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Estimating natural background concentrations for dissolved constituents in groundwater: a methodological review and case studies for geogenic fluoride

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Abstract

Knowledge of the natural background concentrations of groundwater constituents is important for the management of groundwater resources, particularly for the assessment of groundwater contamination and the establishment of clean-up goals and regulatory target levels. In recent years, an increasing number of studies have assessed the natural background concentrations of dissolved constituents in groundwater using a variety of different methods, each with its own assumptions, advantages and limitations. The objective of this paper is to provide a methodological basis for improving the estimation of natural background concentrations of groundwater constituents. To this end, this paper critically reviews the different approaches used to determine natural background concentrations of dissolved constituents in groundwater. In addition, two regional case studies of fluoride in Canadian groundwater are presented to illustrate the estimation of background concentrations for natural groundwater constituents. The review of existing methods shows that the use of pristine groundwater samples is not possible in many cases, due to the widespread influence of human activities. The widely used pre-selection method can provide misleading results because of inadequate selection criteria and poor statistical significance associated with the reduction of the dataset. A variety of model-based methods have been developed, but these methods are all based on assumptions that cannot be verified. Relying on the user's experience and previous knowledge of the groundwater system, exploratory data analysis has many advantages and can be applied for both anthropogenic and natural constituents. The case studies show that the exploratory data analysis approach provides critical information to determine the sources of groundwater constituents and to properly delineate groundwater bodies for which background values will be established. Natural background concentrations should always be considered as theoretical values due to their spatio-temporal variability and scale dependence, and thresholds as concentration values above which further investigation is required.

Keywords: Groundwater contamination, Exploratory data analysis, Pristine groundwater, Pre-selection, Alberta, Quebec.

1. Introduction

Groundwater contamination is a major global concern, as groundwater is a vital source of water for domestic, agricultural and industrial purposes in many parts of the world ([World Water Assessment Programme, 2009](#)). Groundwater contaminants may originate from anthropogenic sources, natural sources, or a mixture of both. In this context, the concept of natural background has been developed to support the management of groundwater resources, particularly the assessment of groundwater contamination and the establishment of clean-up goals and regulatory target levels ([Griffioen et al., 2008](#); [Molinari et al., 2012](#)). The natural background refers to the concentration of a substance in a pristine environment, i.e. unaffected by anthropogenic influence ([Nisi et al., 2016](#); [Panno et al., 2006](#); [Reimann and Garrett, 2005](#)). The natural groundwater chemistry results from the chemical composition of recharge water (i.e. precipitation or infiltrated surface water) that is modified in the soil, the unsaturated zone and the aquifer (or aquitard) by biogeochemical reactions involving interrelated factors such as soil composition, aquifer mineralogy, groundwater flow, recharge rate and residence time ([Biddau et al., 2017](#); [Edmunds and Shand, 2009](#); [Molinari et al., 2012](#)). Natural background values are typically expressed as a concentration range that describes the variability of groundwater composition over space and time ([Reimann and Garrett, 2005](#)). The terms “natural”, “geochemical” or “environmental” background usually refer to undisturbed natural conditions ([Lee and Helsel, 2005](#); [Reimann et al., 2005](#)). In contrast, the term “baseline” usually relates to existing conditions at a given point in time, which may include anthropogenic influences such as diffuse pollution ([Lee and Helsel, 2005](#); [Nisi et al., 2016](#); [Reimann and Garrett, 2005](#)). The geochemical baseline can be defined as the concentration range of a groundwater constituent in a limited area and depth interval over a specific period of time ([Bondu et al., 2021](#)). It is worth mentioning that in the literature the term “natural baseline” has been used as a synonym for natural background (e.g. [Edmunds et al., 2003](#); [Morgenstern and Daughney, 2012](#)). In this paper, the term “threshold” is used to designate the upper limit of background variation, independent of any regulatory standard ([Reimann and Garrett, 2005](#)). In line with the European Groundwater Directive (2006/118/EC), a number of studies have used “threshold values” as quality standards for the determination of chemical status in groundwater bodies, the upper limit of background variation being described as the “natural background level”, the lower limit being technically constrained by the detection or quantification limits” (e.g. [Coetsiers et al., 2009](#); [Hinsby et al., 2008](#)).

