km^2) of California, we find groundwater has a "nonlinear" ($R^2<0.8$) but monotonic relationship between TDS measurements and depth (**Figure 5**) and 23% (98,584 km^2) of California, by area, is lacking sufficient TDS measurement data to determine the BFW. (We define areas lacking sufficient data as having less than 11 TDS measurements within the defined search radius or lacking TDS measurements associated with depths >300 m.) In the Central Valley, 3% of the valley's total area does not have sufficient data for BFW calculations. Across California, 49% (209,026.76 km^2) of the state's area has sufficient data but a nonlinear and nonmonotonic TDS-depth relationship, and the BFW concept may not be appropriate for identifying groundwater subject to management and protection in these areas.

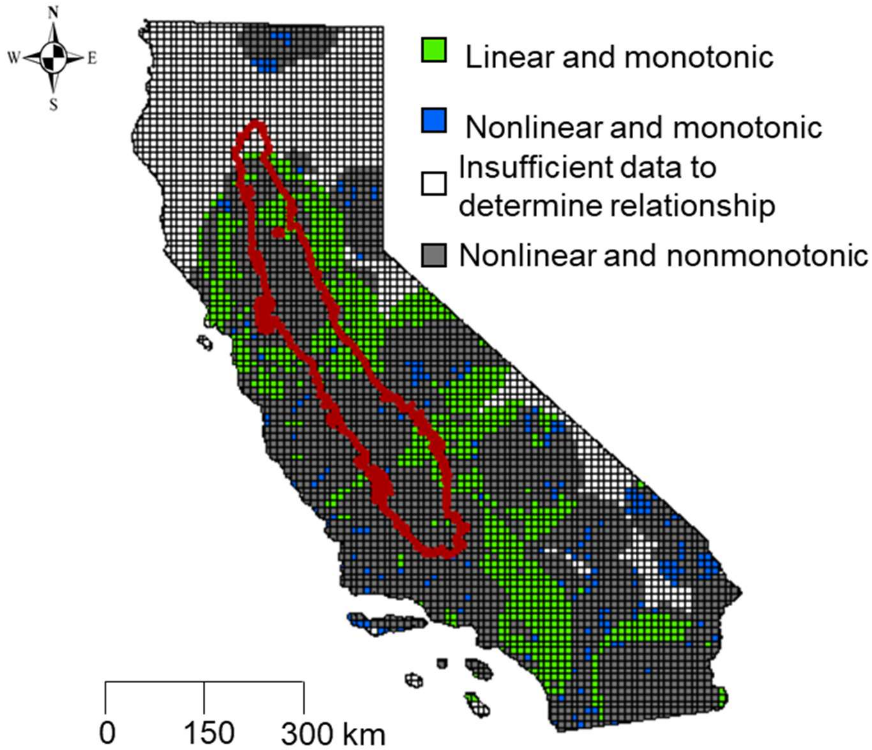


Figure 5. TDS-depth relationship by grid sections in California. Areas with a linear (R^2>0.8) and monotonic relationship are in green, nonlinear (R^2<0.8) and monotonic in blue, and insufficient data in white. Areas in grey have a nonlinear nonmonotonic TDS-depth relationship.

4.3.3. Maps of base of fresh (TDS<3,000 mg/L) and brackish (TDS<10,000 mg/L) water

We calculate the BFW and the base of brackish water using data from the nearest 10 TDS measurements to the center of each grid section. Focusing on the Central Valley, we can calculate the BFW and the base of brackish water in 22% (10,461 km^2) of the valley, which accounts for 2% of the total area of California (**Figure 6A**). We estimate the shallowest BFW to be 155 m and the shallowest base of brackish water to be 691 m. The deepest BFW is 590 m and 59% of BFW estimates are deeper than 400 m.

Additionally, all base of brackish water estimates exceed 400 m in depth and 68% of estimates are deeper than 1,000 m. The deepest base of brackish water estimate is 1,845 m. Where we calculate the BFW and the base of brackish water, an additional volume of at least 8,377 km^3 is managed and protected when using the base of brackish water compared to our estimated BFW, calculated using a TDS limit of 3,000 mg/L.

4.3.4. Comparison between our estimated base of fresh water values and previously-estimated bases of fresh water

We compare our BFW estimates for the Central Valley (**Figure 6A**) with the USGS-estimated BFW contours (both based on a TDS limit of 2,000 mg/L) [2] in 22% (10,552 km^2) of the Central Valley. We find that the USGS-estimated BFW is deeper in 65% (6,841 km^2) of this estimated area and shallower in 35% (3,637 km^2) of the estimated area (**Figure 6B**). The largest difference between our BFW and the USGS-estimated BFW is found to be 801 m where the USGS-estimated value is deeper than our estimated BFW. In areas of the Central Valley where the USGS estimates are deeper than our estimates, 57% of areas have a difference greater than 100 m, and in areas where the USGS estimates are shallower than the BFW estimated in this paper, 19% have a difference greater than 100 m. Where the USGS estimate is shallower than our estimates, the largest difference is 140 m. The USGS-estimated BFW is deeper than our estimated BFW in a majority of the area for which we calculate the BFW. The areas where our estimated BFW are deeper than the USGS-estimated BFW are found in regions of the Central Valley located north of Fresno County, whereas the areas where the USGS estimates are deeper are found in Fresno, King, Tulare, and Kern counties (**Figure 6B**). We find the USGS-estimated BFW conservatively protects more than 1,000 km^3 of groundwater when compared to our estimated BFW. We cannot estimate the BFW in the majority (85%) of the Central Valley due to a nonlinear and nonmonotonic TDS-depth relationship. Therefore, our results cannot be used to determine if the USGS-estimated BFW is a conservative option for groundwater management and protection.

Figure 6A. Maps of the base of fresh water

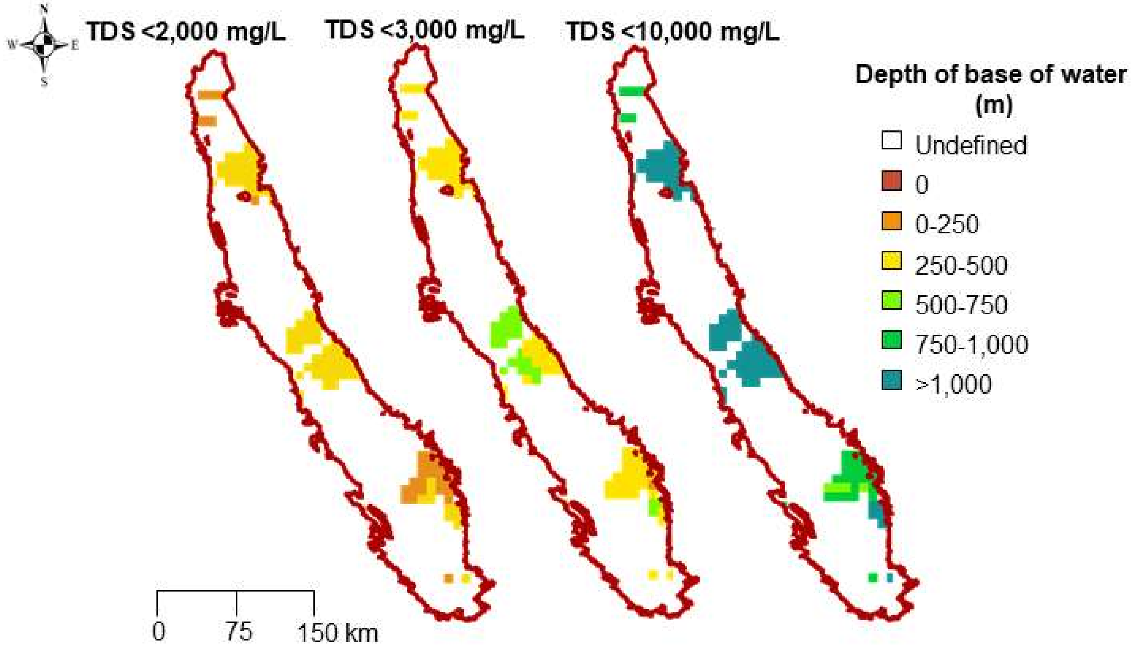


Figure 6B. Differences between the USGS-estimated BFW and the BFW estimated in this paper using TDS <2,000 mg/L

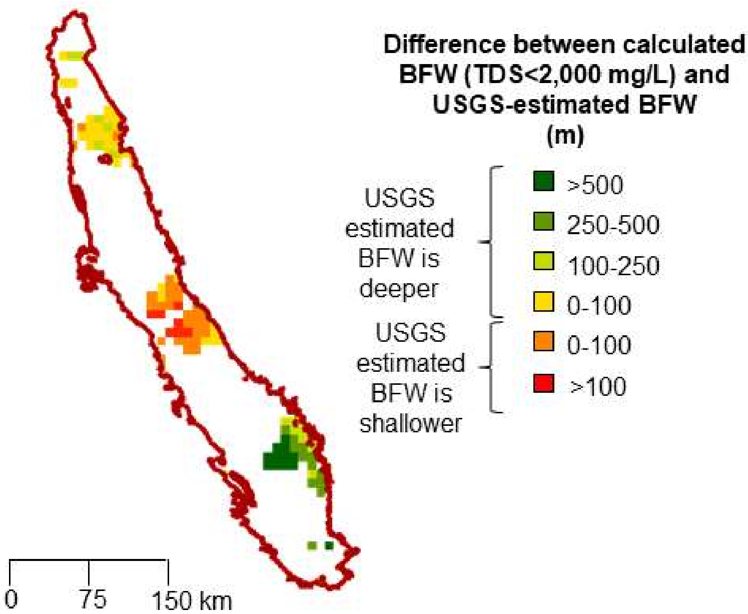


Figure 6. Maps of the base of water (Panel A) using TDS<2,000 mg/L (left), TDS < 3,000 mg/L (center), and TDS < 10,000 mg/L (right). Differences between the USGS-estimated BFW and our estimated BFW using TDS<2,000 mg/L (Panel B). In Panel B, green/yellow areas show where the USGS-estimated BFW is deeper and red/orange areas show where the USGS-estimated BFW is shallower, compared to our BFW estimate using TDS<2,000 mg/L.

4.4. Discussion

Anthropogenic contamination on the ground surface from sources such as agriculture can impact groundwater quality [163]. Although we do not find a noticeable impact in the ability to determine the TDS-depth relationship when removing TDS measurements taken in the first 25 m of the surface, the impact of agriculture on groundwater quality is site-specific [164] and it has been hypothesized that irrigated agriculture may be responsible for the salinization of groundwater deeper than 25 m in the San Joaquin Valley [165, 166]. Based on our dataset of TDS measurements, anthropogenic contamination may affect depths up to 75 m deep as TDS measurements range from 0.06 mg/L to 14,000,000 mg/L between 50 and 75 m of depth. Additional sampling and analysis are needed to identify areas with naturally high TDS concentrations near the surface and areas affected by anthropogenic contamination. Removal of high TDS measurements in areas with contamination could assist in clarifying the TDS-depth relationship and subsequently determining where the BFW is located.

Although we find that the USGS-estimated BFW appears to be a conservative option for groundwater management and protection, this comparison may not be representative as we are only able to estimate the BFW in 22% of the Central Valley and only 2% of California. Nevertheless, the USGS-estimated BFW is deeper than our estimated BFW in the counties of Fresno, King, Tulare, and Kern, where many critically overdrafted groundwater basins are found, and possibly protects more than 1,000 km^3 of groundwater when compared to our estimated BFW using TDS measurements. Therefore, in some regions, the use of the USGS-estimate BFW may be beneficial, indicating the importance of methods catered to local hydrogeological conditions and data availability.

Even with a large data set of 216,754 TDS measurements, we are unable to estimate the BFW across 75% of California's area. There are data limitations that prevent characterization of the TDS-depth relationship in 23% of the state. Moreover, even where there is sufficient data, the BFW (or base of brackish water) concept may not be appropriately applied for groundwater management because the TDS-depth relationship is nonmonotonic, which is the case for a majority (52%) of the state.

Given the challenges to estimating the BFW across California and the limitations of the BFW concept in general, there may be a need for alternative approaches to define groundwater subject to management and protection. One approach may be to use the more conservative base of brackish water instead. However, estimating the base of brackish water is challenging because of data gaps and is likely to contain large uncertainties. Nevertheless, the deeper depths associated with the base of brackish water would lead to management and protection of more potentially usable groundwater – both fresh and brackish. Additional studies with new TDS measurement and other hydrogeological and subsurface data are needed to fully evaluate BFW and alternative strategies, such as the base of brackish water, to determine groundwaters to be managed and protected in California and elsewhere.

4.5. References

2. Kang, M. and R.B. Jackson, *Salinity of deep groundwater in California: Water quantity, quality, and protection.* Proceedings of the National Academy of Sciences of the United States of America, 2016. **113**(28): p. 7768-73.

41. Kang, M., et al., *Base of fresh water, groundwater salinity, and well distribution across California.* Proceedings of the National Academy of Sciences of the United States of America, 2020. **117**(51): p. 32302-32307.

42. Davis, T., M.K. Landon, and G.L. Bennett V, *Prioritization of oil and gas fields for regional groundwater monitoring based on a preliminary assessment of petroleum resource development and proximity to California's groundwater resources*, in *Scientific Investigations Report*. 2018: Reston, VA. p. 128.

46. Government of Saskatchewan, *Total Dissolved Solids (For Private Water and Health Regulated Public Water Supplies)*, Sask H2O, Editor. 2008.

47. Government of Canada, *Guidelines for Canadian Drinking Water Quality: Guideline Technical Document – Total Dissolved Solids (TDS)*. 1991.

48. Gray, S., et al., *4.04 - Seawater Use and Desalination Technology*, in *Treatise on Water Science*, P. Wilderer, Editor. 2011, Elsevier: Oxford. p. 73-109.

49. Shevah, Y., *1.4 - Adaptation to Water Scarcity and Regional Cooperation in the Middle East*, in *Comprehensive Water Quality and Purification*, S. Ahuja, Editor. 2014, Elsevier: Waltham. p. 40-70.

50. Driscoll, D.G., *Hydrology of the Black Hills area, South Dakota*. Water-resources investigations report ; 02-4094. 2002, Rapid City, SD (1608 Mt. View Rd., Rapid City 57702) Denver, CO: U.S. Dept. of the Interior, U.S. Geological Survey ; U.S. Geological Survey, Information Services [distributor].

51. Rhoades, J.D., A. Kandiah, and A.M. Mashali, *The use of saline waters for crop production*. FAO irrigation and drainage paper ; 48. 1992, Rome: Food and Agriculture Organization of the United Nations.

52. Berkstresser Jr, C.F., *Base of fresh ground water approximately 3,000 micromhos in the Sacramento Valley and Sacramento-San Joaquin Delta, California*, in *Water-Resources Investigations Report*. 1973.
53. United States Geological Survey. *Saline Water Use in the United States*. 2019; Available from: https://www.usgs.gov/special-topic/water-science-school/science/saline-water-use-united-states?qt-science_center_objects=0#qt-science_center_objects.
54. Karagiannis, I.C. and P.G. Soldatos, *Water desalination cost literature: review and assessment.* Desalination, 2008. **223**(1): p. 448-456.
55. Kahsar, R., *The potential for brackish water use in thermoelectric power generation in the American southwest.* Energy Policy, 2020. **137**: p. 111170.
56. Cassaniti, C., et al., *Growing floricultural crops with brackish water.* Environmental and Experimental Botany, 2013. **92**: p. 165-175.
89. Babbitt, C., et al., *The Future of Groundwater in California: Lessons in Sustainable Management from Across the West*, Environmental Defense Fund and Robert B. Daugherty Water for Food Global Institute at the University of Nebraska, Editors. 2018.
90. Stokstad, E., *Droughts exposed California's thirst for groundwater. Now, the state hopes to refill its aquifers*, in *Science*. 2020.
91. University of California, Division of Agriculture and Natural Resources, . *Sustainable Groundwater Management Act*. 2015 [cited 2021.
93. Page, R.W., *Base of fresh ground water approximately 3,000 micromhos, in the San Joaquin Valley, California*, in *Open-File Report*. 1971.
94. Pfost, D.L., C.D. Fulhage, and S. Casteel, *Water Quality for Livestock Drinking*, University of Missouri, Editor. 2001.
95. Pang, H.-C., et al., *Effect of brackish water irrigation and straw mulching on soil salinity and crop yields under monsoonal climatic conditions.* Agricultural Water Management, 2010. **97**(12): p. 1971-1977.
148. State of California, *Sustainable Groundwater Management Act 2019 Basin Prioritization*, Department of Water Resources, Editor. 2020.

149. MacLeod, C. and L.E. Méndez-Barrientos, *Groundwater Management in California’s Central Valley: A Focus on Disadvantaged Communities.* Case Studies in the Environment, 2019. **3**(1): p. 1-13.
150. Ojha, C., et al., *Sustained Groundwater Loss in California's Central Valley Exacerbated by Intense Drought Periods.* Water resources research, 2018. **54**(7): p. 4449-4460.
151. Famiglietti, J.S., et al., *Satellites measure recent rates of groundwater depletion in California's Central Valley.* Geophysical Research Letters, 2011. **38**(3).
152. California State Water Resources Control Board, *Groundwater Information Sheet: Salinity*, Division of Water Quality, Editor. 2017.
153. Robbins, J. *As Water Scarcity Increases, Desalination Plants Are on the Rise*. 2019 [cited 2021; Available from: https://e360.yale.edu/features/as-water-scarcity-increases-desalination-plants-are-on-the-rise.
154. Calsbad Desalination Plant. *About: What We Do*. 2017 [cited 2021; Available from: https://www.carlsbaddesal.com/what-we-do.html.
155. Condon, L.E., et al., *Where Is the Bottom of a Watershed?* Water Resources Research, 2020. **56**(3): p. e2019WR026010.
156. Kang, M., J.E. Ayars, and R.B. Jackson, *Deep groundwater quality in the southwestern United States.* Environmental Research Letters, 2019. **14**(3): p. 034004.
157. Perrone, D. and S. Jasechko, *Dry groundwater wells in the western United States.* Environmental Research Letters, 2017. **12**(10): p. 104002.
158. Bertoldi, G.L., R.H. Johnston, and K.D. Evenson, *Ground water in the Central Valley, California; a summary report*, in *Professional Paper*. 1991.
159. Scanlon, B.R., et al., *Groundwater depletion and sustainability of irrigation in the US High Plains and Central Valley.* Proceedings of the National Academy of Sciences, 2012. **109**(24): p. 9320.
160. California Department of Water Resources. *Critically Over Drafted Basins*. 2019; Available from: https://water.ca.gov/Programs/Groundwater-Management/Bulletin-118/Critically-Overdrafted-Basins.

161. esri. *Proximity toolset: Buffer*. 2016 [cited 2021; Available from: https://desktop.arcgis.com/en/arcmap/10.3/tools/analysis-toolbox/buffer.htm.
162. esri. *Overlay toolset: Spatial Join*. 2016 [cited 2021; Available from: https://desktop.arcgis.com/en/arcmap/10.3/tools/analysis-toolbox/spatial-join.htm.
163. Ferguson, G., et al., *Competition for shrinking window of low salinity groundwater.* Environmental Research Letters, 2018. **13**(11): p. 114013.
164. Suarez, D.L., *Impact of agricultural practices on groundwater salinity.* Agriculture, Ecosystems & Environment, 1989. **26**(3): p. 215-227.
165. Gerrit, S., et al., *Sustainability of Irrigated Agriculture in the San Joaquin Valley, California.* Proceedings of the National Academy of Sciences of the United States of America, 2005. **102**(43): p. 15352-15356.
166. Gillespie, J., D. Kong, and S.D. Anderson, *Groundwater salinity in the southern San Joaquin Valley.* AAPG Bulletin, 2017. **101**(8): p. 1239-1261.

5. General Discussion

5.1. Usefulness of geospatial and statistical analysis in identifying anthropogenic groundwater contamination

Our results demonstrate that the combination of geospatial and statistical analysis is useful for managing and visualising large sets of groundwater contamination data. Although we are able to draw conclusions in regions with sufficient data, we also identify areas where data availability is limited. These data limitations affect the ability to utilize geospatial analysis accurately on a global scale.

5.1.1. Limitations of current available data

Effective monitoring of groundwater and the ability for researchers and regulators to access groundwater data are essential for data-driven, science-based sustainable groundwater management strategies. Unfortunately, establishing a robust groundwater monitoring system is not a cheap or easy task with a single groundwater monitoring well costing approximately $100,00 USD [167]. As a result, there are gaps in existing monitoring programs in many countries, and some countries lack groundwater monitoring networks altogether. A 2020 study published by the International Groundwater Resources Assessment Centre reported that of the 185 countries where we find groundwater P concentrations to be lacking, 115 (62%) do not have an established groundwater monitoring program [168]. Even in countries with groundwater monitoring networks, only 51% have a web-based data portal to access the data collected [168]. Therefore, there is a need for new groundwater monitoring networks and expansions in existing networks, along with platforms for data accessibility.

In Canada, where groundwater management is conducted on a provincial basis, we find that groundwater monitoring systems vary significantly among and within provinces/territories. Saskatchewan does not test for P in groundwater while Manitoba's groundwater monitoring system was implemented to understand water supply capacity and to monitor groundwater levels, not to monitor anthropogenic impacts on groundwater. Thus, many of the groundwater monitoring wells in Manitoba are installed in aquifers that are covered by thick clay or till sediments, meaning anthropogenic contamination of these aquifers is most likely not occurring from surface activities [169]. Alberta, British Columbia, Ontario, and Quebec have comparatively dense P monitoring systems in place, but placement of these sites are based on accessibility and existing monitoring well locations [170]. Potentially because of inaccessible terrain, there is an underrepresentation of monitoring networks in natural land use types such as treed areas and wetlands across these provinces, and Canada as a whole. Moreover, provinces are responsible for choosing the type of contaminants to monitor and in the specific case of P, the analysis method. Beyond designing and implementing groundwater monitoring systems, provinces are also responsible for regulating and managing groundwater withdrawal and for approving well licenses that specify the rate, duration, quantity and/or the purpose of groundwater extractions [171]. Except for Quebec and British Columbia, all provinces implemented a licensing system for groundwater extractions by 1972. Quebec began licensing in 2004 [171] and although British Columbia began requiring licenses for groundwater withdrawal in 2016 [172], only 20% of groundwater users have registered since the law was implemented 4 years ago [173]. This uncoordinated and inconsistent data collection makes cohesive groundwater management difficult. Cooperation between provinces and the federal government could produce more sustainable groundwater management for all Canadians.

Groundwater monitoring in the United States is conducted by monitoring networks operated at federal, state, and local levels [174, 175]. However, not all monitoring wells collect data on water quality and wells that do monitor for water quality may not test for all contaminants. The National Ground-Water Monitoring Network compiles groundwater data from across the United States and covers 17,145 monitoring wells. Only 19%

(3,290) of monitoring wells in the database collect groundwater chemistry data, the rest only monitor water levels [176]. Even in California, a state with complex groundwater laws and large groundwater demands, there are spatial gaps in the available data. A 2016 report found that for the Sustainable Groundwater Management Act to ensure sustainable management, additional steps must be taken to expand current groundwater monitoring networks in the state [177]. Effective and sustainable groundwater management requires sufficient data and existing monitoring networks need to be expanded to fill critical data gaps. With adequate funding and cooperative data collection across the country, researchers can utilize the data to provide the results necessary to implement sustainable groundwater management.

For regulators to implement effective and sustainable groundwater management, it is necessary to have an in-depth understanding of the hydrogeology. A current lack of available data, and inconsistencies in the available data between, and within, countries means it is difficult to identify and isolate existing problems. However, there are many challenges that regulators face when designing a groundwater monitoring network. First, the purpose of the groundwater monitoring network determines the number of wells required, sampling frequency, and the depth at which these wells must be drilled [178]; a groundwater monitoring network designed for monitoring anthropogenic P contamination may not be adequate for monitoring groundwater depths. Second, groundwater monitoring wells are expensive. A groundwater monitoring system in South Korea with a target of 0.1 monitoring wells/km^2 was estimated to cost nearly 800 million USD over a 50-year lifetime [179]. Based on contamination modelling, a density of 0.1 monitoring wells/km^2 is recommended to ensure adequate information is collected with the lowest number of wells [180]. With an area of nearly 10 million km^2, roughly 100 times larger than South Korea, a groundwater monitoring system in Canada with a similar coverage of 0.1 monitoring wells/km^2 would be significantly more expensive than the estimated 800 million USD budget proposed for the South Korean monitoring network. Because the cost to implement a robust groundwater monitoring system is so high, it is necessary to use modelling that optimizes the placement and density of wells based on the sampling requirements of the region [181-184]. Finally, as with any subsurface activity, groundwater monitoring wells can have a potential environmental impact. Drilling through the earth's crust creates a pathway for surface contamination to reach the subsurface [185]. Moreover, the average lifetime of a groundwater monitoring well is 30 years [179], after which they must be appropriately decommissioned to prevent future contamination of groundwater and remove the physical obstruction a well may pose on the surface [186]. Ultimately, a global standardization of groundwater monitoring is not possible as individualized monitoring networks by region ensures a customized data collection campaign that focuses on the needs of the region, environmentally and economically. However, ensuring there are some monitoring wells in each region that collect data on all contaminants and groundwater levels would make it simpler to collect and analyze data which is essential for identifying regions of concern.

5.2. Managing anthropogenic impacts on groundwater

Identifying anthropogenic activities that have a potentially negative impact on groundwater quality introduces new opportunities for mitigative actions that could prevent contamination of groundwater aquifers around the world. This thesis focuses primarily on anthropogenic groundwater pollution from agriculture and oil and gas development, two activities that have been identified as consequential contributors to groundwater pollution [5, 6, 187, 188]. Moreover, globally 70% of all freshwater withdrawals are used for agriculture while 19% are used for industrial purposes including energy generation [189]. Over-abstraction of groundwater as a result of these industries poses a risk to both groundwater quality and quantity [188].

In agricultural areas, there are several techniques and mitigation efforts that could be implemented to protect groundwater from nutrient pollution. Good management practices including proper irrigation techniques, and managing fertilizer, pesticide, and land use are all essential components to preventing agricultural contamination of groundwater. Focused irrigation that prevents overwatering ensures pesticides and fertilizers are not lost to the environment through runoff or leaching and reduces water use [188, 190, 191]. While managing fertilizer use by conducting soil tests for nutrients, customizing fertilizer applications based on crop needs, and ensuring fertilizers are properly stored reduces the risk excess nutrients will be lost to the environment [65, 190, 191]. Finally, understanding the geochemical qualities of aquifer systems can help regulators establish recommendations based on the region as storage capacity of the aquifer, unsaturated zone travel time, and aquifer residence times are all important when determining the contamination risk and the capability of an aquifer to naturally attenuate contamination [192]. Agricultural areas are necessary to meet the food demands of a growing population and focusing on better management of these areas will be essential for preserving groundwater quality in the future.

Oil and gas development is a necessary part of the global landscape, fossil fuels still account for 80% of total energy consumption [193] and petroleum is used to produce many everyday products including plastics, electronics, textiles, and other household products including dish detergents and non-stick pans [194]. Therefore, mitigating the environmental impacts of this industry are essential for sustainable groundwater management. Developing effective mitigation strategies requires a full understanding of the pathways through which groundwater contamination is occurring. Currently, it is understood that unplugged or leaky oil and gas wells can leak gases and other hydrocarbons from deep underground formations to shallow groundwater aquifers and the atmosphere [37, 67]. We hypothesize that anthropogenic contamination from the surface can also reach groundwater aquifers through these pathways. Unfortunately, leaky oil and gas wells are difficult to identify due to the high density of oil and gas wells in most areas with oil and gas development and the wide range of factors that may contribute to a well being leaky [37-39, 42, 195, 196]. Targeted case studies that include field sampling of groundwater could identify contamination plumes resulting from leaking oil and gas wells. Examining these contamination plumes will help regulators to better identify which wells are responsible for anthropogenic contamination of groundwater.

5.3. Sustainability of current groundwater management

Current groundwater management does not sufficiently prevent gaps in groundwater monitoring around the world, making it difficult for regulators to ensure sustainable groundwater use. A lack of existing monitoring for certain contaminants and the slow movement of groundwater through the subsurface means that potential problems occurring in groundwater aquifers now may not be identified in a timely manner. Because remediating groundwater is an expensive and time-consuming process and contaminated groundwater aquifers can be impossible to restore for human consumption, implementing groundwater management that prevents contamination is crucial [197].

Globally, sustainable groundwater management requires countries to implement regulations on P, a previously overlooked contaminant. A lack of monitoring regarding certain types of contamination overlooks the interconnectedness of groundwater with other essential earth systems. Groundwater pollution is capable of affecting oceans, rivers, lakes, and the atmosphere if not properly managed [58]. Additionally, it is important for agencies to continue to update groundwater regulations as new research, such as the work done in this thesis, identifies previously understudied contaminants (phosphorus) and unregulated contamination pathways (oil and gas wells). Even in regions like California where there is existing legislation to sustainably manage groundwater, there is a lack of data - a major barrier to effective groundwater management. Many countries are trying to implement sustainable groundwater policies and there remain many challenges to overcome to achieve global groundwater governance in a sustainable manner.

6. General Conclusions

6.1. Summary of results

In this thesis, we conduct a geospatial and statistical analysis using large datasets of phosphorus (P) and total dissolved solids (TDS) concentrations in groundwater to identify previously unstudied pathways through which anthropogenic contamination may be occurring and discuss the ability for current legislation to adequately preserve groundwater quality.

Our global collection of data on P concentrations in groundwater shows that every country with available data reports P concentrations may pose a eutrophication risk to surface waters. Moreover, we find that several regions with significant agricultural activity, including South America, Europe, and Asia, are lacking data on P concentrations in groundwater. These data gaps are concerning because our geospatial analysis of land use in Canada and the United States, shows that agricultural regions are likely responsible for elevated P concentrations in groundwater. We also show that that oil and gas wells may be acting as a previously unidentified pathway through which surface P is contaminating groundwater, exacerbating the impacts of agricultural P inputs. The results from this section of the thesis can be used to implement more effective management of P inputs, considering agricultural and oil and gas wells.

In California, we use available TDS measurements to plot salinity profiles and determine a method to estimate the BFW, where possible. Although we find that the existing USGS-estimated BFW appears to be a conservative option for groundwater management, we are only able to produce estimates for the BFW in 2% of California. Even with a large dataset of 216,754 TDS measurements, we encounter data limitations that prevent estimation of the BFW in 23% of the state. We also find that the assumptions governing the BFW for use in groundwater management are not valid in a majority (52%)

of California. Given the challenges in estimating the BFW and the limitations embedded in the BFW concept in general, it may be necessary to implement alternative approaches to define depths at which groundwater is managed and protected.

6.2. Limitations and recommendations

This thesis identifies oil and gas wells as a potential previously unstudied pathway through which anthropogenic contamination of groundwater may occur and highlights oversights in current groundwater management efforts. There are many opportunities and avenues to expand on the findings. The following recommendations or continued research could provide additional insights into groundwater contamination.

Conducting a field sampling campaign aimed at producing independent data that can be used to verify and validate existing government records would reduce any errors and ensure that all data collected could be utilized in the analysis. For example, with regards to the P data, there were several samples that reported orthophosphate concentrations higher than total phosphorus concentrations, a phenomenon that is physically impossible. In Canada, it would be valuable to conduct sampling in the northern regions of Manitoba, Ontario, and Quebec. The northern portions of these provinces is relatively untouched by anthropogenic activities and comparing contaminant concentrations in relatively natural aquifers to aquifers with similar hydrogeologic properties overlaid by anthropogenic activities could elucidate the impact of anthropogenic activities on groundwater quality.

Similarly, additional sampling campaigns in under-represented regions of the world that have heavy agricultural influences including Asia, South America and Africa could provide valuable insights on the link between crop/pastureland and P concentrations in groundwater. Even within Canada and the United States, increased sampling in areas that are typically more difficult to access and have therefore remain unassessed is necessary to provide sufficient data in regions with minimal anthropogenic impacts.

Moreover, although this thesis identifies leaking oil and gas wells as a potential pathway for anthropogenic phosphorus to reach groundwater, additional analysis of the oil and gas wells in Alberta and Ontario with close proximity to groundwater samples with high concentrations of P and other contaminants are needed.

A multi-scale assessment that synthesizes global, regional, and local studies can help in developing effective groundwater management practices and facilitate knowledge transfer. For California, we show that it may be valuable to replace the BFW concept with an alternative approach to delineating groundwater to be managed and protected. Such challenges to using the BFW likely exist in many other regions around the world. If regulators choose to rely on the BFW, BFW estimates should be updated more frequently, and the definition should be regularly updated to include higher TDS groundwater (e.g., up to 10,000 mg/L) depending on the technology and economics of the time and location. Continual improvements to groundwater management with new monitoring and data are needed to ensure that groundwater resources are available and protected for future generations.

References

1. Kemper, K.E., *Groundwater—from development to management.* Hydrogeology Journal, 2004. **12**(1): p. 3-5.
2. Kang, M. and R.B. Jackson, *Salinity of deep groundwater in California: Water quantity, quality, and protection.* Proceedings of the National Academy of Sciences of the United States of America, 2016. **113**(28): p. 7768-73.
3. Food and Agriculture Organization of the United Nations (FAO), et al., *Global diagnostic on groundwater governance*. 2016, Rome, Italy: FAO.
4. Margat, J.F. and J.v.d. Gun, *Groundwater around the world : a geographic synopsis*. 2013, CRC Press, Taylor & Francis Group: Boca Raton.
5. Sampat, P. and J.A. Peterson, *Deep trouble : the hidden threat of groundwater pollution*. Worldwatch paper ; 154. 2000, Washington, DC: Worldwatch Institute.
6. Burri, N.M., et al., *A review of threats to groundwater quality in the anthropocene.* Science of The Total Environment, 2019. **684**: p. 136-154.
7. Scozzari, A. and E. Dotsika, *Threats to the quality of groundwater resources : prevention and control*. 2016, Springer: Heidelberg.
8. Palomino, J., O.C. Muellerklein, and M. Kelly, *A review of the emergent ecosystem of collaborative geospatial tools for addressing environmental challenges.* Computers, Environment and Urban Systems, 2017. **65**: p. 79-92.
9. Sun, A.Y. and B.R. Scanlon, *How can Big Data and machine learning benefit environment and water management: a survey of methods, applications, and future directions.* Environmental Research Letters, 2019. **14**(7): p. 073001.
10. Government of Canada, *Canadian Geospatial Data Infrastructure*. 2016.
11. U.S. Environmental Protection Agency, *Open Government 2017 Progress Report*. 2017.
12. Zwirowicz-Rutkowska, A. and A. Michalik, *The Use of Spatial Data Infrastructure in Environmental Management:an Example from the Spatial Planning Practice in Poland.* Environmental Management, 2016. **58**(4): p. 619-635.
13. Longley, P.A., et al., *17. Information and Decision Making*, in *Geographic Information Science & Systems (4th Edition)*. John Wiley & Sons.

14. Wironen, M.B., E.M. Bennett, and J.D. Erickson, *Phosphorus flows and legacy accumulation in an animal-dominated agricultural region from 1925 to 2012.* Global Environmental Change, 2018. **50**: p. 88-99.
15. Mackie, C., et al., *Groundwater-surface water interactions and agricultural nutrient transport in a Great Lakes clay plain system.* Journal of Great Lakes Research, 2021. **47**(1): p. 145-159.
16. Liao, X., et al., *Subsurface transport and potential risk of phosphorus to groundwater across different land uses in a karst springs basin, Florida, USA.* Geoderma, 2019. **338**: p. 97-106.
17. Oenema, O., L. van Liere, and O. Schoumans, *Effects of lowering nitrogen and phosphorus surpluses in agriculture on the quality of groundwater and surface water in the Netherlands.* Journal of Hydrology, 2005. **304**(1): p. 289-301.
18. Meinikmann, K., M. Hupfer, and J. Lewandowski, *Phosphorus in groundwater discharge – A potential source for lake eutrophication.* Journal of Hydrology, 2015. **524**: p. 214-226.
19. United States Environmental Protection Agency, *Preventing Eutrophication: Scientific Support for Dual Nutrient Criteria*, Office of Water, Editor. 2015.
20. Yuan, Z., et al., *Understanding the anthropogenic phosphorus pathway with substance flow analysis at the city level.* Journal of Environmental Management, 2011. **92**(8): p. 2021-2028.
21. Schindler, D.W., *The dilemma of controlling cultural eutrophication of lakes.* Proceedings. Biological sciences, 2012. **279**(1746): p. 4322-4333.
22. Holman, I.P., et al., *Phosphorus in groundwater—an overlooked contributor to eutrophication?* Hydrological Processes, 2008. **22**(26): p. 5121-5127.
23. Holman, I.P., et al., *An assessment of the risk to surface water ecosystems of groundwater P in the UK and Ireland.* Science of the Total Environment, 2010. **408**(8): p. 1847-1857.
24. McCobb T.D., et al., *Phosphorus in a Ground-Water Contaminant Plume Discharging to Ashumet Pond, Cape Cod, Massachusetts*. 2003, 1999: U.S. Geological Survey Water Resources Investigations. p. 70 p.

25. Stollenwerk, K.G., *Simulation of phosphate transport in sewage-contaminated groundwater, Cape Cod, Massachusetts.* Applied Geochemistry, 1996. **11**(1): p. 317-324.
26. Domagalski, J.L. and H.M. Johnson, *Subsurface transport of orthophosphate in five agricultural watersheds, USA.* Journal of Hydrology, 2011. **409**(1): p. 157-171.
27. Program, U.S.G.S.T.S.H., H.T. Buxton, and D.W. Morganwalp, *U.S. Geological Survey Toxic Substances Hydrology Program: proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999*. US Geological Survey Toxic Substances Hydrology Program :proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999. 1999, West Trenton, N.J. : Denver, Colo.: U.S. Dept. of the Interior, U.S. Geological Survey ; Branch of Information Services [distributor]. 3 v.
28. Roy, J.W., et al., *Contribution of phosphorus to Georgian Bay from groundwater of a coastal beach town with decommissioned septic systems.* Journal of Great Lakes Research, 2017. **43**(6): p. 1016-1029.
29. EPA, U.S., *2018 Edition of the Drinking Water Standards and Health Advisories Table*, in *Drinking Water Standards and Health Advisories*. 2018.
30. Canadian Council of Ministers of the Environment, *Canadian Water Quality Guidelines for the Protection of Aquatic Life*, in *Phosphorus: Canadian Guidance Framework for the Management of Freshwater Systems*. 2004.
31. Government of Canada, *Guidelines for Canadian Drinking Water Quality - Summary Table*. 2017.
32. EPA. *State Progress Toward Developing Numeric Nutrient Water Quality Criteria for Nitrogen and Phosphorus*. 2019; Available from: https://www.epa.gov/nutrient-policy-data/state-progress-toward-developing-numeric-nutrient-water-quality-criteria.
33. McDowell, R.W., et al., *A National Assessment of the Potential Linkage between Soil, and Surface and Groundwater Concentrations of Phosphorus.* JAWRA Journal of the American Water Resources Association, 2015. **51**(4): p. 992-1002.

34. Rudel, T.K., et al., *Agricultural intensification and changes in cultivated areas, 1970–2005.* Proceedings of the National Academy of Sciences, 2009. **106**(49): p. 20675.
35. Bindraban, P.S., C.O. Dimkpa, and R. Pandey, *Exploring phosphorus fertilizers and fertilization strategies for improved human and environmental health.* Biology and Fertility of Soils, 2020. **56**(3): p. 299-317.
36. Sherwood, O.A., et al., *Groundwater methane in relation to oil and gas development and shallow coal seams in the Denver-Julesburg Basin of Colorado.* Proceedings of the National Academy of Sciences, 2016. **113**(30): p. 8391.
37. Kang, M., et al., *Identification and characterization of high methane-emitting abandoned oil and gas wells.* Proceedings of the National Academy of Sciences of the United States of America, 2016. **113**(48): p. 13636-13641.
38. Kang, M., et al., *Direct measurements of methane emissions from abandoned oil and gas wells in Pennsylvania.* Proceedings of the National Academy of Sciences, 2014. **111**(51): p. 18173.
39. Williams, J.P., A. Regehr, and M. Kang, *Methane Emissions from Abandoned Oil and Gas Wells in Canada and the United States.* Environmental Science & Technology, 2021. **55**(1): p. 563-570.
40. Alberta Energy Regulator, *Frequently Asked Questions: Base of Groundwater Protection*. 2016.
41. Kang, M., et al., *Base of fresh water, groundwater salinity, and well distribution across California.* Proceedings of the National Academy of Sciences of the United States of America, 2020. **117**(51): p. 32302-32307.
42. Davis, T., M.K. Landon, and G.L. Bennett V, *Prioritization of oil and gas fields for regional groundwater monitoring based on a preliminary assessment of petroleum resource development and proximity to California's groundwater resources*, in *Scientific Investigations Report*. 2018: Reston, VA. p. 128.
43. United States Geological Survey. *Chloride, Salinity, and Dissolved Solids*. Water Resources 2020 [cited 2021; Available from: https://www.usgs.gov/mission-

areas/water-resources/science/chloride-salinity-and-dissolved-solids?qt-science_center_objects=0#qt-science_center_objects.

44. Government of Canada, *Total Dissolved Solids (TDS)*, Health Canada, Editor. 1991.

45. World Health Organization, *Guidelines for Drinking-Water Quality*. 2011, Gutenberg: Malta.

46. Government of Saskatchewan, *Total Dissolved Solids (For Private Water and Health Regulated Public Water Supplies)*, Sask H2O, Editor. 2008.

47. Government of Canada, *Guidelines for Canadian Drinking Water Quality: Guideline Technical Document – Total Dissolved Solids (TDS)*. 1991.

48. Gray, S., et al., *4.04 - Seawater Use and Desalination Technology*, in *Treatise on Water Science*, P. Wilderer, Editor. 2011, Elsevier: Oxford. p. 73-109.

49. Shevah, Y., *1.4 - Adaptation to Water Scarcity and Regional Cooperation in the Middle East*, in *Comprehensive Water Quality and Purification*, S. Ahuja, Editor. 2014, Elsevier: Waltham. p. 40-70.

50. Driscoll, D.G., *Hydrology of the Black Hills area, South Dakota*. Water-resources investigations report ; 02-4094. 2002, Rapid City, SD (1608 Mt. View Rd., Rapid City 57702) Denver, CO: U.S. Dept. of the Interior, U.S. Geological Survey ; U.S. Geological Survey, Information Services [distributor].

51. Rhoades, J.D., A. Kandiah, and A.M. Mashali, *The use of saline waters for crop production*. FAO irrigation and drainage paper ; 48. 1992, Rome: Food and Agriculture Organization of the United Nations.

52. Berkstresser Jr, C.F., *Base of fresh ground water approximately 3,000 micromhos in the Sacramento Valley and Sacramento-San Joaquin Delta, California*, in *Water-Resources Investigations Report*. 1973.

53. United States Geological Survey. *Saline Water Use in the United States*. 2019; Available from: https://www.usgs.gov/special-topic/water-science-school/science/saline-water-use-united-states?qt-science_center_objects=0#qt-science_center_objects.

54. Karagiannis, I.C. and P.G. Soldatos, *Water desalination cost literature: review and assessment.* Desalination, 2008. **223**(1): p. 448-456.
55. Kahsar, R., *The potential for brackish water use in thermoelectric power generation in the American southwest.* Energy Policy, 2020. **137**: p. 111170.
56. Cassaniti, C., et al., *Growing floricultural crops with brackish water.* Environmental and Experimental Botany, 2013. **92**: p. 165-175.
57. Gorelick, S.M. and C. Zheng, *Global change and the groundwater management challenge.* Water Resources Research, 2015. **51**(5): p. 3031-3051.
58. Gleeson, T., et al., *Global Groundwater Sustainability, Resources, and Systems in the Anthropocene.* Annual Review of Earth and Planetary Sciences, 2020. **48**(1): p. 431-463.
59. McGrath, S.P., *POLLUTION | Industrial*, in *Encyclopedia of Soils in the Environment*, D. Hillel, Editor. 2005, Elsevier: Oxford. p. 282-287.
60. Nieder, R., D.K. Benbi, and F.-X. Reichl, *Soil components and human health*. 2018, Springer: Dordrecht, Netherlands.
61. Smil, V., *PHOSPHORUS IN THE ENVIRONMENT: Natural Flows and Human Interferences.* Annual Review of Energy and the Environment, 2000. **25**(1): p. 53-88.
62. Maïté, S.G., et al. *Impacts of Nitrogen and Phosphorus: From Genomes to Natural Ecosystems and Agriculture*. Frontiers in Ecology and Evolution, 2017. DOI: 10.3389/fevo.2017.00070.
63. Ruttenberg, K.C., *Phosphorus Cycle*, in *Encyclopedia of Ocean Sciences*, J.H. Steele, Editor. 2001, Academic Press: Oxford. p. 2149-2162.
64. Mekonnen, M.M. and A.Y. Hoekstra, *Global Anthropogenic Phosphorus Loads to Freshwater and Associated Grey Water Footprints and Water Pollution Levels: A High-Resolution Global Study.* Water Resources Research, 2018. **54**(1): p. 345-358.
65. Le Moal, M., et al., *Eutrophication: A new wine in an old bottle?* Science of The Total Environment, 2019. **651**: p. 1-11.

66. King, K.W., et al., *Phosphorus Transport in Agricultural Subsurface Drainage: A Review.* Journal of Environmental Quality, 2015. **44**(2): p. 467-485.

67. Wisen, J., et al., *A portrait of wellbore leakage in northeastern British Columbia, Canada.* Proceedings of the National Academy of Sciences of the United States of America, 2020. **117**(2): p. 913-922.

68. Wisen, J., et al., *Assessing the potential of cross-contamination from oil and gas hydraulic fracturing: A case study in northeastern British Columbia, Canada.* Journal of Environmental Management, 2019. **246**: p. 275-282.

69. Llewellyn, G.T., et al., *Evaluating a groundwater supply contamination incident attributed to Marcellus Shale gas development.* Proceedings of the National Academy of Sciences, 2015. **112**(20): p. 6325.

70. Osborn, S.G., et al., *Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing.* Proceedings of the National Academy of Sciences, 2011. **108**(20): p. 8172.

71. McMahon, P.B., et al., *Methane in groundwater from a leaking gas well, Piceance Basin, Colorado, USA.* Science of The Total Environment, 2018. **634**: p. 791-801.

72. Vengosh, A., et al., *A Critical Review of the Risks to Water Resources from Unconventional Shale Gas Development and Hydraulic Fracturing in the United States.* Environmental Science & Technology, 2014. **48**(15): p. 8334-8348.

73. Watson, T.L. and S. Bachu, *Evaluation of the Potential for Gas and CO2 Leakage Along Wellbores.* SPE Drilling & Completion, 2009. **24**(01): p. 115-126.

74. Jordan, P., *Chronic well leakage probability relative to basin and fluid characteristics.* Proceedings of the National Academy of Sciences, 2020. **117**(3): p. 1249.

75. Tveit, M.R., et al., *The fate of hydrocarbon leaks from plugged and abandoned wells by means of natural seepages.* Journal of Petroleum Science and Engineering, 2021. **196**: p. 108004.

76. Hyland, C., et al., *Agronomy Fact Sheet Series (Fact Sheet 12): Phosphorus Basics - The Phosphorus Cycle*, Cornell University Cooperative Extension, Editor. 2005.

77. Sims, J.T., R.R. Simard, and B.C. Joern, *Phosphorus Loss in Agricultural Drainage: Historical Perspective and Current Research.* Journal of Environmental Quality, 1998. **27**(2): p. 277-293.
78. Fouzia, H.B., *Monitoring of Marine Pollution*. 2019, IntechOpen: [S.l.].
79. Geng, Y., et al., *Increasing temperature reduces the coupling between available nitrogen and phosphorus in soils of Chinese grasslands.* Scientific Reports, 2017. **7**(1): p. 43524.
80. Jones, A.S., et al., *Surrogate Measures for Providing High Frequency Estimates of Total Suspended Solids and Total Phosphorus Concentrations.* JAWRA Journal of the American Water Resources Association, 2011. **47**(2).
81. Government of Canada, *Guidelines for Canadian Drinking Water Quality - Summary Table*. 2017.
82. EPA, U.S., *2018 Edition of the Drinking Water Standards and Health Advisories Table*, in *Drinking Water Standards and Health Advisories*. 2018.
83. Turner, B.L. and P.M. Haygarth, *Phosphorus Forms and Concentrations in Leachate under Four Grassland Soil Types.* Soil Science Society of America Journal, 2000. **64**(3): p. 1090-1099.
84. Government of Ontario Ministry of the Environment, *Lakeshore Capacity Assessment Handbook: Protecting Water Quality in Inland Lakes on Ontario's Precambrian Shield Appendix A: Rationale for a Revised Phosphorus Criterion for Precambian Shield Lakes in Ontario*, Environmental Sciences & Standards Division Standards Development Branch, Editor. 2010: Toronto, Ontario, Canada.
85. United States Environmental Protection Agency. *State-Specific Water Quality Standards Effective under the Clean Water Act (CWA)*. 2020; Available from: https://www.epa.gov/wqs-tech/state-specific-water-quality-standards-effective-under-clean-water-act-cwa.
86. Jr., E.T., *Agricultural Land Loss & Conservation* American Farmland Trust, Editor. 2009.
87. U.S. Energy Information Administration. *Oil and petroleum products explained: where are oil comes from*. Where U.S. crude oil is produced 2021 [cited 2021.

88. Thomas, B.F., et al., *GRACE Groundwater Drought Index: Evaluation of California Central Valley groundwater drought.* Remote Sensing of Environment, 2017. **198**: p. 384-392.
89. Babbitt, C., et al., *The Future of Groundwater in California: Lessons in Sustainable Management from Across the West*, Environmental Defense Fund and Robert B. Daugherty Water for Food Global Institute at the University of Nebraska, Editors. 2018.
90. Stokstad, E., *Droughts exposed California's thirst for groundwater. Now, the state hopes to refill its aquifers*, in *Science*. 2020.
91. University of California, Division of Agriculture and Natural Resources, . *Sustainable Groundwater Management Act*. 2015 [cited 2021.
92. Government of California, Department of Water Resources. *SGMA Portal: All Submitted GSP Annual Reports*. 2020 [cited 2021; Available from: https://sgma.water.ca.gov/portal/gspar/submitted.
93. Page, R.W., *Base of fresh ground water approximately 3,000 micromhos, in the San Joaquin Valley, California*, in *Open-File Report*. 1971.
94. Pfost, D.L., C.D. Fulhage, and S. Casteel, *Water Quality for Livestock Drinking*, University of Missouri, Editor. 2001.
95. Pang, H.-C., et al., *Effect of brackish water irrigation and straw mulching on soil salinity and crop yields under monsoonal climatic conditions.* Agricultural Water Management, 2010. **97**(12): p. 1971-1977.
96. Kröger, R., et al., *Downstream approaches to phosphorus management in agricultural landscapes: Regional applicability and use.* Science of The Total Environment, 2013. **442**: p. 263-274.
97. USGS. *Phosphorus Doesn't Migrate in Ground Water? Better Think Again!* 2002; Available from: https://toxics.usgs.gov/highlights/phosphorous_migration.html.
98. Demirel, Z., Z. Özer, and O. gülçiçek, *Nitrogen and phosphate contamination stress of groundwater in an internationally protected area of the göksu delta, Turkey.* Fresenius Environmental Bulletin, 2010. **19**: p. 2509-2517.

99. Izbicki, J.A., *Fate of Nutrients in Shallow Groundwater Receiving Treated Septage, Malibu, CA.* Groundwater, 2014. **52**(S1): p. 218-233.
100. Johnson, J.L.D.a.H., *Phosphorus and Groundwater: Establishing Links Between Agricultural Use and Transport to Streams.* U.S. Geological Survey Fact Sheet 2012-3004, 2012.
101. Lewandowski, J., et al., *Groundwater – The disregarded component in lake water and nutrient budgets. Part 2: effects of groundwater on nutrients.* Hydrological Processes, 2015. **29**(13): p. 2922-2955.
102. Robertson, W.D., S.L. Schiff, and C.J. Ptacek, *Review of Phosphate Mobility and Persistence in 10 Septic System Plumes.* Groundwater, 1998. **36**(6): p. 1000-1010.
103. Robertson, W.D., D.R. Van Stempvoort, and S.L. Schiff, *Review of phosphorus attenuation in groundwater plumes from 24 septic systems.* Science of The Total Environment, 2019.
104. Weihrauch, C. and C.J. Weber, *Phosphorus enrichment in floodplain subsoils as a potential source of freshwater eutrophication.* Science of The Total Environment, 2020. **747**: p. 141213.
105. Waller, D.H., et al., *Estimation of the contribution of phosphorus from on-site sewage disposal systems to lakes*. Research report. 1996, [Ottawa]: CMHC.
106. Spiteri, C., et al., *Modelling the geochemical fate and transport of wastewater-derived phosphorus in contrasting groundwater systems.* Journal of Contaminant Hydrology, 2007. **92**(1): p. 87-108.
107. Chen, X., et al., *Seasonal changes in the concentrations of nitrogen and phosphorus in farmland drainage and groundwater of the Taihu Lake region of China.* Environmental Monitoring and Assessment, 2010. **169**(1): p. 159-168.
108. Chambers, P.A., A. Canada, and C. Agri-Food, *Nutrients and their impact on the Canadian environment*. 2001, [Ottawa]: [Environment Canada].
109. Darrah, T.H., et al., *Noble gases identify the mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus and Barnett Shales.* Proceedings of the National Academy of Sciences, 2014. **111**(39): p. 14076.

110. Warner, N.R., et al., *Geochemical and isotopic variations in shallow groundwater in areas of the Fayetteville Shale development, north-central Arkansas.* Applied Geochemistry, 2013. **35**: p. 207-220.
111. Rosecrans, C.Z., et al., *Groundwater Quality of Aquifers Overlying the Oxnard Oil Field, Ventura County, California.* Science of The Total Environment, 2021. **771**: p. 144822.
112. U.S Environmental Protection Agency, *Design and Installation of Monitoring Wells*, Science and Ecosystem Support, Editor. 2018.
113. U.S. Energy Information Administration, *Average Depth of Crude Oil and Natural Gas Wells*. 2021.
114. Kang, M., et al., *Orphaned oil and gas well stimulus—Maximizing economic and environmental benefits.* Elementa: Science of the Anthropocene, 2021. **9**(1).
115. Haygarth, P.M. and A.N. Sharpley, *Terminology for Phosphorus Transfer.* Journal of Environmental Quality, 2000. **29**(1): p. 10-15.
116. Minnesota Pollution Control Agency, *Data Analysis Protocol for the Ground Water Monitoring and Assessment Program*. 1999.
117. McHugh, M.L., *The chi-square test of independence.* Biochemia medica, 2013. **23**(2): p. 143-149.
118. S.J. Rodvang, et al., *Groundwater quality in the eastern portion of the Lethbridge Northern Irrigation District: 1995 to 2001*, Alberta Agriculture, Food and Rurual Development, Lethbridge, Alberta, Canada,, Editor. 2002.
119. Tao, Y., et al., *Sources and enrichment of phosphorus in groundwater of the Central Yangtze River Basin.* Science of The Total Environment, 2020. **737**: p. 139837.
120. Wang, S., et al., *Effects of dissolved oxygen supply level on phosphorus release from lake sediments.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2008. **316**(1): p. 245-252.
121. Kim, L.-H., et al., *Phosphorus release rates from sediments and pollutant characteristics in Han River, Seoul, Korea.* Science of The Total Environment, 2004. **321**(1): p. 115-125.

122. Kent, R., T.D. Johnson, and M.R. Rosen, *Status and trends of orthophosphate concentrations in groundwater used for public supply in California.* Environmental Monitoring and Assessment, 2020. **192**(8): p. 550.
123. Marengo, J.A., et al., *Changes in Climate and Land Use Over the Amazon Region: Current and Future Variability and Trends.* Frontiers in Earth Science, 2018. **6**(228).
124. Souza, C., *Federal Republic of Brazil.* der.), A Global Dialogue on Federalism, 2005. **1**: p. 76-102.
125. Souza, C.M., et al., *Reconstructing Three Decades of Land Use and Land Cover Changes in Brazilian Biomes with Landsat Archive and Earth Engine.* Remote Sensing, 2020. **12**(17): p. 2735.
126. Shigaki, F., A. Sharpley, and L.I. Prochnow, *Animal-based agriculture, phosphorus management and water quality in Brazil: options for the future.* Scientia Agricola, 2006. **63**: p. 194-209.
127. Campos, V., *Arsenic in groundwater affected by phosphate fertilizers at São Paulo, Brazil.* Environmental Geology, 2002. **42**(1): p. 83-87.
128. Roy, E., et al., *Soil phosphorus sorption capacity after three decades of intensive fertilization in Mato Grosso, Brazil.* Agriculture Ecosystems & Environment, 2017. **249**: p. 206-214.
129. Hanjra, M.A., et al., *Wastewater irrigation and environmental health: Implications for water governance and public policy.* International Journal of Hygiene and Environmental Health, 2012. **215**(3): p. 255-269.
130. Siebe, C. and E. Cifuentes, *Environmental impact of wastewater irrigation in central Mexico: An overview.* International Journal of Environmental Health Research, 1995. **5**(2): p. 161-173.
131. Zhang, Y. and Y. Shen, *Wastewater irrigation: past, present, and future.* WIREs Water, 2019. **6**(3): p. e1234.
132. Singh, A., *A review of wastewater irrigation: Environmental implications.* Resources, Conservation and Recycling, 2021. **168**: p. 105454.

133. Organisation for Economic Co-operation and Development (OECD) and Food and Agriculture Organization of the United Nations (FAO), *OECD-FAO Agricultural Outlook 2019-2028*. 2019. p. 70-71.
134. European Environment Agency (EEA), *Landscapes in transition an account of 25 years of land cover change in Europe*. 2017.
135. Dixon, J., et al., *Farming Systems and Poverty: Improving Farmers' Livelihoods in a Changing World*, ed. M. Hall. 2001.
136. Gale, S., G. Thomson, and F. Zarlenga, *Capter 5 - Underground geological storage*. 2005. p. 195-265.
137. Ritchie, H. and M. Roser. *Land Use*. 2013; Available from: https://ourworldindata.org/land-use.
138. Dupas, R., et al., *The role of mobilisation and delivery processes on contrasting dissolved nitrogen and phosphorus exports in groundwater fed catchments.* Sci Total Environ, 2017. **599-600**: p. 1275-1287.
139. Porder, S. and S. Ramachandran, *The phosphorus concentration of common rocks—a potential driver of ecosystem P status.* Plant and Soil, 2013. **367**(1-2): p. 41-55.
140. Geisseler, D. and G. Miyao, *Soil testing for P and K has value in nutrient management for annual crops.* California Agriculture, 2016. **70**(3): p. 152-159.
141. Sharpley, A., *Managing agricultural phosphorus to minimize water quality impacts.* Scientia agricola., 2016. **73**(1): p. 1-8.
142. Canadian Council of Ministers of the Environment, *Water Quality for the Protection of Agriculture*. 2007.
143. Government of Manitoba. *Nutrient Management Regulation*. 2020 January, 2020]; Available from: https://www.manitoba.ca/sd/pubs/water/lakes-beaches-rivers/limitsandthresholds.pdf.
144. Government of British Columbia, D. Poon, and O. Schmidt, *Phosphorus Considerations for Nutrient Management*. 2010.

145. Government of Saskatchewan, *Surface Water Quality Objectives.* Environmental and Municipal Management Services Division of Saskachewan Water Security Agency,, 2015. **EPB 356**: p. 4.
146. Government of Alberta, *Environmental Quality Guidelines for Alberta Surface Waters*, Water Policy Branch, Alberta Environment and Parks, Editor. 2018: Edmonton, Alberta.
147. Government of Ontario, *Water management: policies, guidelines, provincial water quality objectives*, Environment and energy, Editor. 2016.
148. State of California, *Sustainable Groundwater Management Act 2019 Basin Prioritization*, Department of Water Resources, Editor. 2020.
149. MacLeod, C. and L.E. Méndez-Barrientos, *Groundwater Management in California's Central Valley: A Focus on Disadvantaged Communities.* Case Studies in the Environment, 2019. **3**(1): p. 1-13.
150. Ojha, C., et al., *Sustained Groundwater Loss in California's Central Valley Exacerbated by Intense Drought Periods.* Water resources research, 2018. **54**(7): p. 4449-4460.
151. Famiglietti, J.S., et al., *Satellites measure recent rates of groundwater depletion in California's Central Valley.* Geophysical Research Letters, 2011. **38**(3).
152. California State Water Resources Control Board, *Groundwater Information Sheet: Salinity*, Division of Water Quality, Editor. 2017.
153. Robbins, J. *As Water Scarcity Increases, Desalination Plants Are on the Rise*. 2019 [cited 2021; Available from: https://e360.yale.edu/features/as-water-scarcity-increases-desalination-plants-are-on-the-rise.
154. Calsbad Desalination Plant. *About: What We Do*. 2017 [cited 2021; Available from: https://www.carlsbaddesal.com/what-we-do.html.
155. Condon, L.E., et al., *Where Is the Bottom of a Watershed?* Water Resources Research, 2020. **56**(3): p. e2019WR026010.
156. Kang, M., J.E. Ayars, and R.B. Jackson, *Deep groundwater quality in the southwestern United States.* Environmental Research Letters, 2019. **14**(3): p. 034004.

157. Perrone, D. and S. Jasechko, *Dry groundwater wells in the western United States.* Environmental Research Letters, 2017. **12**(10): p. 104002.
158. Bertoldi, G.L., R.H. Johnston, and K.D. Evenson, *Ground water in the Central Valley, California; a summary report*, in *Professional Paper*. 1991.
159. Scanlon, B.R., et al., *Groundwater depletion and sustainability of irrigation in the US High Plains and Central Valley.* Proceedings of the National Academy of Sciences, 2012. **109**(24): p. 9320.
160. California Department of Water Resources. *Critically Over Drafted Basins*. 2019; Available from: https://water.ca.gov/Programs/Groundwater-Management/Bulletin-118/Critically-Overdrafted-Basins.
161. esri. *Proximity toolset: Buffer*. 2016 [cited 2021; Available from: https://desktop.arcgis.com/en/arcmap/10.3/tools/analysis-toolbox/buffer.htm.
162. esri. *Overlay toolset: Spatial Join*. 2016 [cited 2021; Available from: https://desktop.arcgis.com/en/arcmap/10.3/tools/analysis-toolbox/spatial-join.htm.
163. Ferguson, G., et al., *Competition for shrinking window of low salinity groundwater.* Environmental Research Letters, 2018. **13**(11): p. 114013.
164. Suarez, D.L., *Impact of agricultural practices on groundwater salinity.* Agriculture, Ecosystems & Environment, 1989. **26**(3): p. 215-227.
165. Gerrit, S., et al., *Sustainability of Irrigated Agriculture in the San Joaquin Valley, California.* Proceedings of the National Academy of Sciences of the United States of America, 2005. **102**(43): p. 15352-15356.
166. Gillespie, J., D. Kong, and S.D. Anderson, *Groundwater salinity in the southern San Joaquin Valley.* AAPG Bulletin, 2017. **101**(8): p. 1239-1261.
167. Choy, J., *High Quality Groundwater Data Isn't Always Easy or Cheap, But It Is Necessary*, in *Standford: Water in the West,*. 2016: Online.
168. International Groundwater Resources Assessment Centre, *National Groundwater Monitoring Programmes: A global overview of quantatitive groundwater monitoring networks*. 2020.
169. Phipps, G., *RE: Groundwater Quality Data*, J. Warrack, Editor. 2019.

170. Deri-Takacs, J. and Alberta Environment, *Groundwater Quality Data*, J. Warrack, Editor. 2020.
171. Bakker, K., *Eau Canada : the future of Canada's water*. 2007, Vancouver: UBC Press.
172. Government of British Columbia, *New Requirements for Groundwater Users*, Environmental protection and sustainability, Editor. 2016: Online.
173. Shaw, R., *B.C. government failing to register groundwater users, say critics*, in *Vancouver Sun*. 2020: Online.
174. United States Geological Survey, *Fact Sheet FS-128-02*, National Water Information System Web, Editor. 2002.
175. National ground-Water Monitoring Network. *Interactive map on groundwater monitoring information in the United States*. 2021; Available from: https://www.americangeosciences.org/critical-issues/maps/interactive-map-groundwater-monitoring-information-united-states.
176. National Ground-Water Monitoring Network. 2021.
177. Moran, T., et al., *From the Ground Down: Understanding Local Groundwater Data Collection and Sharing Practices in California*, Standford: Water in the West, Editor. 2016, Standford Law School: Martin Daniel Gould Center for Conflict Resolution.
178. Thyssen, N., W. European Topic Centre on Inland, and A. European Environment, *European freshwater monitoring network design*. Topic report (European Environment Agency) ; no. 10/1996. 1997, Luxembourg: OOPEC.
179. Sun, G.K. and K. Gyoo-Bum *Are Groundwater Monitoring Networks Economical? Cost-Benefit Analysis on the Long-Term Groundwater Supply Project of South Korea*. Water, 2019. **11**, DOI: 10.3390/w11040753.
180. Grabow, G.L., et al., *Groundwater Monitoring Network Design Using Minimum Well Density.* Water Science and Technology, 1993. **28**(3-5): p. 327-335.
181. Azadi, S., et al., *Optimal design of groundwater monitoring networks using gamma test theory.* Hydrogeology Journal, 2020. **28**(4): p. 1389-1402.

182. Kavusi, M., A. Khashei Siuki, and M. Dastourani, *Optimal Design of Groundwater Monitoring Network Using the Combined Election-Kriging Method.* Water Resources Management, 2020. **34**(8): p. 2503-2516.
183. Mirzaie-Nodoushan, F., O. Bozorg-Haddad, and H.A. Loáiciga, *Optimal design of groundwater-level monitoring networks.* Journal of Hydroinformatics, 2017. **19**(6): p. 920-929.
184. Thakur, J.K., *Hydrogeological modeling for improving groundwater monitoring network and strategies.* Applied Water Science, 2017. **7**(6): p. 3223-3240.
185. Chesnaux, R., *Uncontrolled Drilling: Exposing a Global Threat to Groundwater Sustainability.* Journal of Water Resource and Protection, 2012. **04**.
186. Government of New Brunswick, *Guidelines for the Decommissioning (abandonment) of Groundwater Wells and Boreholes*, Department of Environment, Editor. 2021.
187. Foster, S., et al., *Groundwater—a global focus on the 'local resource'.* Current Opinion in Environmental Sustainability, 2013. **5**(6): p. 685-695.
188. Lall, U., L. Josset, and T. Russo, *A Snapshot of the World's Groundwater Challenges.* Annual Review of Environment and Resources, 2020. **45**(1): p. 171-194.
189. Ritchie, H. and M. Roser. *Water Use and Stress*. 2017 [cited 2021; Available from: https://ourworldindata.org/water-use-stress.
190. Rutgers University. *Preventing Water Pollution for Agriculture*. 2013; Available from: https://salem.njaes.rutgers.edu/nre/agriculture/agriculture.html.
191. Agriculture and Rural Delivery Directorate, *Prevention of environmental pollution from agricultural activity : a code of good practice*. 2005, Edinburgh: Scottish Executive.
192. Adams, B., et al., *Groundwater and its susceptibility to degradation : a global assessment of the problem and options for management*. Early Warning and Assessment Report Series. Vol. RS. 03-3. 2003, Nairobi, Kenya: United Nations Environment Programme.

193. Ritchie, H. and M. Roser. *Energy*. 2020 [cited 2021; Available from: https://ourworldindata.org/energy.
194. Canadian Association of Petroleum Producers. *Uses for Oil*. 2020 [cited 2021; Available from: https://www.capp.ca/oil/uses-for-oil/.
195. Jackson, R.B., *The integrity of oil and gas wells.* Proceedings of the National Academy of Sciences, 2014. **111**(30): p. 10902.
196. Davies, R.J., et al., *Oil and gas wells and their integrity: Implications for shale and unconventional resource exploitation.* Marine and Petroleum Geology, 2014. **56**: p. 239-254.
197. National Research Council . Committee on Future Options for Management in the Nation's Subsurface Remediation, E., *Alternatives for managing the nation's complex contaminated groundwater sites*. 2013, National Academies Press: Washington, D.C.
198. Iheagwara, O.S., et al., *Phosphorus, phosphorous, and phosphate.* Hemodial Int, 2013. **17**(4): p. 479-82.
199. Stainton, M., *Errors in Molybdenum Blue Methods for Determining Orthophosphate in Freshwater.* Canadian Journal of Fisheries and Aquatic Sciences, 2011. **37**: p. 472-478.
200. Croghan, W. and P. Egeghy. *Methods of Dealing with Values Below the Limit of Detection using SAS Carry*. 2003.
201. Huisman, N.L.H. and K.G. Karthikeyan, *Using radiometric tools to track sediment and phosphorus movement in an agricultural watershed.* Journal of Hydrology, 2012. **450-451**: p. 219-229.
202. Gilley, J.E., A.J. Sindelar, and B.L. Woodbury, *REMOVAL OF CATTLE MANURE CONSTITUENTS IN RUNOFF FROM NO-TILL CROPLAND AS AFFECTED BY SETBACK DISTANCE.* Transactions of the ASABE, 2016. **59**(6): p. 1681-1693.
203. Whiting, P.J., et al., *Suspended sediment sources and transport distances in the Yellowstone River basin.* Geological Society of America Bulletin, 2005. **117**(3): p. 515.

204. Wetzel, R.G., *13 - THE PHOSPHORUS CYCLE*, in *Limnology (Third Edition)*, R.G. Wetzel, Editor. 2001, Academic Press: San Diego. p. 239-288.
205. Government of Canada and Agriculture and Agri-Food Canada. *Land Use*. 2019; Available from: http://www.agr.gc.ca/atlas/landu.
206. United States Geological Survey. *Land Cover Data*. 2011; Available from: https://www.usgs.gov/core-science-systems/science-analytics-and-synthesis/gap/science/land-cover-data-download?qt-science_center_objects=0#qt-science_center_objects.
207. Government of Canada. *Land Use 2010*. 2010; Available from: https://open.canada.ca/data/en/dataset/9e1efe92-e5a3-4f70-b313-68fb1283eadf.
208. Maxe, L., *Groundwater Monitoring (2020:2431)*, J. Warrack, Editor. 2020.
209. Government of British Columbia Ministry of Environment, *Phosphorus Mangement in Vancouver Island Streams*, Environmental Protection Division and Environmental Sustainability and Strategic Policy Division, Editors. 2014.

Appendix A: Groundwater phosphorus concentrations: global distribution and links with agricultural and oil and gas activities

Treatment of phosphorus (P) data

Phosphorus (P) is naturally reactive meaning that in biological systems, phosphorus is found in the form of phosphates and the two terms (phosphorus and phosphate) are often used interchangeably [198]. All concentration data is converted to mg P/L to compare the different types of concentrations reported in the literature (Table S1). Many countries in the world have recommendations for surface water that are expressed as mg P/L. In Canada, the Canadian Council for Minsters of the Environment (CCME) [30] voluntary recommendations consider surface waters that have TP concentrations greater than 0.1 mg P/L "hyper eutrophic", which is the most severe classification of nutrient pollution. The CCME recommendations are consistent with lake quality models that have found TP concentrations ranging from 0.035 and 0.1 mg P/L to cause eutrophication in surface waters [83]. The United States Environmental Protection Agency (EPA) approves TP limits set by individual states; these limits are region specific and based on the type of water body. Because they are site specific, TP limits in the United States for freshwater lakes range from 0.005 mg P/L in California to 1 mg P/L in Arizona [85]. The voluntary recommendations by the CCME are chosen for this paper because they cover lakes and rivers and fall within the range of TP limits in other jurisdictions.

Analysis methods for peer-reviewed papers and studies were included in the materials and methods sections of the publications. To determine analysis methods for government agencies, we contacted individuals responsible for the monitoring of phosphorus in groundwater at the respective agency. The raw data consist of 12 different concentration types: total phosphorus, phosphorus as inorganic phosphate, phosphorus as P, dissolved phosphorus, total dissolved phosphorus, total filtered phosphorus, particulate phosphorus, total recoverable P, orthophosphate as P, orthophosphate, dissolved orthophosphate as P and inorganic phosphorus. Table S1 presents the total number of samples collected in each country by original sampling type. To facilitate comparisons, we combine P concentration data based on the analysis method of the groundwater sample (Table S4). This simplification results in 5 sample analysis methods: (1) total phosphorus using molybdate blue and ultraviolet-visible absorption spectroscopy (20%, TP ICP-OES), (2) total phosphorus as determined by inductively coupled argon plasma emission spectroscopy (<1%, TP ICP-MS), (3) dissolved orthophosphate as P (78%, DP), (4) total dissolved P (2%, TDP), and (5) particulate P (<1%) [115] (Table S4).

The 5 different final methods chosen for this paper are based on the analysis method used on the sample:

1. Total phosphorus (TP ICP-OES): acid digestion of sample using sulphuric acid, calculation of P concentration using molybdate blue reaction (Many samples (20%) are analyzed using ICP-OES, while a small portion (<1%) are analyzed using ICP-MS. All of the samples analyzed using ICP-MS were taken in Alberta from the Alberta Groundwater Observation Well Network and range in date from June 10, 2010 to February 12, 2014. All of the samples measured with ICP-MS were also analyzed using ICP-OES.)
2. Total phosphorus as determined by inductively coupled argon plasma emission spectrometry (TP ICP-MS): acid digestion of sample using sulphuric acid, calculation of P concentration using inductively coupled argon plasma emission spectrometry
3. Dissolved orthophosphate (DP): no digestion, calculation of concentration using molybdate blue reaction
4. Total dissolved phosphorus (TDP): sample is filtered through 0.45 um membrane, acid digestion of sample using sulphuric acid, calculation of P concentration using molybdate blue reaction
5. Particulate phosphorus: calculated value of TP minus DP

To estimate the extent of P pollution in groundwater worldwide, we characterize P concentration data as greater or less than 0.1 mg P/L. Total P concentrations are theoretically largest in any water sample as this value consists of all P in the sample, including organic and inorganic P compounds. This means that using TP ranges for other concentration types may underestimate P pollution. For example, orthophosphate as P concentrations are expected to be lower than TP values. However, measurement methods for the calculation of DP tend to overestimate P concentrations in the sample [199]. Although there is some uncertainty, we look at all data types globally, and we remove sites where any concentration type, except TP measured by ICP-MS, is larger than TP ICP-OES as this is physically impossible.

Canada, Ireland, and Mexico all report P concentrations below the detection limit. Because we treat values below the detection limit as zeros, this may impact the results of the data analysis. A small percentage of samples in Canada (11%) and Mexico (2%) have concentrations below the corresponding detection limit. Studies find that for data with a small percentage (<10%) of values below the detection limit, there is little bias introduced by replacing values with zeros [200]. For Ireland, where the majority (58%) of samples are below the detection limit, the mean and the median P concentrations are biased low for all methods. However, the analysis conducted in Ireland consists mainly of sorting data by greater and less than 0.1 mg P/L. Because the detection limit in Ireland is 0.007 mg P/L, our findings should remain the same with regards to the percentage of samples that pose a eutrophication risk.

Geospatial analysis

We determine well density for oil and gas wells and P sampling locations using the Point Density tool in ArcMap. Based on the 30 m spatial resolution of the Canadian land use and United States land cover data and the abundance of oil and gas well location data, we choose a rectangular search area of 100 km^2 for the Neighborhood setting with a length and width of 10 km. Due to the data sparsity of P monitoring sites, we use a search area of 900 km^2 for the Neighborhood in the calculation of TP monitoring site density with a length and width of 30 km. We also use the ArcMap tool, Near, to calculate the closest distance between TP monitoring sites and oil and gas wells and the Buffer tool to calculate the land use types within specified radii. Because the main transport mechanism for phosphorus is sediment transport of adsorbed P [201, 202], P transport can vary from a few km via runoff to hundreds of km if the high P sediment reaches a river. We choose radii of 0.5, 1, 10 and 50 km based on our analysis of DO concentrations and enhanced P concentrations with respect to crop/pastureland distance (Table S8) and findings from other studies [202, 203].

We use all types of P concentrations for our analysis because total phosphorus (TP) measurements are an important measure of lake health [204], but other P concentration types such as TDP and orthophosphate determine the amount of biologically available P. Therefore, other P concentration types besides TP are important indicators of eutrophication potential. Because P recommendations for surface waters in Canada and the United States are stated in terms of TP, we use only the TP concentrations for the oil and gas analysis in Alberta and Ontario. Additionally, all sites in Ontario test for TP, and a majority of sites in Alberta (54%) test for TP. Moreover, the environmental limits in both provinces are stated using TP concentrations. In British Columbia, all P concentrations collected are in terms of TDP. Therefore, we compare TDP concentrations to TP ranges, which is a conservative approach given dissolved P concentrations only represent a fraction of TP concentrations.

For Canada, we use the land use open source geographic information data set collected from the Government of Canada website [205]. For the United States, we use the United States Geological Survey (USGS) land cover data [206]. There are some land use classifications excluded from our land use data, primarily a differentiation between forest types and a direct classification for animal feedlots, golf courses, and residential yards, which are sources of non-point P pollution. The managed grassland category for Canadian land use includes “natural shrubs for cattle grazing” [207] and the USGS land cover data includes a classification for “Agricultural and Developed Vegetation” that has been reclassified to cropland [206]. Different forest types may also affect P concentrations in groundwater although this data is not available in the Canadian land use data and is beyond the scope of this paper, which focuses on anthropogenic impacts.

We translate the land cover data to land use data to develop one unified set of land use types for data from the two countries. We convert land cover and land use data using a key-word search criterion based on the chosen land use (Table S5). The chosen land use categories are: unclassified, other, settlements, roads, water, forest, wetland, cropland, grassland (managed), and grassland (unmanaged). Settlements are described as “built up and urban areas” [207], managed grassland is classified as “natural grass and shrubs used for cattle grazing” [207], while unmanaged grasslands are areas with no anthropogenic use. The “other” category encompasses rocks, beaches, ice and other barren land. There is uncertainty in the conversion of land cover to land use because some Canadian land use categories, such as forests, are not named similarly in the USGS land cover data while other Canadian categories, such as roads, are not available in the USGS land cover data.

We obtain data for the location of the oil and gas wells from the British Columbia Oil and Gas Commission Open Data Portal Well Surface Hole Locations (accessed July 2021), the Alberta Energy Regulator ST37 List of Wells in Alberta Shapefile (accessed October 2019) and the Oil, Gas and Salt Resources Library of Ontario (accessed July 2020). All oil and gas wells, including those that are active, abandoned, and orphaned, are considered, assuming all wells can act as a pathway through which P could reach groundwater aquifers.

We consider the top percentiles of P measurements within a specified radius from oil and gas wells (Table S6). For example, in British Columbia, the top 30^{th} percentile is 93 P measurements (30%), the top 20^{th} percentile is 59 P measurements (19%), and the 10^{th} percentile is 25 P measurements (8%). To ensure we have a sufficiently large dataset within all radii considered for our statistical analysis, we use the top 30^{th} percentile of P measurements.

Conversion between phosphorus concentration types

We find that 0.8% (1,257) of sites we analyze are tested for more than one type of P concentration. We analyze the ratios for TP (ICP-MS):TP (ICP-OES) at 146 sites and for DP:TP (ICP-OES) at 929 sites. Particulate P:TP (ICP-OES) is collected at six sites in total and has the smallest range with two orders of magnitude difference between the highest and lowest ratios. The largest ratio recorded from the data is TP (ICP-MS):TP (ICP-OES) with a value of 27.8 and the lowest ratio is DP:TP (ICP-OES) with a value of 4.0×10^{-6} (Table S7 and Table S8). Because these ratios are highly variable, it is difficult to create a universal conversion factor between different types of P concentration data.

Representativeness of land use surrounding P monitoring sites in Canada and the United States

We find significant relationships between land use and P concentrations, especially when we compare the data to P measurements throughout the province. Within a 1 km radius of P monitoring sites in Canada, the proportion of areas designated as crop/pastureland are over-represented by more than +15% when compared to overall provincial land use in all provinces with available data (Alberta, Manitoba, Ontario, and Quebec), except British Columbia (over-represented by +8%). Settlements within a 1 km radius of P monitoring sites are also over-represented when compared to overall provincial land use in British Columbia (+23%), Ontario (+14%), and Quebec (+8%). In all provinces, natural land use types, such as forests are under-represented when compared to overall provincial land use: British Columbia (-32%), Alberta (-30%), Manitoba (-14%), Ontario (-18%), and Quebec (-10%) (Table S10). In the United States, the only land use type that is substantially under-represented is unmanaged grasslands with a 19% difference from overall land use composition. Forests and settlements in the United States are slightly over-represented when compared to overall land use with a difference of 11% and 5%, respectively (Table S11). The discrepancy in the land use within a 1 km radius of P monitoring sites and overall national land use is larger in Canada than the United States.

The distribution of sample locations by land use is not proportional to nation-wide land use distributions as some countries, including Canada, select sites for P monitoring in groundwater based on accessibility and existing monitoring site networks [170]. Other countries, like Sweden [208], utilize land use as a criterion for selection of groundwater monitoring sites. Therefore, in Canada, the under-representation of natural land use types such as forested areas and wetlands may be a result of inaccessible terrain or lack of existing groundwater sampling infrastructure and need. Sampling campaigns in these regions could prove beneficial to characterize P concentrations in groundwater in areas that are generally undisturbed by anthropogenic activities.

Analysis of oil and gas well proximity impact on phosphorus concentrations in British Columbia

British Columbia is selected to provide context for the analysis in Ontario and Alberta. Previous studies have found that population growth and urban development are the main drivers of P pollution in the southern portion of British Columbia, where elevated P concentrations are found and there is no oil and gas development (Figure 2 and Figure S4) [209].

In British Columbia, there are 34,890 oil and gas wells, the majority (99%) of which are in the northeastern region of the province (Figure S4). Because the elevated P concentrations are found in the southern portion of the province and oil and gas wells are found in the northeastern portion of the province, we expect no to very weak relationships between oil and gas wells and elevated P concentrations. We conduct an analysis using all oil and gas wells and all TDP concentrations across the entire province. (We conduct the analysis with TDP concentrations as all concentrations in the province are reported in terms of TDP.) The maximum TDP concentration in British Columbia is 5.76 mg P/L and the monitoring site is located 11.4 km from the nearest oil and gas well in the southwest of the province near Abbotsford, a prominent agricultural area. This finding may be an indication that the oil and gas well is exacerbating groundwater P contamination in the area but additional data collection and analysis is needed to obtain a statistically significant relationship. At 171.9 km, the farthest distance from an oil and gas well, the TDP concentration is 0.1 mg P/L, above the CCME recommendation for surface waters. We find that 9% (28) TDP monitoring sites are within 1 km of any oil and gas well, 9% (28) TDP monitoring sites are within 5 km of any oil and gas well, and 47% (147) TDP monitoring sites are within 1 km of crop/pastureland. Of the 28 sites found within 1 km of any oil and gas well, 20 (71%) are found within 1 km of crop/pastureland. Therefore, we find a strong link between crop/pastureland and elevated P concentrations.

We conduct a Chi^2 analysis of the top 30^{th} percentile of TDP concentrations in British Columbia, but we do not find a statistical difference in the populations of TDP samples using the median distance of 26 km (Table S15). This finding is consistent with our hypothesis that based on the available P monitoring site and oil and gas well distributions, we are unable to find statistically significant link leaking oil and gas wells to elevated TDP concentrations in British Columbia. In contrast, in Alberta and Ontario where crop/pastureland are co-located with oil and gas wells, we are able to find statistically significant relationships using the Chi^2 method. Overall, our finding suggest that oil and gas wells may be acting as a pathway for anthropogenic P to reach groundwater.

Table S1. Sources of data collected and number of data points available by P concentration type

Source	Type	TP (mg/L)	Phosphorus as Phosphate (mg/L)	Phosphorus as P (mg/L)	DP (mg/L)	DP (ug/L)	TDP (mg/L)	Total Filtered P (mg/L)	Particulate P (mg/L)	Total Recoverable P (ug/L)	Orthophosphate as P (mg/L)	Orthophosphate (mg/L)	Dissolved Orthophosphate as P (mg/L)	Inorganic P (mg/L)	Total
Brazil															
Geological Survey of Brazil	G	5202													5202
Canada															
Alberta Groundwater Observation Well Network	G	475			41	275	6		6	146					949
Alberta Agriculture and Forestry (Battersea area data)	IS	154					154				185				493
Alberta Agriculture and Forestry (BMP project)	IS	264					264				264				792
Alberta Agriculture and Forestry (feedlot groundwater study)	IS										825				825
Alberta Agriculture and Forestry (small-plot manure study)	IS	70									240				310
British Columbia Provincial Groundwater Observation Well Network	G	3243													3243
Manitoba Groundwater Management	G				892										892
Provincial Groundwater Monitoring Network (Ontario)	G	3807	3730												7537
Quebec Environment	G	312		19										1135	1466
China															
Spatial distribution and sources of groundwater phosphorus in Dezhou Region	IS	27					27				27		27		108
Ireland															

Environmental Protection Agency (Ireland)	G	8505													8505
Mexico															
The effects of wastewater irrigation on groundwater quality in Mexico	IS	12										13			25
A survey of groundwater quality in Tulum region, Yucatan Peninsula, Mexico	IS	39													39
New Zealand															
National Groundwater Monitoring Programme (NGMP)	G	4		2									2990		
Northern Ireland															
Department of Agriculture, Environment and Rural Affairs	G	834		75							1159				2068
South Africa															
National Groundwater Quality Monitoring Project (NGwQMP)	G										104194				104194
Sweden															
Geological Survey of Sweden	G	6059		74				18			564	7920			14635
United States															
Water Quality Data USA	G	811			408						259				1478
Characterization of Groundwater Phosphorus Input to Torch Lake	IS	43													43
National groundwater monitoring network (NGWMN)	G	467									61	29			557
Germany															
Umweltbundesamt	G										4504				4504
Wales															
Natural Resources Wales	G				118										
TOTAL		30328	3730	288	1341	275	451	18	6	146	112282	7962	3017	1135	157983

Table S2: Available depth and date ranges and phosphorus detection limits by data source.

Source	Type	Depths Available?	Depth Range (m)	Detection Limits Available?	Detection Limits (mg/L)	Date Range
Brazil						
Geological Survey of Brazil	G	No	N/A	No	N/A	1962-2019
Canada						
Alberta Groundwater Observation Well Network	G	Yes	3-189	No	N/A	2006-2013
Alberta Agriculture and Forestry (Battersea area data)	IS	Yes	1-35	No	N/A	1998-2001
Alberta Agriculture and Forestry (BMP project)	IS	Yes	0.03-4	Yes	0.005	2009-2012
Alberta Agriculture and Forestry (feedlot groundwater study)	IS	No	N/A	No	N/A	1996-2000
Alberta Agriculture and Forestry (small-plot manure study)	IS	No	N/A	No	N/A	1998-1999
British Columbia Provincial Groundwater Observation Well Network	G	No	N/A	Yes	0.001	1985-2019
Manitoba Groundwater Management	G	Yes	5-190	No	N/A	N/A
Provincial Groundwater Monitoring Network (Ontario)	G	No	N/A	Yes	0.0005-0.5	2002-2016
Quebec Environment	G	No	N/A	Yes	0.03	1978-2014
China						
Spatial distribution and sources of groundwater phosphorus in Dezhou Region	IS	Yes	2-40	No	N/A	N/A
Ireland						
Environmental Protection Agency (Ireland)	G	No	N/A	Yes	0.007	2010-2018
Mexico						
The effects of wastewater irrigation on groundwater quality in Mexico	IS	Yes	7-37	Yes	0.005-0.01	1995
A survey of groundwater quality in Tulum region, Yucatan Peninsula, Mexico	IS	No	N/A	No	N/A	2017
New Zealand						
National Groundwater Monitoring Programme (NGMP)	G	No	N/A	No	N/A	N/A
Northern Ireland						
Department of Agriculture, Environment and Rural Affairs	G	No	N/A	Yes	0.015	2015-2018
South Africa						
National Groundwater Quality Monitoring Project (NGwQMP)	G	No	N/A	Yes	0.001-0.2	1971-2018
Sweden						
Geological Survey of Sweden	G	No	N/A	No	N/A	1995-2019

United States						
Water Quality Data USA	G	No	N/A	Yes	0.004-0.01	1930-2015
Characterization of Groundwater Phosphorus Input to Torch Lake	IS	Yes	1.5-3	No	N/A	2005
National groundwater monitoring network (NGWMN)	G	No	N/A	Yes	0.005-0.01	1975-2018
Germany						
Umweltbundesamt	G	No	N/A	Yes	0.005-0.01	1989-2017
Wales						
Natural Resources Wales	G	No	N/A	Yes	0.001-0.02	2002-2019

G = government database

IS = individual study

Table S3: Countries with data below the detection limits. Samples that report concentrations less than detection limits are assumed to have a concentration of 0 mg/L.

Country	Below-Detection Samples?	Number of Below-Detection Samples	% of Samples that are below detection
Brazil	No	0	0
Canada	Yes	1,796	11
China	No	0	0
Ireland	Yes	4,925	58
Mexico	Yes	1	2
New Zealand	No	0	0
Northern Ireland	No	0	0
South Africa	No	0	0
Sweden	No	0	0
United States	No	0	0
Germany	No	0	0
Wales	No	0	0
Total		6,722	

Table S4. Number of measurements by phosphorus concentration types based on analysis method of sample and the statistics for each country and each sample type by country. Rows highlighted in grey show country totals and rows highlighted in grey show provincial totals for Canada. Monitoring sites where any concentration type (other than TP ICP-MS) is greater than TP are removed as this is physically impossible.

Sample Location		TP ICP-OES (mg p/L)	TP ICP-MS (mg p/L)	DP (mg p/L)	TDP (mg p/L)	Particulate Phosphorus (mg p/L)	TOTAL	Mean	Median	Max	Min
Brazil		5202	0	0	0	0	5,202	0.642	0.18	156	0.00
Canada		9460	146	6804	159	6	18,047	0.220	0.02	250	0.00
Alberta		963	146	2163	159	6	4,011	0.090	0.031	7.165	0.00
Mean		0.204	0.118	0.077	0.058	0.071					
Median		0.07	0.04	0.02	0.02	0.01					
Max		3.922	0.905	7.165	0.542	0.282					
Min		0	0.0000036	0	0	0.001					
British Columbia			0	0	3243	0	3,243	0.073	0.02	5.76	0.00
Mean					0.073						
Median					0.02						
Max					5.76						
Min					0						
Manitoba		0	0	892	0	0	1,784	0.017	0.071	1.67	0.00
Mean											
Median											
Max											
Min											
Ontario		3807	0	3730	0	0	7,537	0.370	0.013	250	0.00
Mean		0.715		0.018							
Median		0.02		0.01							
Max		250		6.18							
Min		0		0							

Quebec		1447	0	19	0	0	1,466	0.094	0.05	11.9	0.00
Mean		0.094		0.055							
Median		0.05		0.15							
Max		11.9		0.34							
Min		0		0							
China		27	0	27	27	0	108	0.130	0.155	1.49	0.04
Mean		0.312		0.014	0.196						
Median		0.24		0.04	0.13						
Max		1.49		0.11	0.69						
Min		0		0	0.04						
Germany		0	0	4504	0	0	4,504	0.375	0.03	5.8	0.01
Mean				0.375							
Median				0.03							
Max				5.8							
Min				0.005							
Ireland		8505	0	0	0	0	8,505	0.020	0.019	4.6	0.00
Mean		0.020									
Median		0.02									
Max		4.6									
Min		0									
Mexico		51	0	12	0		63	0.237	0.08	4.273	0.00
Mean		0.272		0.370							
Median		0.08		0.04							
Max		4.273		3.082							
Min		0		0							
New Zealand		4	0	2	2990		2,996	0.061	0.03	8.9	0.00
Mean		0.018		0.003	0.061						
Median		0.02		0.00	0.03						
Max		0.023		0.005	8.9						
Min		0.014		0.001	0						
Northern Ireland		834	0	1234	0		2,068	0.175	0.05	32	0.00

Mean		0.260		0.118							
Median		0.02		0.05							
Max		32		19.5							
Min		0		0.002							
South Africa		0	0	104194	0		104,194	0.063	0.014	372.781	0.00
Mean				0.063							
Median				0.01							
Max				372.781							
Min				0							
Sweden		6059	0	8558	18		14,635	0.208	0.015	793	0.00
Mean		0.126		0.265	0.562						
Median		0.01		0.02	0.01						
Max		25.4		793	5						
Min		0		0	0.0015						
United States		1321	0	1059	0		2,788	0.658	0.02	72.1	0.00
Mean		1.092		0.055							
Median		0.04		0.00							
Max		72.1		13.8							
Min		0		0							
Wales		0	0	118	0		118	0.249	0.0798	3.82	0.01
		28,220	**146**	**126,512**	**6,437**	**6**	**161,321**	**0.126**	**0.014**	**793**	**0**

Table S5. Key word search criteria for conversion of USGS land cover to chosen land use categories

Key words	Land Use Category
Swamp*, riparian, bog, marsh, floodplain	Wetland
Forest, recently logged, recently burned, recently chained	Trees
Shrubland, badland, grassland	Grassland (unmanaged)
Developed, urban	Settlements
Vineyards, crop	Cropland
Open water	Water
Barren, geysers, dune, tundra, beach, rock, cliff	Other

Table S6. Specified radius of selection for P concentration percentiles from oil and gas wells.

Radius	Total Number of P concentrations	Top 10th percen-tile	Top 20th percen-tile	Top 30th percen-tile
British Columbia				
0-5 km	28	2	5	8
5-10 km	57	5	12	18
10-15 km	32	1	6	10
15-20 km	16	1	3	5
20-30 km	37	3	7	11
30-40 km	8	0	1	2
40-50 km	16	1	3	5
50-75 km	41	3	7	11
75-100 km	60	8	12	18
>100 km	15	1	3	5
Total	310	25	59	93
Alberta				
0-0.1 km	33	3	6	10
0.1-0.2 km	30	3	7	9
0.2-0.3 km	36	3	7	11
0.3-0.4 km	56	5	10	18
0.4-0.5 km	51	5	10	15
0.5-0.6 km	16	1	3	5
0.6-0.7 km	22	2	4	5
0.7-0.8 km	10	1	2	3
0.8-0.9 km	15	1	3	4
0.9-1 km	11	1	2	3
> 1 km	26	2	5	8
Total	306	27	59	91
Ontario				
0-1 km	47	10	10	14
1-2 km	46	5	10	14
2-3 km	50	5	10	15
3-4 km	29	3	6	9
4-5 km	24	2	5	7
5-6 km	27	2	7	9
6-7 km	15	1	3	4
7-8 km	13	1	2	4
8-9 km	11	1	2	3
9-10 km	21	2	4	6
10-15 km	44	4	9	13
15-50 km	52	5	12	17
> 50 km	25	2	5	7
Total	404	43	85	122

Table S7: Ratio of phosphorus testing methods to TP (ICP-OES)

Ratio	Number of Sites	Max	Min	Std Deviation	Std Error	Average
TP(ICP-MS):TP (ICP-OES)	146	27.8	0.0003	3.147	0.260	1.26
DP:TP (ICP-OES)	929	1.0	0.000004	0.260	0.009	0.18
TDP:TP (ICP-OES)	176	1.0	0.0067	0.317	0.024	0.52
Particulate P:TP (ICP-OES)	6	0.7	0.0058	0.343	0.140	0.29

Table S8: Distribution of the ratio values for different phosphorus testing methods Ratios of DP/TP (ICP-OES), TDP/TP (ICP-OES) and Particulate/TP (ICP-OES) that are greater than 1 are removed from the calculations as this is physically impossible.

	Count			Count		
Ratio Value	**TP(ICP-MS)/TP (ICP-OES)**		**Ratio Value**	**DP/TP (ICP-OES)**	**TDP/TP (ICP-OES)**	**Particulate/TP (ICP-OES)**
0-0.25	26		0.05	482	20	1
0.25-0.50	16		0.1	75	8	2
0.50-0.75	25		0.5	247	58	1
0.75-1	44		1	125	90	2
1-2.5	28					
2.5-5	2					
5-10	1					
10-20	3					
>20	1					

Table S9: Spearman's rank correlation between dissolved oxygen (DO) and phosphorus (P) concentrations based on proximity to crop/pastureland.

	Correlation (all)	Count	%	Correlation (P conc <0.1)	Count	%	Correlation (P conc >0.1)	Count	%
All	-0.61	1529		-0.54	1159		-0.16	370	
Crop in 50 km	-0.61	1514	99	-0.54	1147	99	-0.14	367	99
Crop in 10 km	-0.63	1473	96	-0.55	1122	97	-0.17	351	95
Crop in 1 km	-0.63	1440	94	-0.55	1094	94	-0.17	346	94
Crop in 500 m	-0.61	1300	85	-0.53	975	84	-0.12	325	88
Crop in 50 m	-0.61	984	64	-0.46	669	58	-0.11	315	85

Table S10: Land use comparison in Canadian provinces based on land use surrounding TP monitoring sites where orange is minimally (-5-15%) underrepresented, red is significantly under-represented (>-15%), light blue is minimally (5-15%) over-represented, and dark blue is significantly (>15%) over-represented.

		50 km		10 km		1 km		0.5 km	
Land Use		**%**	**Difference**	**%**	**Difference**	**%**	**Difference**	**%**	**Difference**
British Columbia									
Unclassified	0%	0%	0%	0%	0%	0%	0%	0%	0%
Wetlands	5%	1%	-4%	1%	-4%	1%	-4%	1%	-4%
Water	3%	3%	0%	5%	2%	5%	2%	5%	1%
Grassland (managed)	0%	1%	0%	2%	2%	1%	1%	1%	0%
Cropland	1%	3%	2%	8%	8%	15%	14%	14%	13%
Grassland (unmanaged)	1%	0%	-1%	0%	-1%	0%	-1%	0%	-1%
Forest	77%	85%	8%	73%	-4%	45%	-32%	43%	-34%
Roads	0%	1%	0%	3%	3%	8%	8%	9%	9%
Settlements	0%	1%	1%	7%	7%	23%	23%	26%	26%
Other	12%	4%	-7%	1%	-11%	1%	-11%	1%	-11%
Alberta									
Unclassified	0%	0%	0%	0%	0%	0%	0%	0%	0%
Wetlands	18%	6%	-13%	3%	-15%	3%	-15%	2%	-16%
Water	5%	4%	-1%	5%	1%	5%	0%	4%	-1%
Grassland (managed)	7%	16%	9%	16%	9%	15%	8%	14%	7%
Cropland	21%	44%	23%	55%	34%	55%	34%	55%	34%
Grassland (unmanaged)	0%	0%	0%	0%	0%	0%	0%	0%	0%
Forest	45%	26%	-19%	16%	-29%	16%	-30%	16%	-30%
Roads	1%	2%	1%	2%	1%	3%	3%	5%	4%
Settlements	1%	1%	0%	1%	1%	3%	2%	4%	3%
Other	2%	1%	-1%	0%	-2%	0%	-2%	0%	-2%
Manitoba									
Unclassified	0%	0%	0%	0%	0%	0%	0%	0%	0%
Wetlands	34%	14%	-19%	8%	-26%	4%	-30%	3%	-31%
Water	19%	11%	-8%	4%	-15%	2%	-17%	2%	-17%
Grassland (managed)	0%	2%	1%	3%	3%	5%	5%	5%	5%
Cropland	9%	45%	35%	60%	51%	59%	49%	58%	49%
Grassland (unmanaged)	0%	0%	0%	0%	0%	0%	0%	0%	0%
Forest	36%	26%	-10%	21%	-15%	22%	-14%	20%	-16%
Roads	0%	2%	1%	3%	2%	4%	4%	6%	6%
Settlements	0%	1%	1%	2%	1%	5%	4%	5%	5%
Other	1%	0%	-1%	0%	-1%	0%	-1%	0%	-1%
Ontario									
Unclassified	0%	0%	0%	0%	0%	0%	0%	0%	0%

Wetlands	24%	4%	-20%	4%	-20%	4%	-21%	4%	-21%
Water	19%	26%	7%	9%	-10%	5%	-14%	5%	-14%
Grassland (managed)	0%	0%	0%	0%	0%	0%	0%	0%	0%
Cropland	5%	21%	16%	46%	42%	39%	35%	35%	31%
Grassland (unmanaged)	1%	0%	0%	0%	0%	0%	0%	0%	0%
Forest	50%	44%	-6%	29%	-21%	32%	-18%	31%	-18%
Roads	0%	2%	1%	4%	3%	5%	5%	7%	6%
Settlements	1%	4%	3%	8%	7%	15%	14%	18%	17%
Other	0%	0%	0%	0%	0%	0%	0%	0%	0%
Quebec									
Unclassified	0%	0%	0%	0%	0%	0%	0%	0%	0%
Wetlands	6%	3%	-3%	4%	-3%	2%	-4%	2%	-5%
Water	15%	7%	-8%	6%	-9%	6%	-9%	6%	-9%
Grassland (managed)	0%	0%	0%	0%	0%	0%	0%	0%	0%
Cropland	2%	11%	9%	17%	15%	25%	23%	26%	25%
Grassland (unmanaged)	1%	0%	-1%	0%	-1%	0%	-1%	0%	-1%
Forest	64%	75%	11%	68%	4%	54%	-10%	48%	-16%
Roads	0%	1%	1%	2%	2%	4%	4%	6%	6%
Settlements	0%	3%	2%	3%	3%	8%	8%	12%	11%
Other	11%	0%	-11%	0%	-11%	0%	-11%	0%	-11%

Table S11: Land use comparison in United States based on land use surrounding TP monitoring sites where orange is minimally (-5-15%) underrepresented, red is significantly under-represented (>-15%), light blue is minimally (5-15%) over-represented, and dark blue is significantly (>15%) over-represented.

	USA	50 km		10 km		1 km		0.5 km	
Land Use	**%**	**%**	**Difference**	**%**	**Difference**	**%**	**Difference**	**%**	**Difference**
Unclassified	0%	0%	0%	0%	0%	0%	0%	0%	0%
Wetlands	6%	3%	-3%	3%	-3%	3%	-3%	3%	-3%
Water	6%	4%	-2%	3%	-2%	6%	1%	7%	1%
Grassland (managed)	0%	0%	0%	0%	0%	0%	0%	0%	0%
Cropland	24%	30%	6%	30%	5%	27%	3%	25%	1%
Grassland (unmanaged)	29%	17%	-12%	12%	-16%	10%	-19%	11%	-18%
Forest	29%	37%	8%	37%	9%	39%	11%	39%	10%
Roads	0%	0%	0%	0%	0%	0%	0%	0%	0%
Settlements	6%	8%	2%	11%	5%	10%	5%	11%	6%
Other	1%	2%	0%	3%	2%	4%	3%	4%	3%

Table S12: Comparison of the percentage of P concentrations >0.1 mg P/L located directly on each land use type. Land use highlighted in red represents a >15% difference from the total percentage of all P concentrations >0.1 mg/L and land use highlighted in orange represents a 5-14% difference from the total percentage of all P concentrations >0.1 mg/L.

Land Use Category	Total Count	%	P Concentration (mg/L)	Count	%
Wetlands	716	3%	<0.1	606	85%
			>0.1	110	15%
Water	328	1%	<0.1	291	89%
			>0.1	37	11%
Grassland (managed)	296	1%	<0.1	197	67%
			>0.1	99	33%
Cropland	6,861	28%	<0.1	5,893	86%
			>0.1	968	14%
Grassland (unmanaged)	627	3%	<0.1	568	91%
			>0.1	59	9%
Forest	6,390	26%	<0.1	5,707	89%
			>0.1	683	11%
Roads	3,682	15%	<0.1	3,277	89%
			>0.1	405	11%
Settlements	4,920	20%	<0.1	4,450	90%
			>0.1	470	10%
Other	326	1%	<0.1	258	79%
			>0.1	68	21%
Total	24,146	100%	<0.1	21,247	88%
			>0.1	2,899	12%

Table S13: Chi^2 analysis for top 30^{th} percentile of TP concentrations reported at monitoring sites in Alberta using various distances and α values. Null hypothesis (H_0): there is no difference between the two populations.

Distance	<0.1 mg P/L	> 0.1 mg P/L	% > than 0.1 mg P/L	Total	Median (mg P/L)
<0.30 km	1	29	97	30	0.21
>0.30 km	14	47	61	61	0.19
P value = 0.07		α= 0.05 → Accept H_o		α= 0.1 → Reject H_o	
<0.50 km	14	49	78	63	0.19
>0.50 km	1	27	96	28	0.28
P value = 0.03		α = 0.05 → Reject H_o		α = 0.1 → Reject H_o	
<0.75 km	14	59	81	73	0.18
>0.75 km	1	17	94	18	0.29
P value = 0.16		α = 0.05 → Accept H_o		α = 0.1 → Accept H_o	
<1.0 km	15	68	82	83	0.21
>1.0 km	0	8	100	8	0.18
P value = 0.19		α = 0.05 → Accept H_o		α = 0.1 → Accept H_o	
<2.0 km	15	72	83	87	0.21
>2.0 km	0	4	100	4	0.18
P value = 0.37		α = 0.05 → Accept H_o		α = 0.1 → Accept H_o	

Table S14: Chi^2 analysis for top 30^{th} percentile of TP concentrations reported at monitoring sites in Ontario using various distances and α values. Null hypothesis (H_0): there is no difference between the two populations.

Distance	<0.1 mg P/L	> 0.1 mg P/L	% > than 0.1 mg P/L	Total	Median (mg P/L)
<0.30 km	3	1	25	4	0.03
>0.30 km	65	58	47	123	0.08
P value = 0.15		α= 0.05 → Accept H_o		α= 0.1 → Accept H_o	
<0.5 km	4	1	20	5	0.03
>0.5 km	64	58	48	122	0.08
P value = 0.34		α= 0.05 → Accept H_o		α= 0.1 → Accept H_o	
<1.0 km	11	3	21	14	0.03
>1.0 km	57	56	50	113	0.10
P value = 0.01		α= 0.05 → Reject H_o		α= 0.1 → Reject H_o	
<2.0 km	20	8	29	28	0.04
>2.0 km	48	51	52	99	0.10
P value = 0.06		α = 0.05 → Accept H_o		α = 0.1 → Reject H_o	
<15 km	52	51	50	103	0.10
>15 km	16	8	33	24	0.05
P value = 0.1		α = 0.05 → Accept H_o		α = 0.1 → Reject H_o	

Table S15: Chi^2 analysis for top 30^{th} percentile of TP concentrations reported at monitoring sites in British Columbia using various distances and α values. Null hypothesis (H_0): there is no difference between the two populations.

Distance	<0.1 mg P/L	> 0.1 mg P/L	% > than 0.1 mg P/L	Total	Median (mg P/L)
<0.30 km	3	5	8	8	0.1
>0.30 km	27	58	92	85	0.11
P value = 0.87		α= 0.05 → Accept H_o		α= 0.1 → Accept H_o	
<10 km	12	14	22	26	0.1
>10 km	18	49	78	67	0.14
P value = 0.08		α= 0.05 → Accept H_o		α= 0.1 → Reject H_o	
<20 km	14	27	66	41	0.1
>20 km	16	36	69	52	0.14
P value = 0.57		α = 0.05 → Accept H_o		α = 0.1 → Accept H_o	
<26 km	16	33	67	49	0.1
>26 km	14	30	68	44	0.11
P value = 0.48		α = 0.05 → Accept H_o		α = 0.1 → Accept H_o	
<50 km	22	37	63	59	0.1
>50 km	8	26	76	34	0.16
P value = 0.35		α = 0.05 → Accept H_o		α = 0.1 → Accept H_o	

Table S16. References used for data.

References
Olson, B. and Alberta Ministry of Agriculture and Forestry (2000). Feedlot Groundwater Quality Project.
B.M. Olson, et al. (2010). "Nitrate Leaching in Two Irrigated Soils with Different Rates of Cattle Manure." Journal of Environmental Quality 38: 2218-2228.
S.J. Rodvang, et al. (2002). Groundwater quality in the eastern portion of the Lethbridge Northern Irrigation District: 1995 to 2001. Alberta Agriculture, Food and Rural Development, Lethbridge, Alberta, Canada
Olson, B., et al. (2005). "Soil and Groundwater Quality under a Cattle Feedlot in Southern Alberta." Water Quality Research Journal of Canada 40.
Oil, Gas & Salt Resources Library, (2019). Petroleum Data. Government of Ontario.
Moreau-Fournier, M.; Reeves, R.R.; Reshitnyk, L.; Daughney, C.J. 2010 Incorporation of New Zealand regional authority state of the environment groundwater quality data into the GNS Science Geothermal-Groundwater Database Lower Hutt, N.Z.: GNS Science. GNS Science report 2010

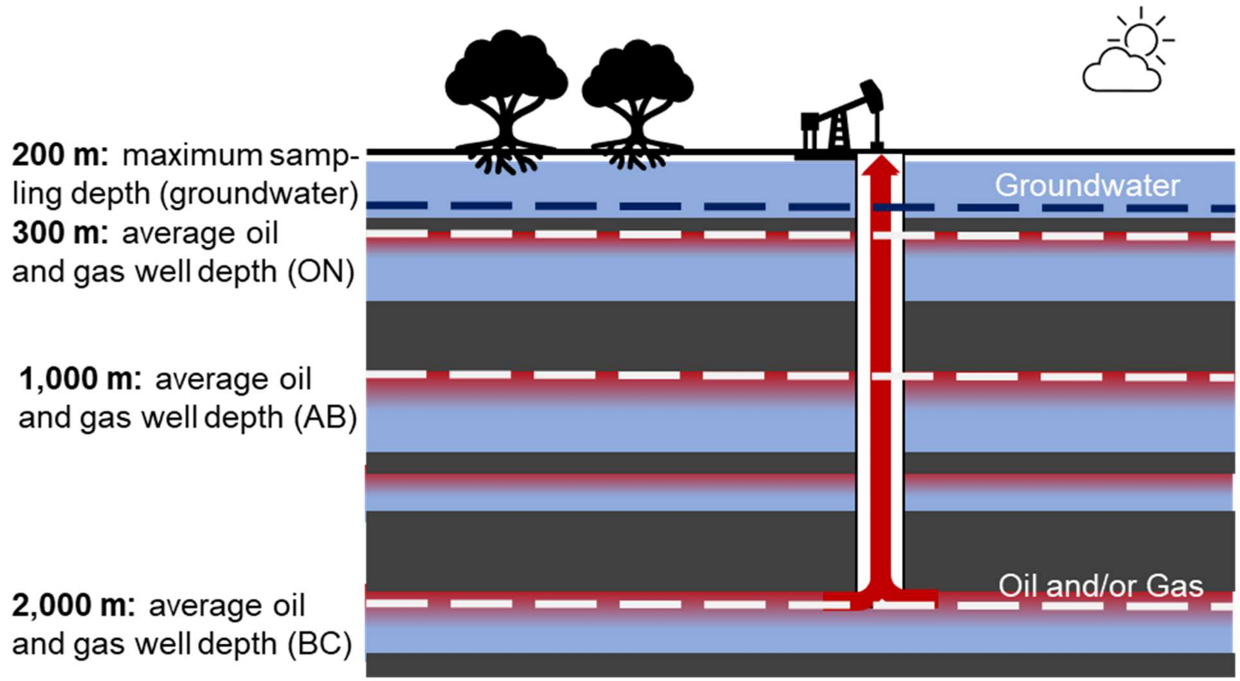


Figure S1: Schematic of a cross section of a typical oil and gas well (white) with depths in the Canadian provinces of British Columbia, Alberta, and Ontario and the maximum sampling depth for a groundwater sample collected for analysis in this paper (dark blue). Red represents oil and/or gas-containing pools/formations and the blue represents groundwater. The gray layers represent low permeability formations that act as barriers to vertical flow.

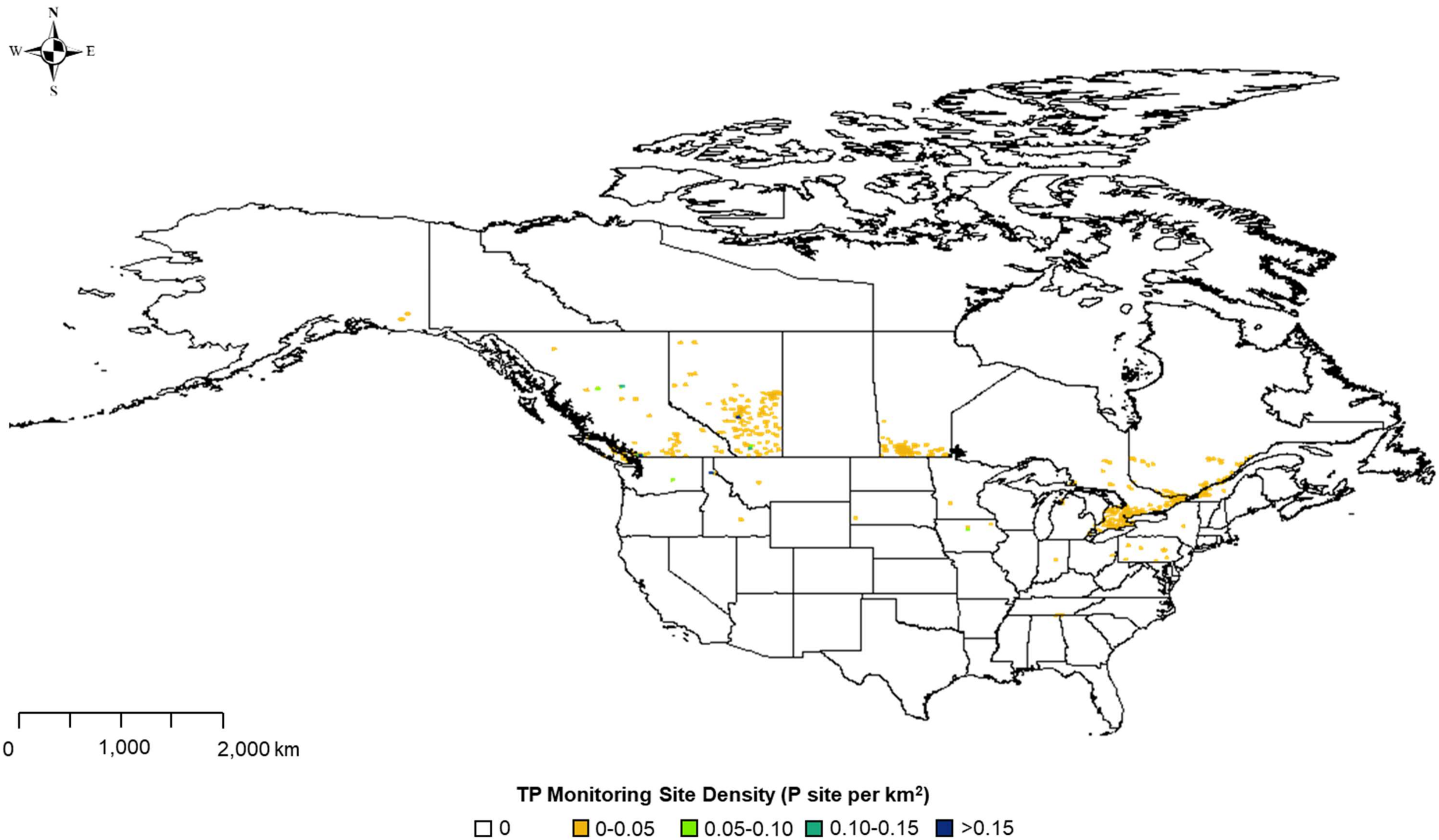


Figure S2. Point density of TP monitoring sites with concentrations greater than 0.1 mg P/L in a search area of 30 km by 30 km.

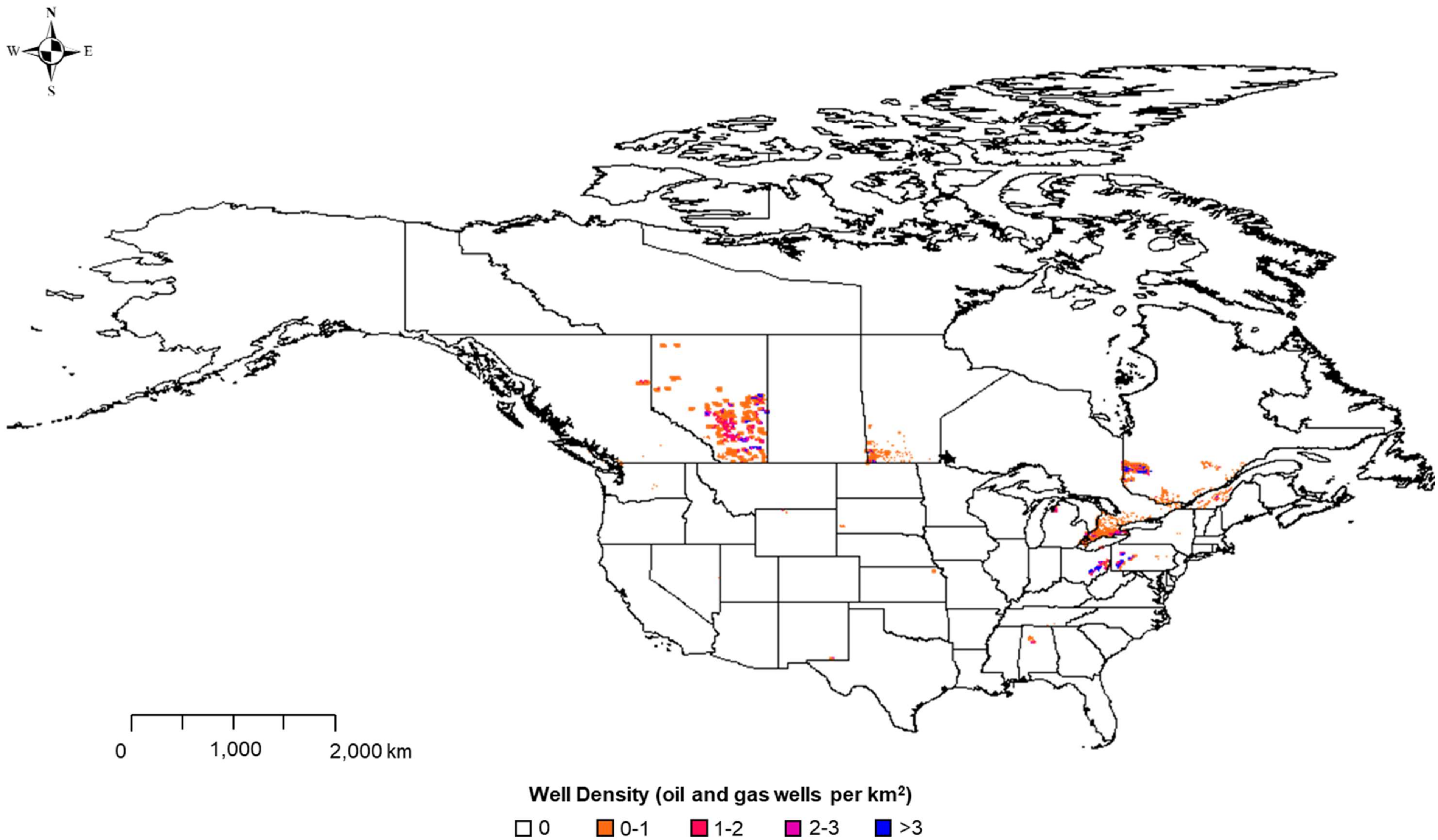


Figure S3. Point density of oil and gas wells in Canada and the United States in areas where the point density of all TP monitoring sites is >0 wells per 900 km^2.

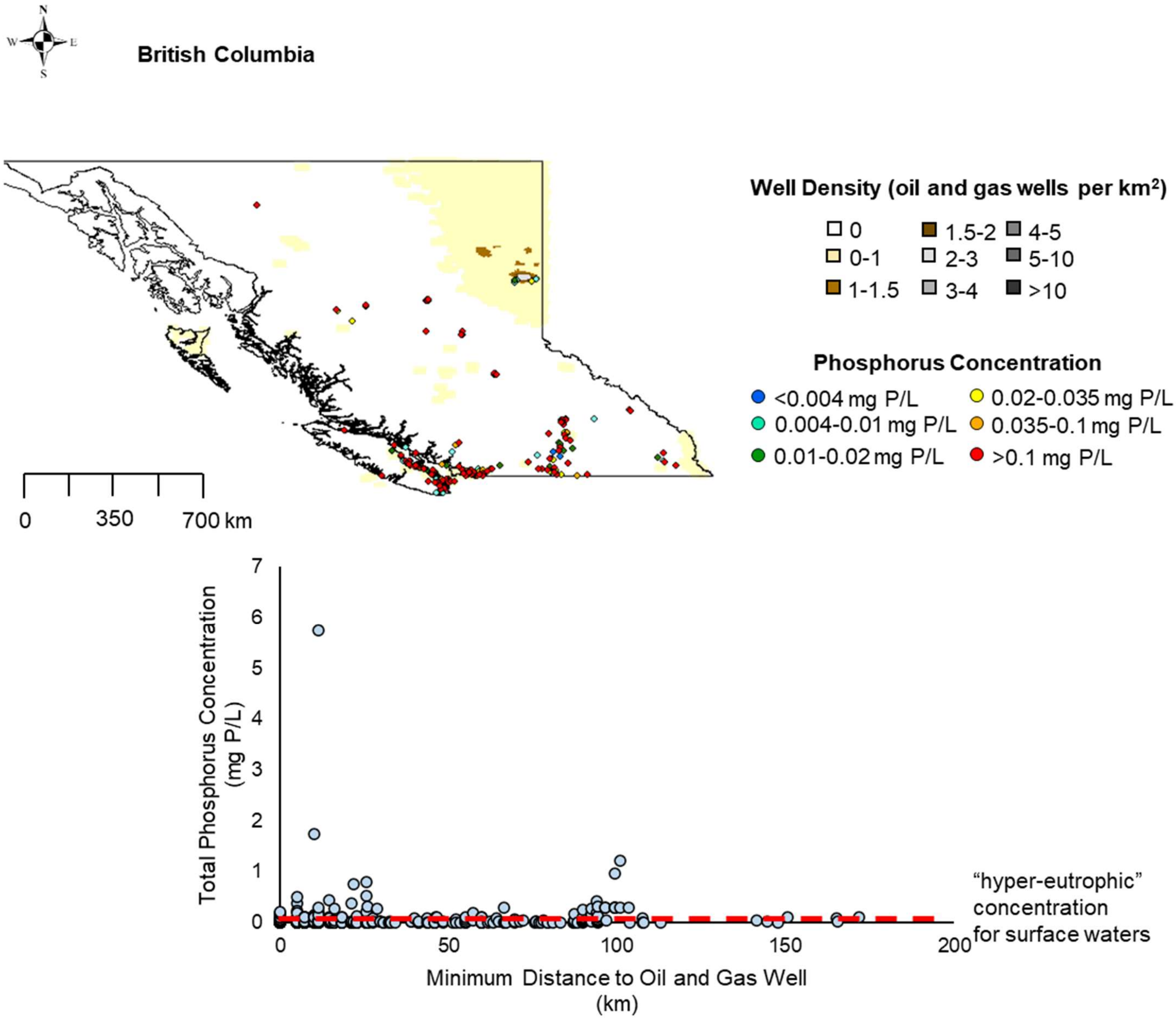


Figure S4. Well density map of all oil and gas wells in British Columbia with P concentration values separated by CCME concentration range. The dotted red lines on the scatter plots represent the CCME "hyper-eutrophic" P concentration of 0.1 mg P/L.

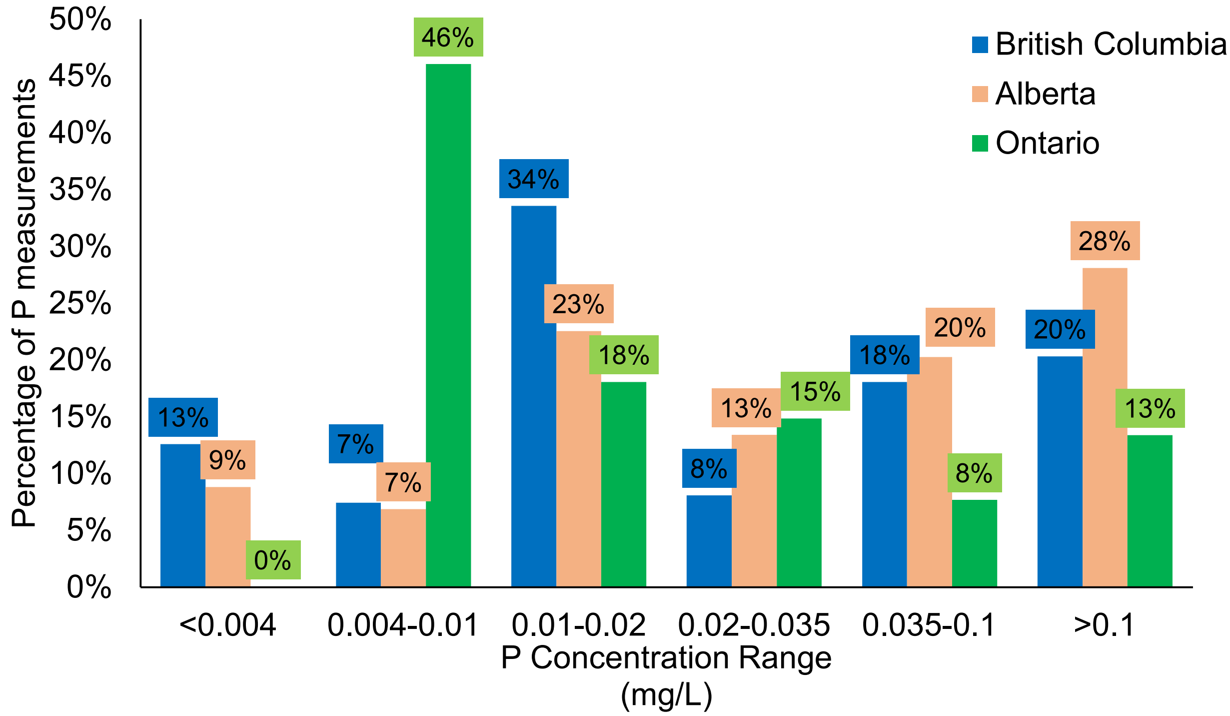


Figure S5: Frequency histogram of phosphorus (P) measurements by concentration range in British Columbia (blue), Alberta (orange), and Ontario (green). The P concentration type is TP for Alberta and Ontario and is TDP for British Columbia.

Appendix B: Estimating the base of fresh water in California

Table S1. Comparison between the data available in the depth zones used by Kang et al (2020) and the depth zones used in this paper.

Kang et al., 2020				This paper		
Depth Zone	**Count**	**%**		**Depth Zone**	**Count**	**%**
				0-25	62667	28.9%
0-75	130796	60.3%		**25-75**	68129	31.4%
75-150	45200	20.9%		**75-150**	45200	20.9%
150-305	32753	15.1%		**150-305**	32753	15.1%
305-1000	6729	3.1%		**305-1000**	6729	3.1%
1000-2000	729	0.3%		**1000-2000**	729	0.3%
>2000	547	0.3%		**>2000**	547	0.3%
All data	216754	100%		**All data**	216754	100%

Table S2. Selection radii implemented for TDS data selection changing with depth zone.

Depth Zone (m)	**Selection Radius (km)**
0-25	10
25-75	10
75-150	30
150-305	30
305-1,000	60
1,000-2,000	90
>2,000	120

Table S3. Selection radii implemented for TDS data selection changing with depth zone and location.

	Grid Section and Selection Radius (km)		
Depth Zone (m)	**17, 18, 19, 20**	**4, 8, 9, 10, 11, 12, 13, 14, 15, 16**	**1, 2, 3, 5, 6, 7**
0-25	10	10	20
25-75	10	10	20
75-150	20	20	20
150-305	20	20	20
305-1,000	60	60	40
1,000-2,000	90	90	90
>2,000	200	150	100

Table S4. Comparison between TDS-depth relationship by area using all TDS measurements associated with depths >25 m and TDS measurements at all depths.

	TDS measurements > 25 m in depth			All TDS measurements	
	Area (km^2)	**%**		**Area (km^2)**	**%**
Linear	88,597.5	20.9%		84,850.5	20.0%
Nonlinear monotonic	30,298.9	7.1%		31,506.0	7.4%
Nonlinear nonmonotonic	206,258.9	48.6%		209,026.8	49.3%
Insufficient data	98,812.7	23.3%		98,584.7	23.3%
Total	42,3967.9	100%		42,3967.9	100%

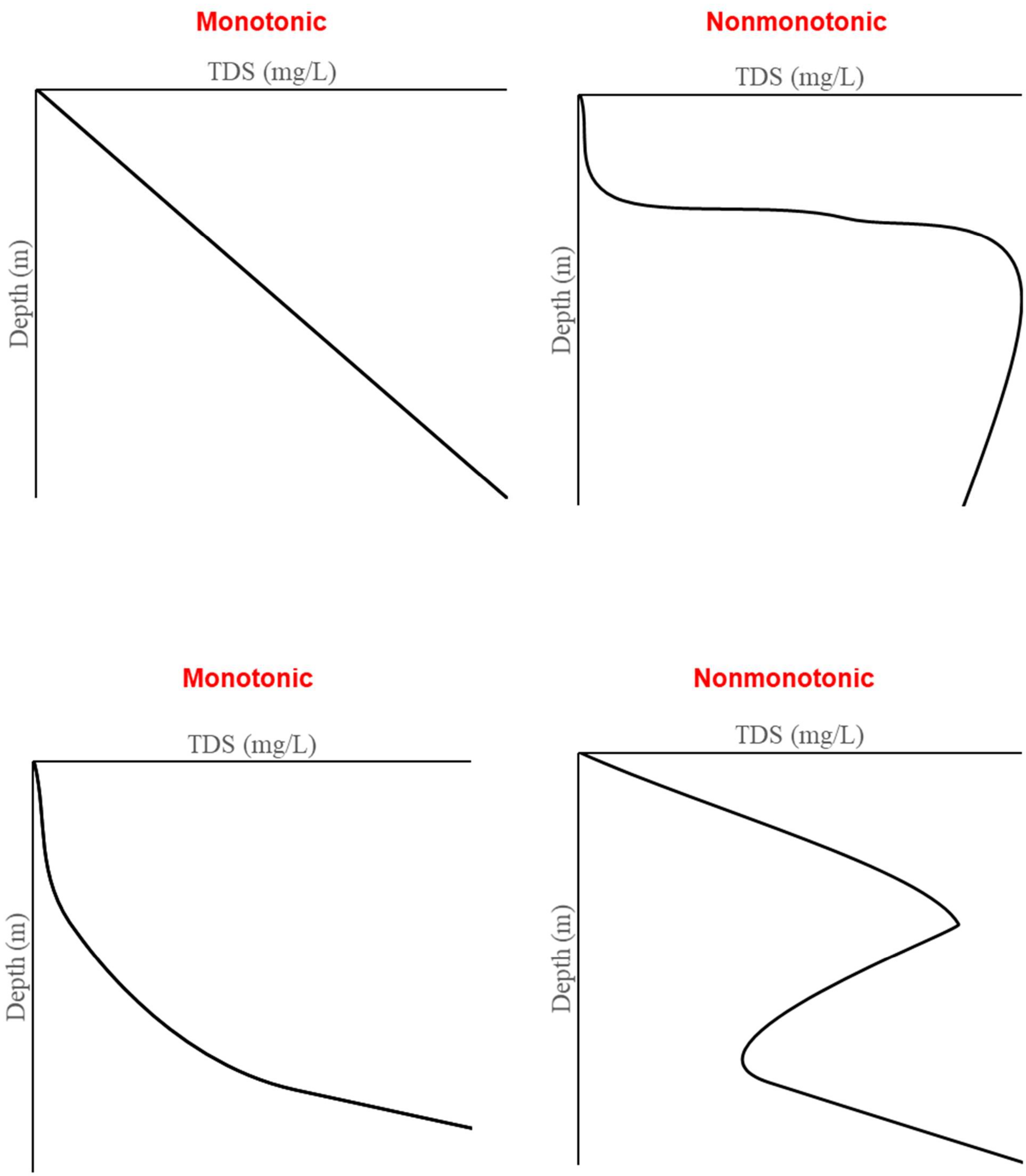


Figure S1. Illustration of the difference between monotonic (left images) and nonmonotonic (right images) TDS-depth relationships.

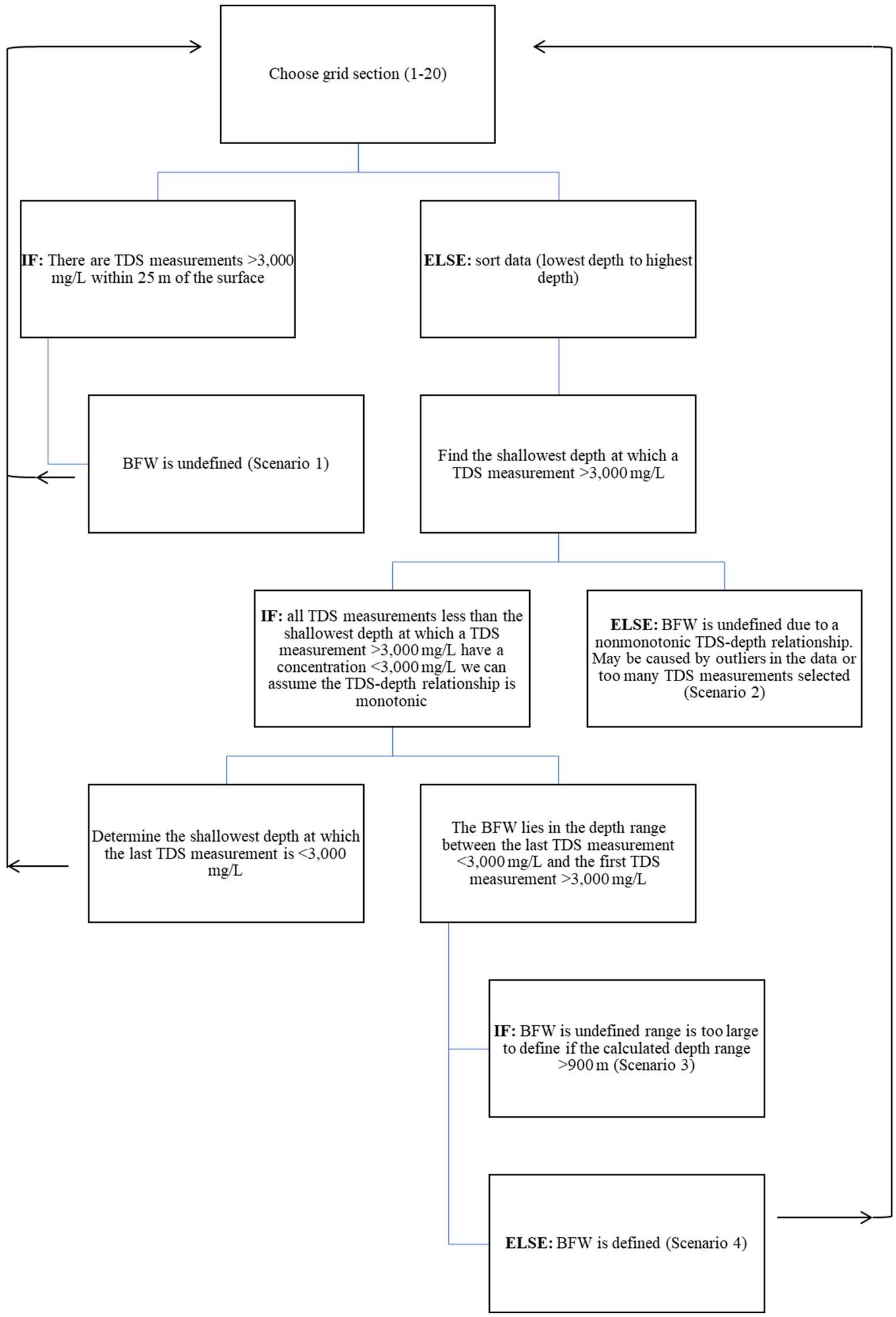


Figure S2. Flow chart illustration of the process used to determine if the BFW can be calculated from the selected TDS measurements for each of the 20 grid sections selected in the Central Valley.

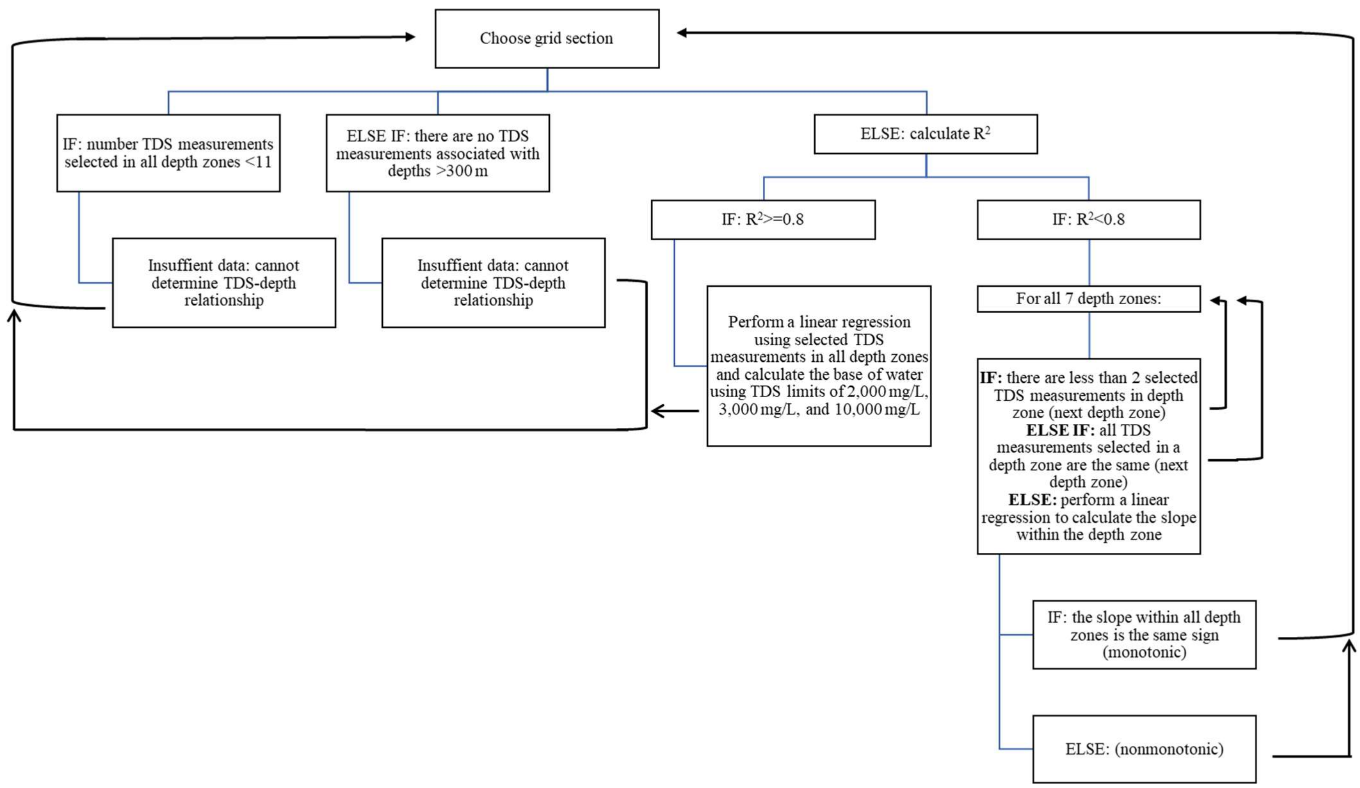


Figure S3. Flow chart illustration of the Python code used to determine TDS-depth relationships for grid sections in California.

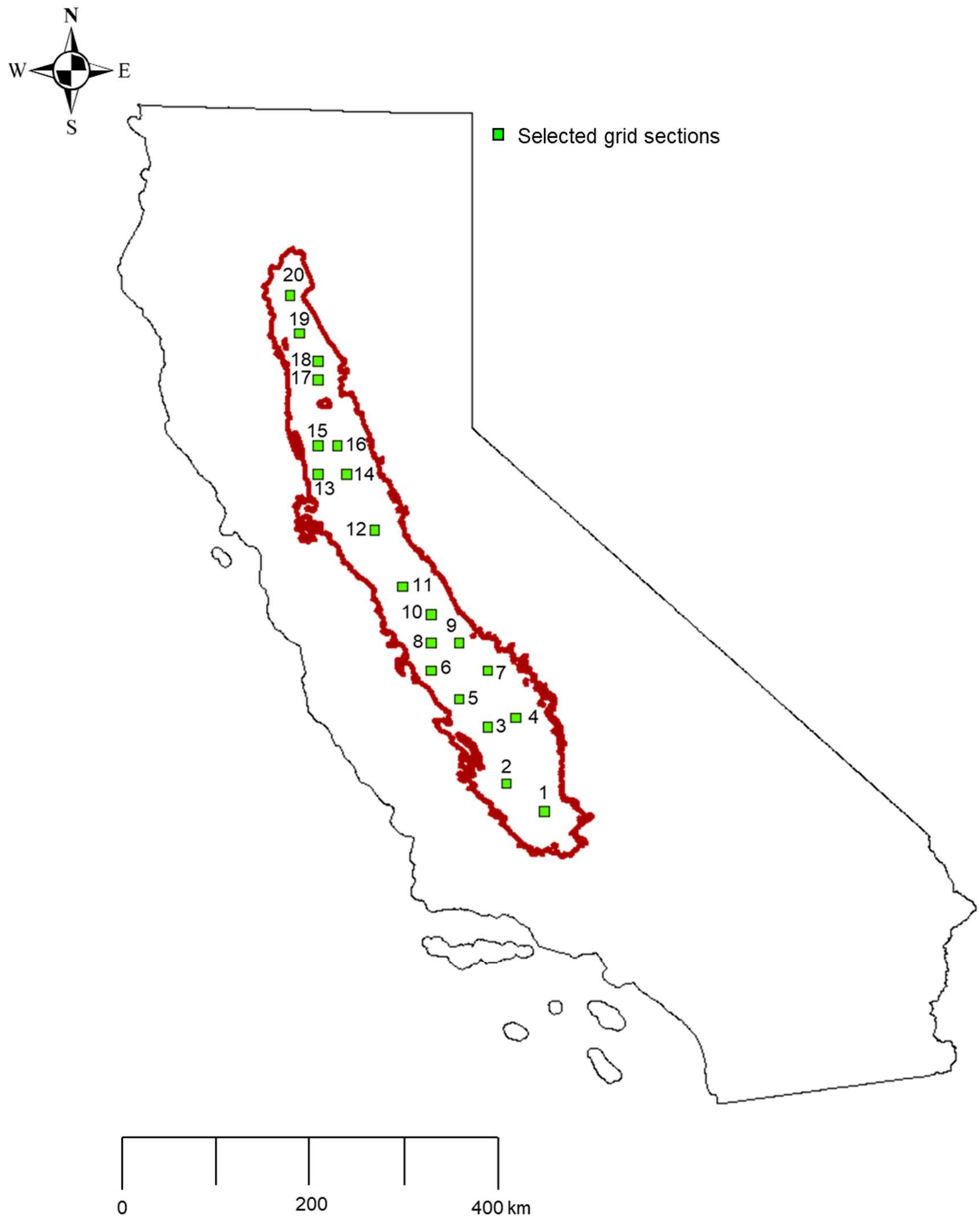


Figure S4. Locations of the 20 selected grid sections in Central Valley.

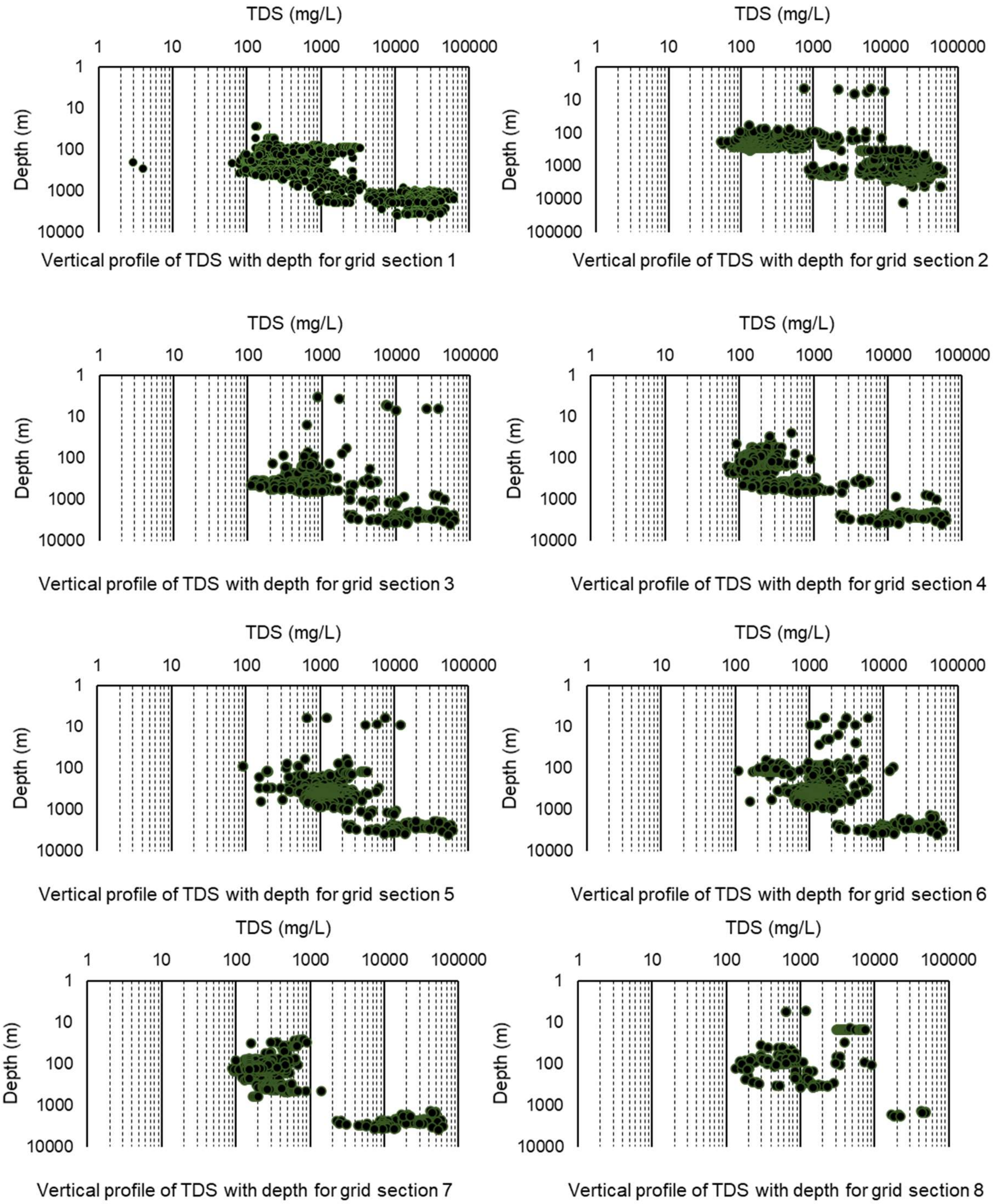
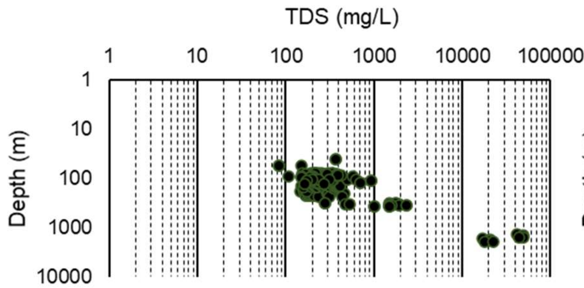
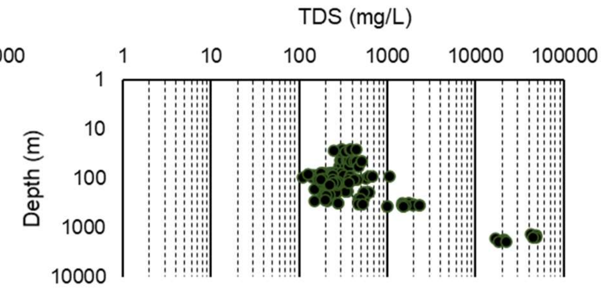


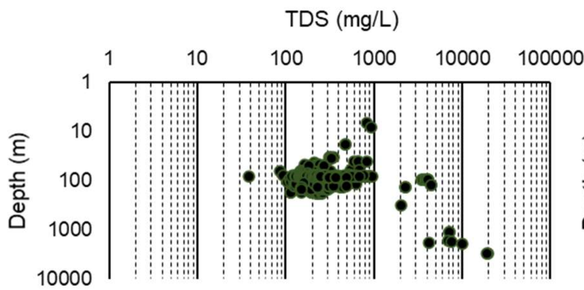
Figure S5. Salinity profiles of 20 selected grid points obtained using varying radius with depth only (grid sections 1-8).



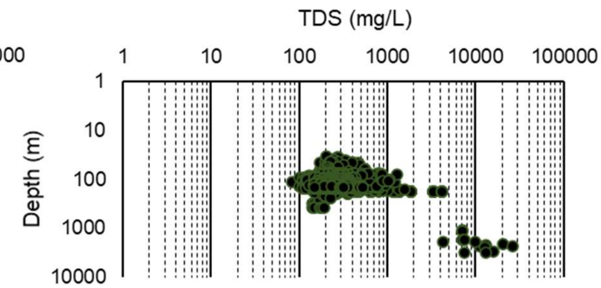
Vertical profile of TDS with depth for grid section 9



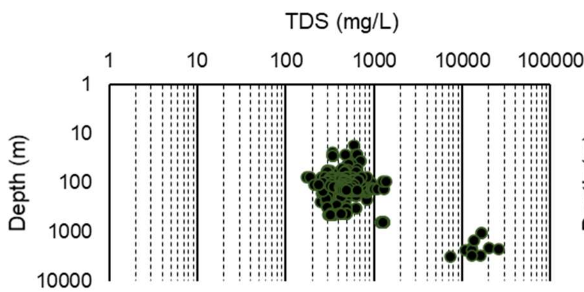
Vertical profile of TDS with depth for grid section 10



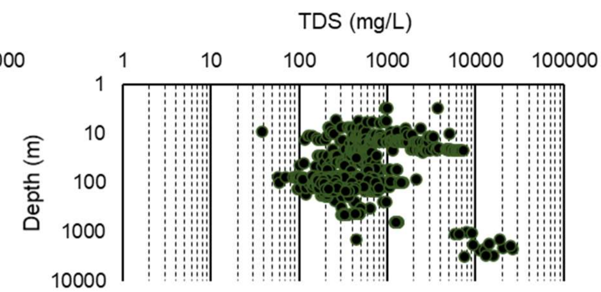
Vertical profile of TDS with depth for grid section 11



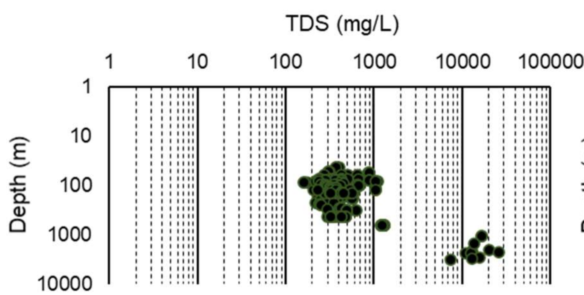
Vertical profile of TDS with depth for grid section 12



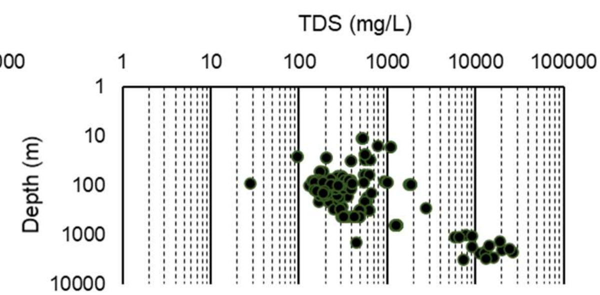
Vertical profile of TDS with depth for grid section 13



Vertical profile of TDS with depth for grid section 14



Vertical profile of TDS with depth for grid section 15



Vertical profile of TDS with depth for grid section 16

Figure S6. Salinity profiles of 20 selected grid points obtained using varying radius with depth only (grid sections 9-16).

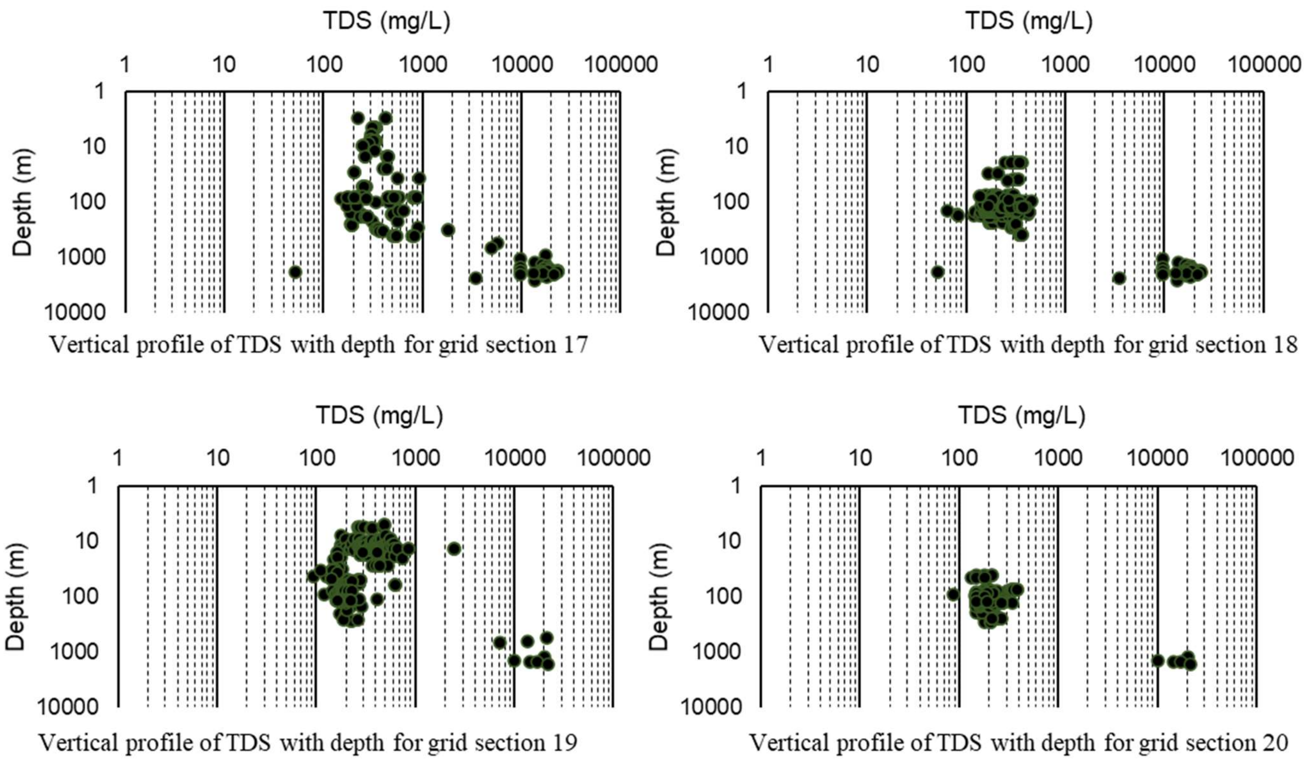
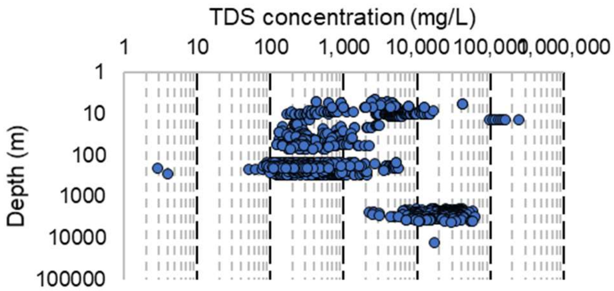
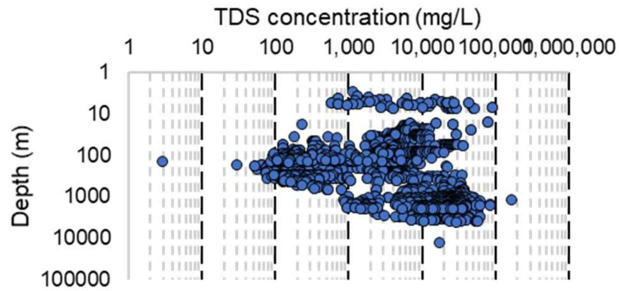


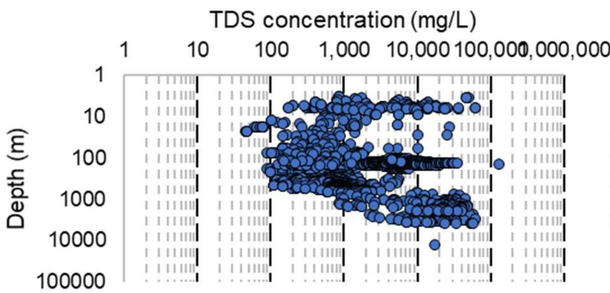
Figure S7. Salinity profiles of 20 selected grid points obtained using varying radius with depth only (grid sections 17-20).



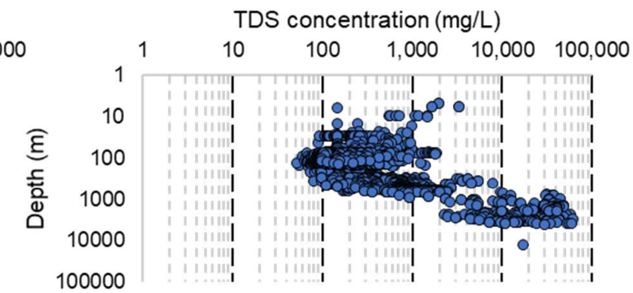
Vertical profile of TDS with depth for grid section 1



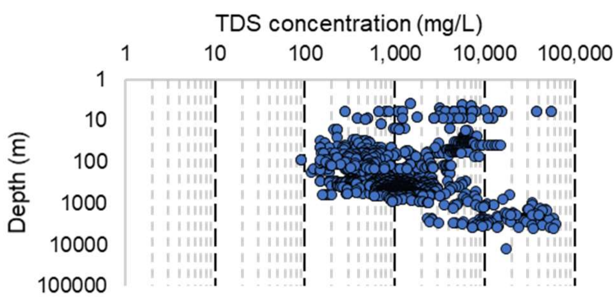
Vertical profile of TDS with depth for grid section 2



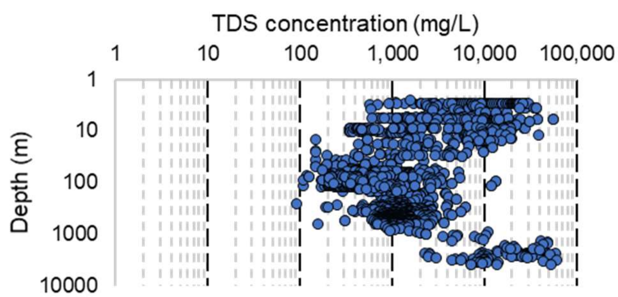
Vertical profile of TDS with depth for grid section 3



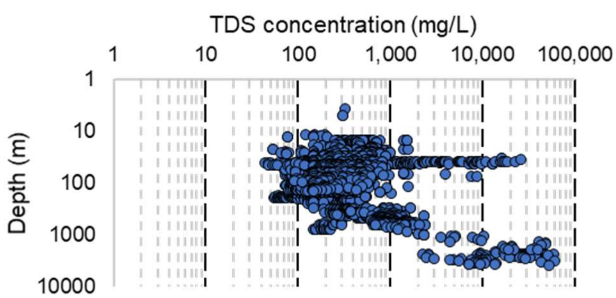
Vertical profile of TDS with depth for grid section 4



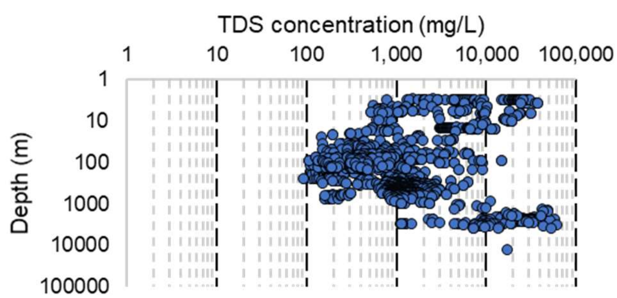
Vertical profile of TDS with depth for grid section 5



Vertical profile of TDS with depth for grid section 6



Vertical profile of TDS with depth for grid section 7



Vertical profile of TDS with depth for grid section 8

Figure S8. Salinity profiles of 20 selected grid points obtained using varying radius with depth and location (grid sections 1-8).

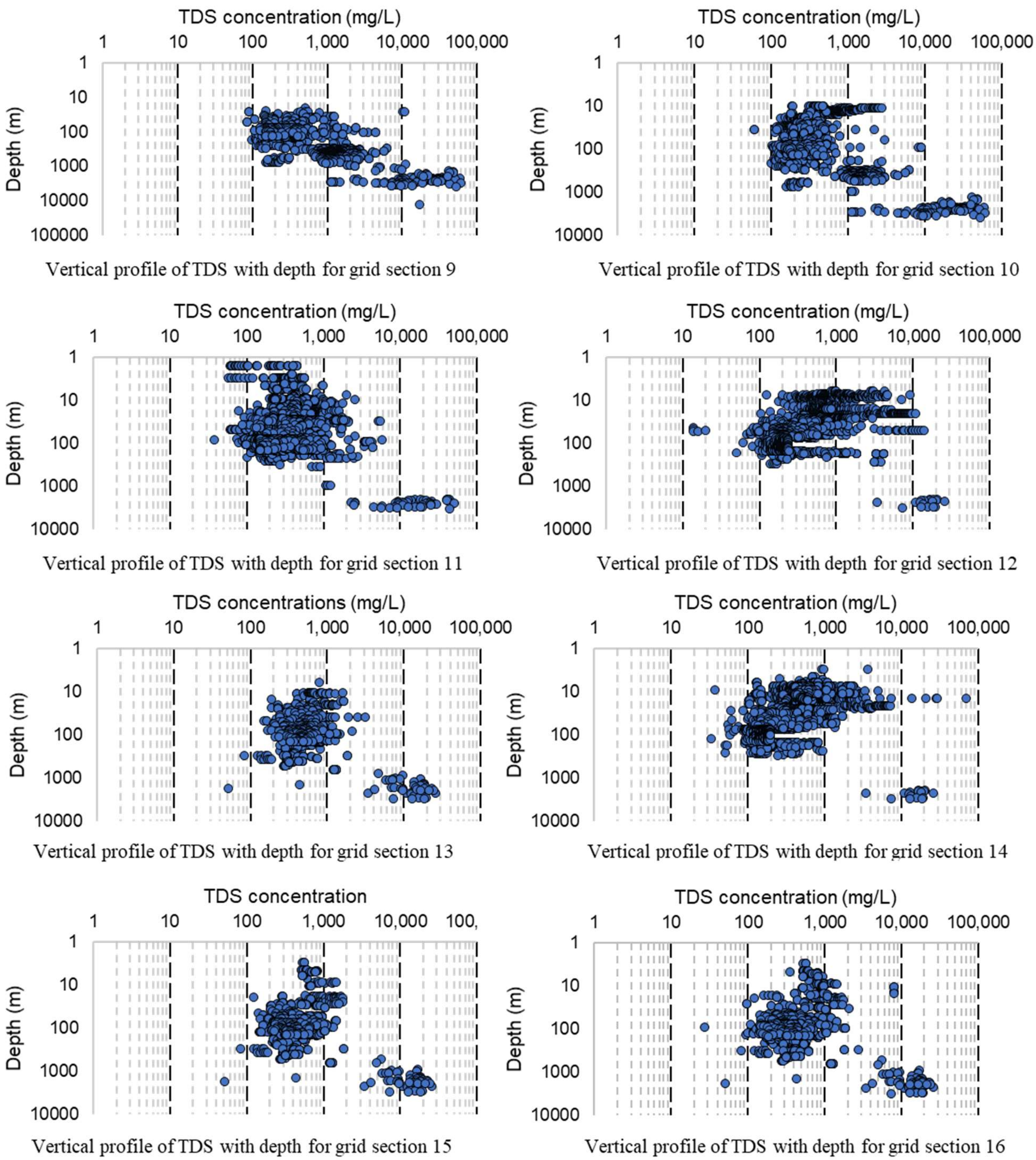
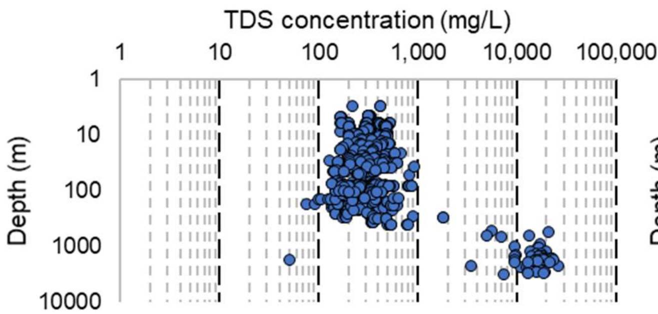
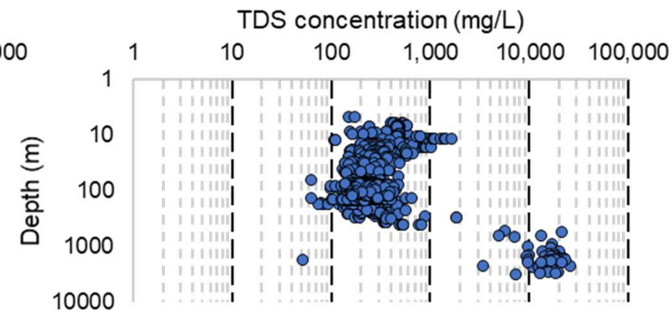


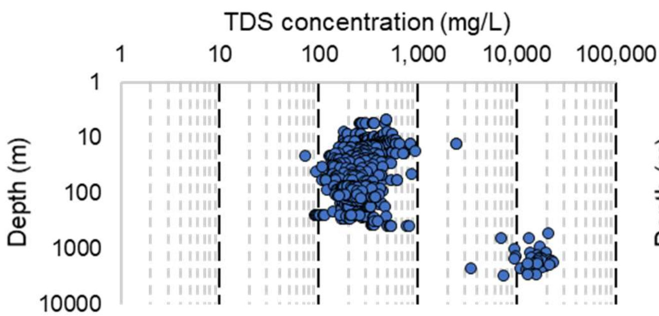
Figure S9. Salinity profiles of 20 selected grid points obtained using varying radius with depth and location (grid sections 9-16).



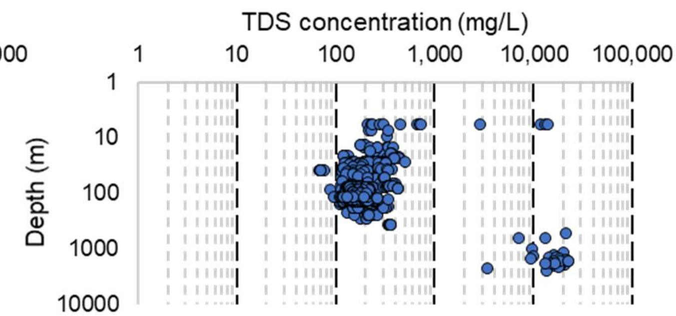
Vertical profile of TDS with depth for grid section 17



Vertical profile of TDS with depth for grid section 18



Vertical profile of TDS with depth for grid section 19



Vertical profile of TDS with depth for grid section 20

Figure S10. Salinity profiles of 20 selected grid points obtained using varying radius with depth and location (grid sections 17-20).

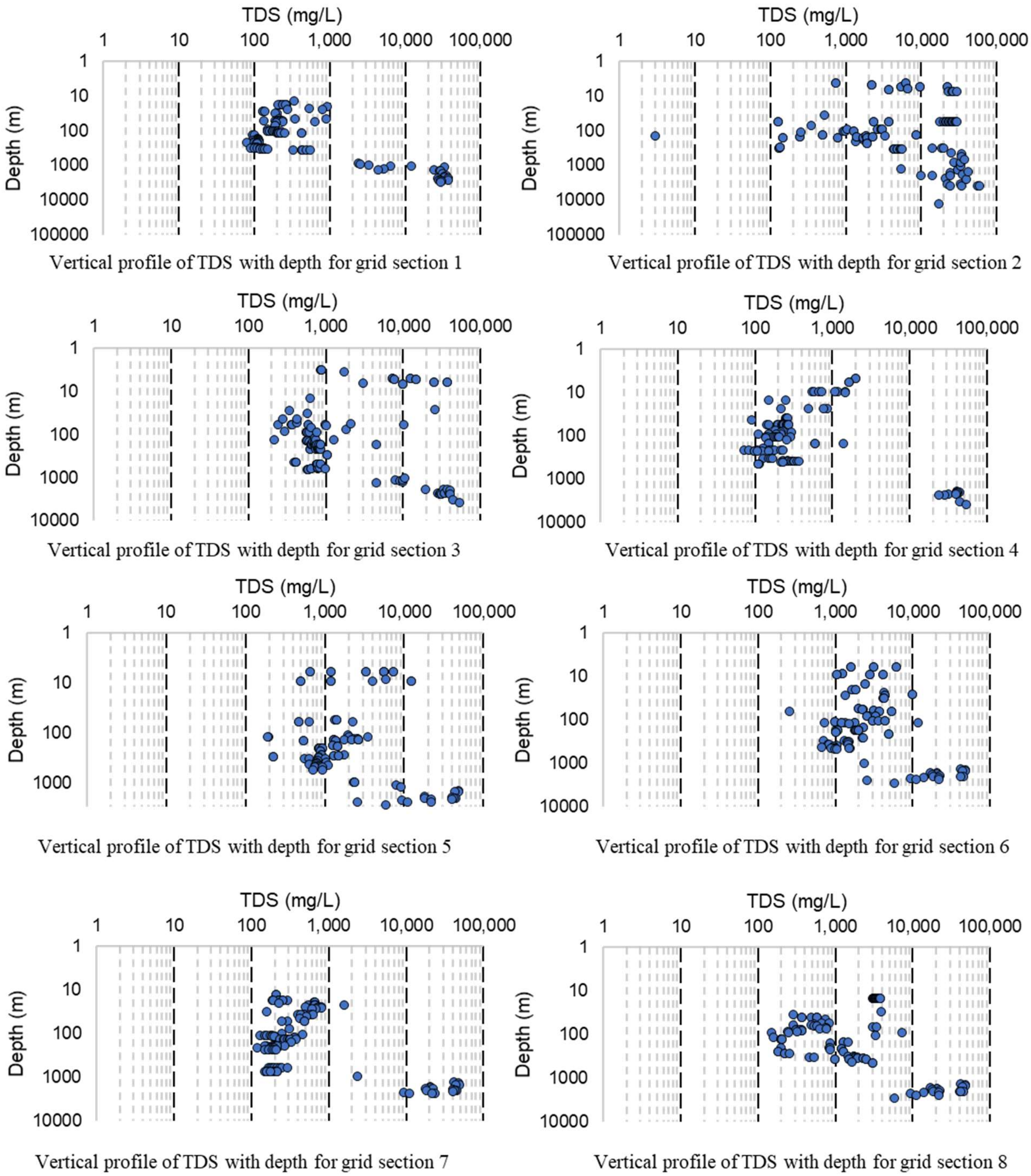
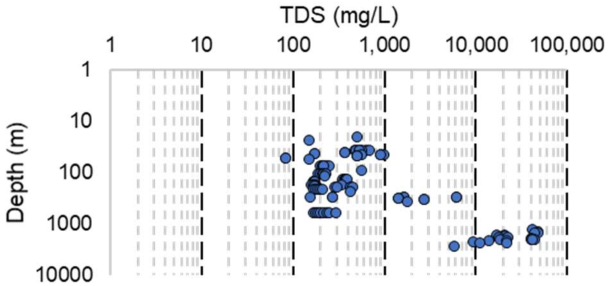
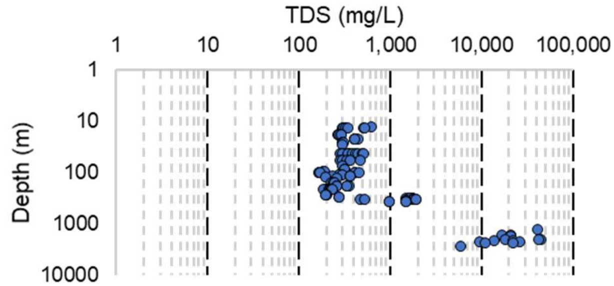


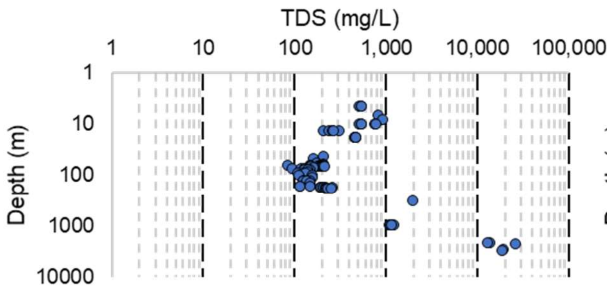
Figure S11. Salinity profiles of 20 selected grid points obtained using the nearest 20 TDS measurements (grid sections 1-8).



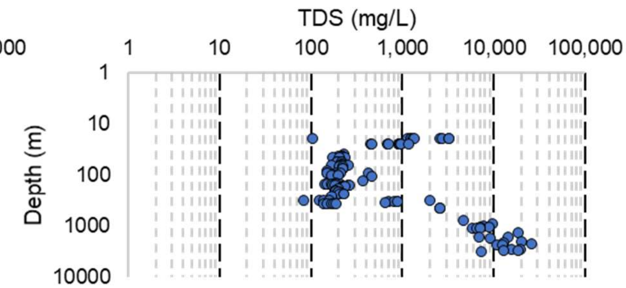
Vertical profile of TDS with depth for grid section 9



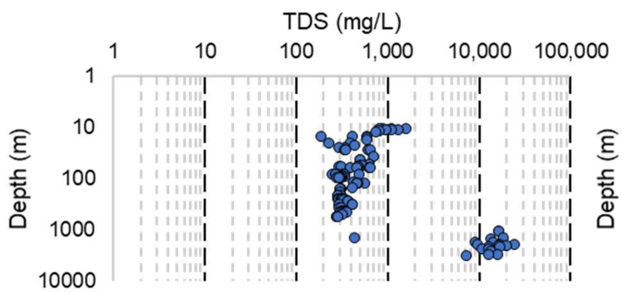
Vertical profile of TDS with depth for grid section 10



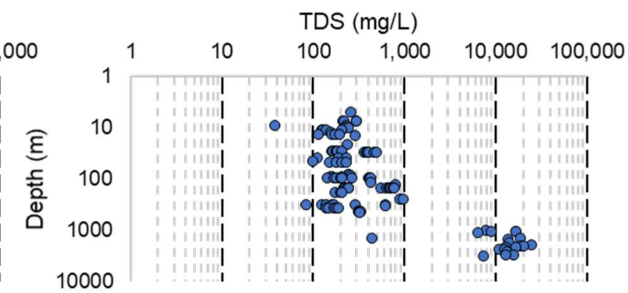
Vertical profile of TDS with depth for grid section 11



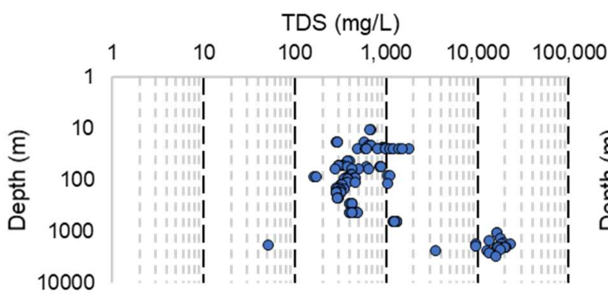
Vertical profile of TDS with depth for grid section 12



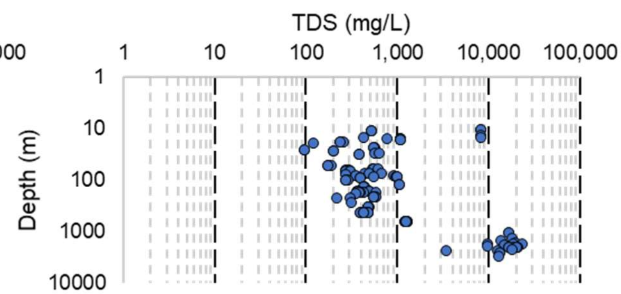
Vertical profile of TDS with depth for grid section 13



Vertical profile of TDS with depth for grid section 14



Vertical profile of TDS with depth for grid section 15



Vertical profile of TDS with depth for grid section 16

Figure S12. Salinity profiles of 20 selected grid points obtained using the nearest 20 TDS measurements (grid sections 9-16).

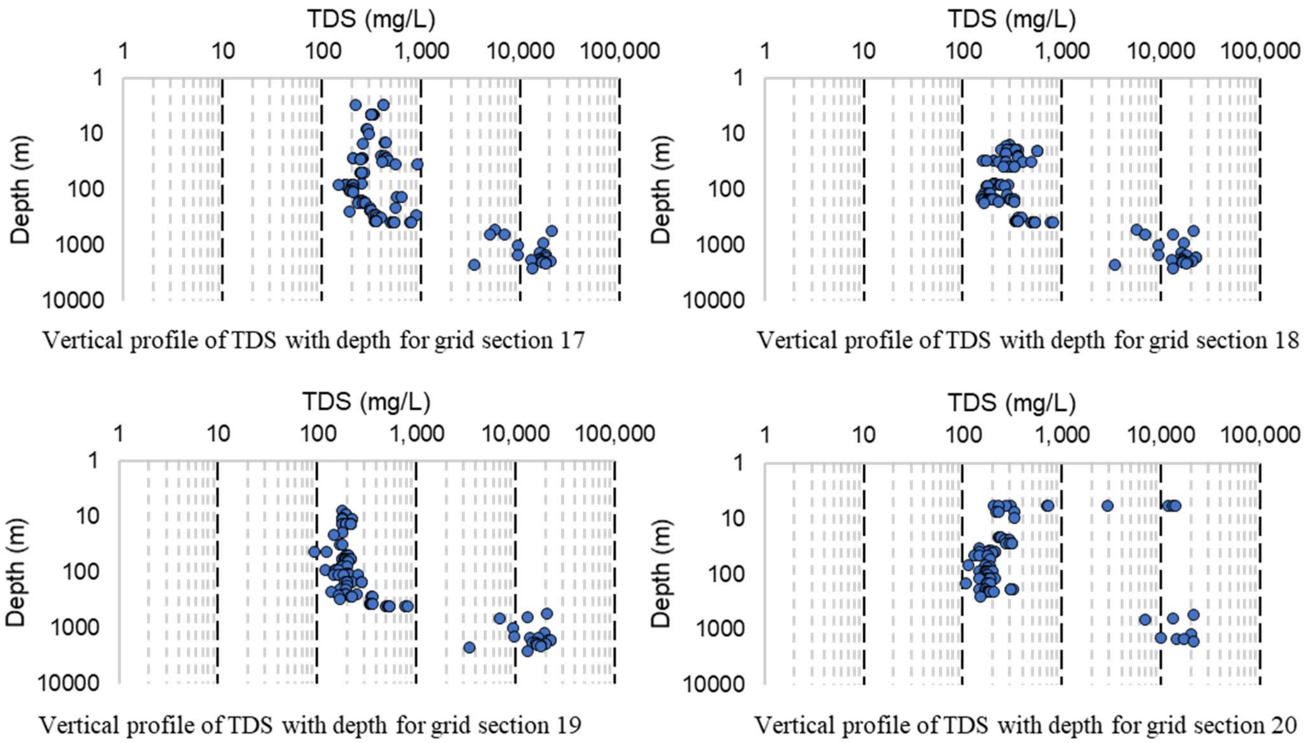
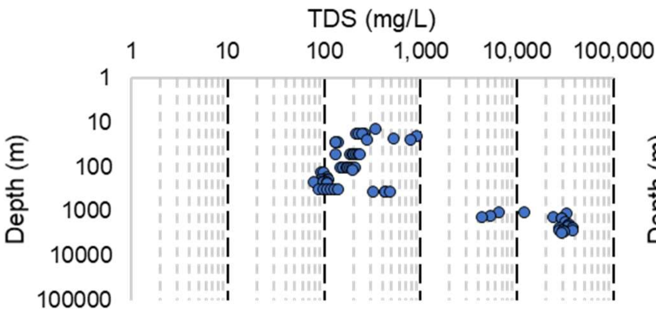
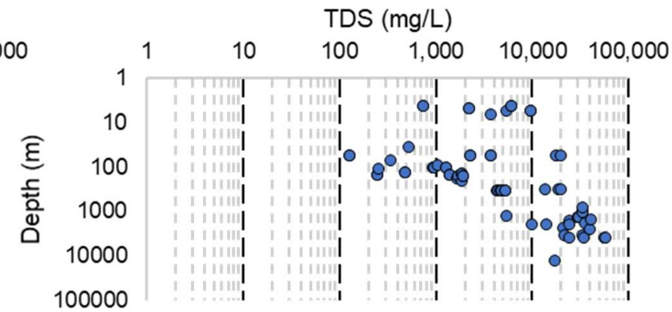


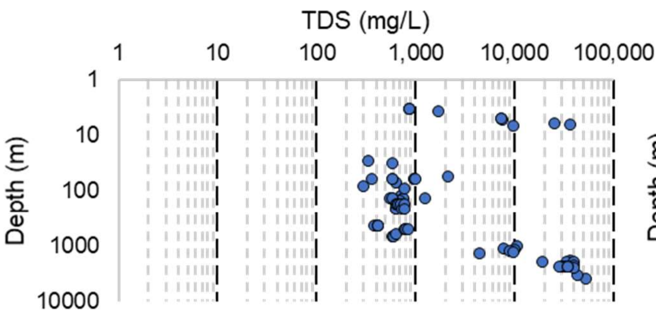
Figure S13. Salinity profiles of 20 selected grid points obtained using the nearest 20 TDS measurements (grid sections 17-20).



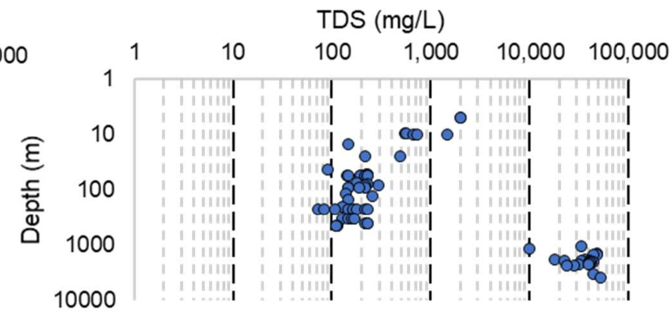
Vertical profile of TDS with depth for grid section 1



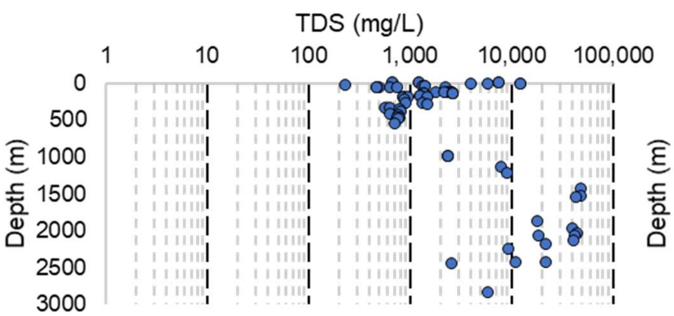
Vertical profile of TDS with depth for grid section 2



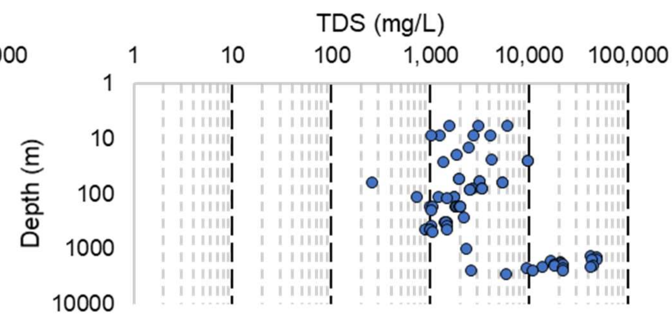
Vertical profile of TDS with depth for grid section 3



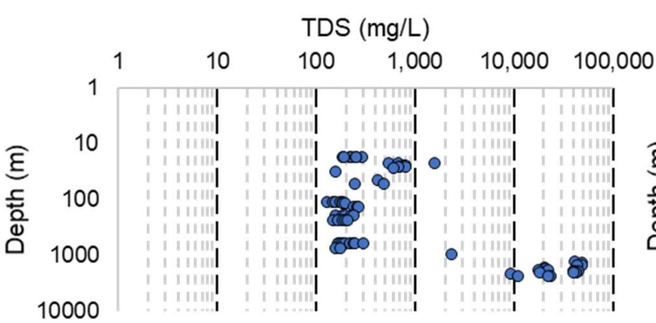
Vertical profile of TDS with depth for grid section 4



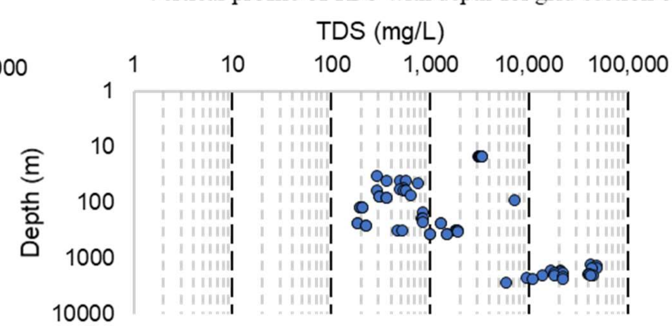
Vertical profile of TDS with depth for grid section 5



Vertical profile of TDS with depth for grid section 6

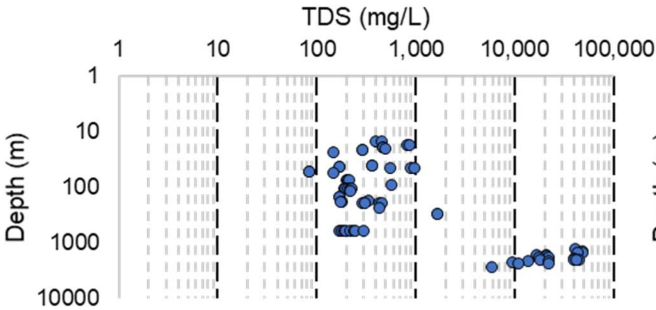


Vertical profile of TDS with depth for grid section 7

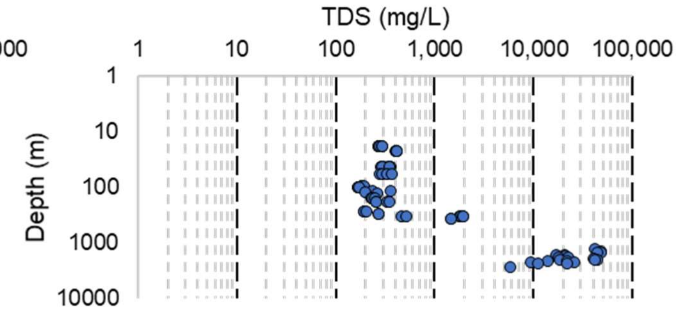


Vertical profile of TDS with depth for grid section 8

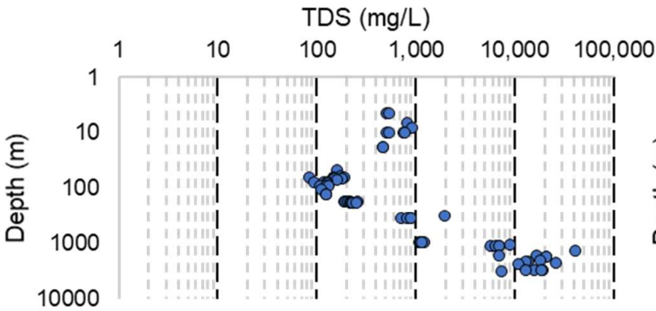
Figure S14. Salinity profiles of 20 selected grid points obtained using the nearest 10 TDS measurements (grid sections 1-8).



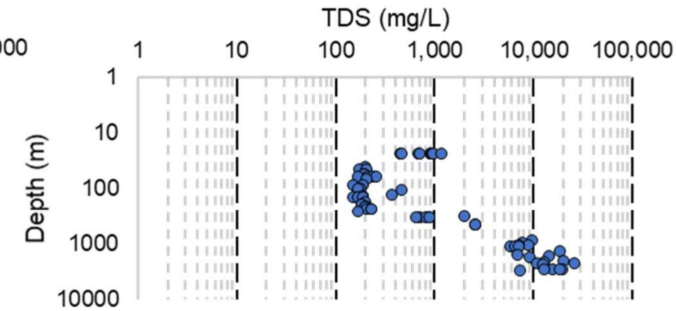
Vertical profile of TDS with depth for grid section 9



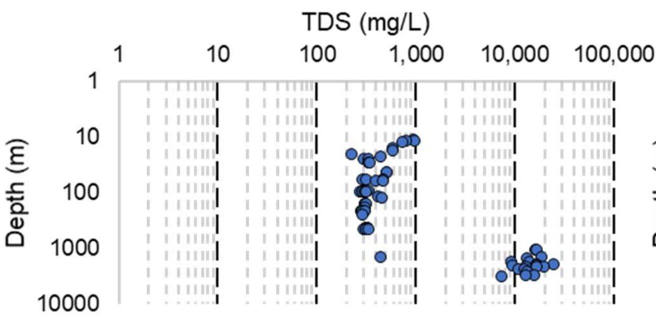
Vertical profile of TDS with depth for grid section 10



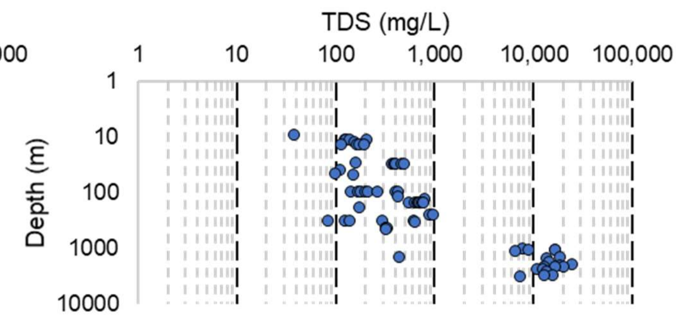
Vertical profile of TDS with depth for grid section 11



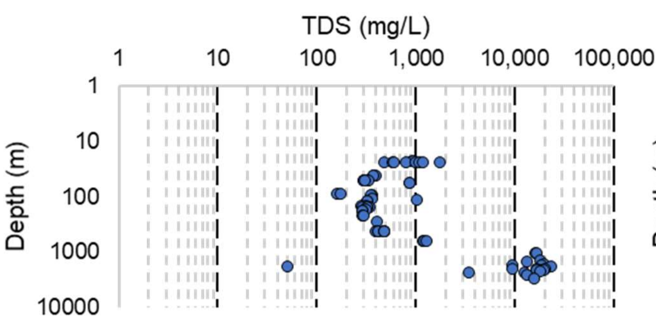
Vertical profile of TDS with depth for grid section 12



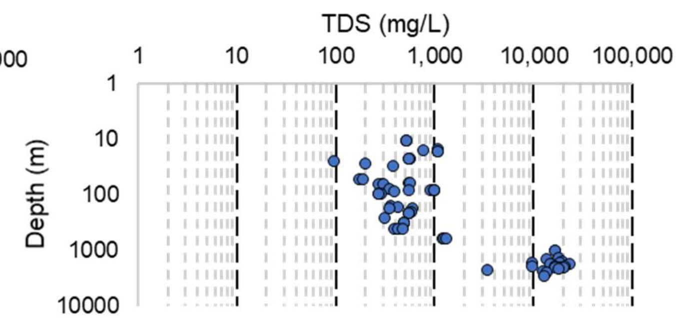
Vertical profile of TDS with depth for grid section 13



Vertical profile of TDS with depth for grid section 14

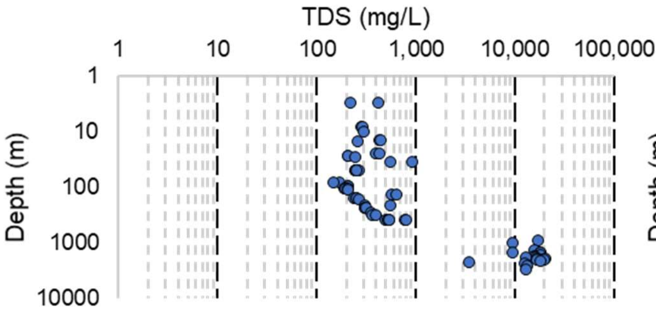


Vertical profile of TDS with depth for grid section 15

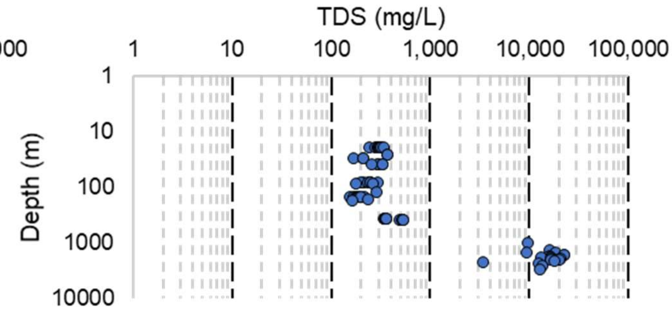


Vertical profile of TDS with depth for grid section 16

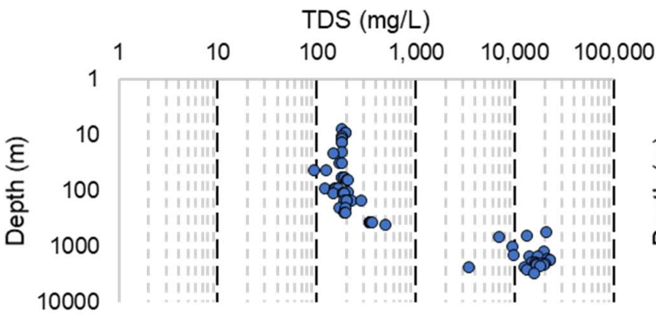
Figure S15. Salinity profiles of 20 selected grid points obtained using the nearest 10 TDS measurements (grid sections 9-16).



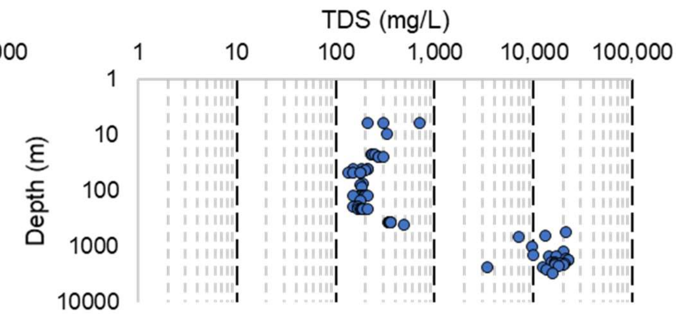
Vertical profile of TDS with depth for grid section 17



Vertical profile of TDS with depth for grid section 18



Vertical profile of TDS with depth for grid section 19



Vertical profile of TDS with depth for grid section 20

Figure S16. Salinity profiles of 20 selected grid points obtained using the nearest 10 TDS measurements (grid sections 17-20).