The concept of natural background is challenging as background values are spatially-dependent, i.e. relative to the location and scale of the groundwater systems ([Reimann and Garrett, 2005](#)). Natural background values are defined for specific groundwater bodies, which often correspond to regional aquifer units (e.g. [Coetsiers et al., 2009](#); [Molinari et al.,](#)

2012; Serianz et al., 2020). However, large-scale groundwater bodies may exhibit significant heterogeneity in groundwater chemistry (Ducci et al., 2016; Edmunds and Shand, 2009; Molinari et al., 2019). In this case, groundwater bodies can be refined (grouped or subdivided) based on the existing knowledge of groundwater geochemistry, the analysis of hydrogeochemical data and depending on the specific objectives of the study (e.g. contaminants of interest, study area). The delineation of groundwater bodies has a major influence on the estimated background values (Edmunds and Shand, 2009; Preziosi et al., 2014, 2010). In recent years, an increasing number of studies have assessed the natural background concentrations of dissolved constituents in groundwater (e.g. Biddau et al., 2017; Bulut et al., 2020; Cruz and Andrade, 2015; De Caro et al., 2017; Ducci and Sellerino, 2012; Gao et al., 2020b; Kim et al., 2015; Molinari et al., 2012, 2014; Parrone et al., 2019; Preziosi et al., 2010, 2014; Sellerino et al., 2019; Serianz et al., 2020; Urresti-Estala et al., 2013; Zabala et al., 2016). These studies have applied a variety of methods to determine natural background values, each with its own assumptions, advantages and limitations. The application of different methods to the same dataset has shown that natural background values may vary significantly depending on the method used (Bulut et al., 2020; Gao et al., 2020a; Molinari et al., 2012; Preziosi et al., 2014; Sellerino et al., 2019). However, there is little discussion in the literature regarding the implications of the different approaches on the estimated background values. Moreover, little consideration has been given to the sources of groundwater constituents, while the determination of natural background concentrations is fundamentally different for constituents influenced by anthropogenic impacts and for constituents derived purely from natural sources. Groundwater studies have often used a single approach to establish natural background concentrations for a wide range of dissolved constituents, regardless of their natural or anthropogenic origin (e.g. Bulut et al., 2020; Coetsiers et al., 2009; Cruz and Andrade, 2015).

The objective of this paper is to provide a methodological basis for improving the estimation of natural background concentrations in groundwater, considering the available groundwater chemistry data, the current understanding of the groundwater system and the sources of groundwater constituents. For this purpose, this paper critically reviews the methods that are commonly used to determine natural background concentrations of constituents dissolved in groundwater. Graphical examples are provided to illustrate statistical methods using a randomly generated, right-skewed distribution typical of geochemical data. This review focuses on groundwater constituents derived from anthropogenic sources, which have been addressed in most studies of natural background concentrations in groundwater. In addition, two regional case studies of fluoride in Canadian groundwater are presented to illustrate the basic case of natural groundwater constituents. In these case studies, the estimation of natural background concentrations is performed using a combination of exploratory data analysis techniques.

90 2. Review of methods for assessing natural background concentrations in groundwater

2.1. Pristine groundwater samples

Natural background values can be reliably determined using groundwater samples that have not been affected by anthropogenic inputs. This is the case for pristine groundwater located in areas with little or no human activities (e.g. [Gunnarsdottir et al., 2015](#)) or protected from surface contamination such as deep confined aquifers (e.g. [Marandi and Karro, 2008](#)). For a pristine groundwater body, the natural background values correspond to the measured concentration range (minimum-maximum concentrations), which reflects the spatio-temporal variations in constituent concentrations. The determination of background concentrations for natural groundwater constituents is illustrated in the case studies (section 3). However, identifying pristine portions of aquifers is often challenging in densely populated and intensively cultivated areas ([Molinari et al., 2014](#); [Panno et al., 2006](#)). Furthermore, establishing background values in pristine areas has limited applications (e.g. mining or hydrocarbon development in remote areas), as there is no need for pollution assessment or remediation. For areas affected by human activities, another approach is to extrapolate background values from groundwater samples collected in similar adjacent pristine areas ([Edmunds and Shand, 2009](#)). This approach is based on the assumption that the natural background varies little for similar hydrogeological environments. However, extrapolating background values is questionable as each area has unique environmental characteristics ([Edmunds and Shand, 2009](#); [Panno et al., 2006](#)). Groundwater chemistry may be strongly influenced by local geological features associated with lithofacies changes and mineralization. In addition, natural groundwater chemistry is likely to vary between pristine upland areas and down-gradient areas as a result of the geochemical evolution of groundwater. For all these reasons, pristine groundwater samples have not been routinely used for estimating natural background concentrations in groundwater.

The use of historical data is an alternate approach to estimate the natural background concentrations of groundwater constituents ([Griffioen et al., 2008](#); [Limbrick, 2003](#)). The assumption is that groundwater samples collected prior to extensive human influence are representative of pristine conditions. Historical data usually refer to samples collected before the 1950s, after which agricultural activities and other anthropogenic activities strongly intensified ([Griffioen et al., 2008](#)). In theory, historical analyses are the best estimate of the natural background groundwater quality in areas currently affected by anthropogenic pollution ([Griffioen et al., 2008](#); [Kelly and Panno, 2008](#)). The primary limitation of this approach is related to the scarcity of groundwater chemistry data collected more than fifty years ago ([Edmunds and Shand, 2009](#); [Kelly and Panno, 2008](#)). In addition, historical datasets often have limited hydrochemical parameters and uncertainties/biases associated with the sampling procedures (e.g. filtration, well purging) and analytical methods (e.g. detection limits) used at that time ([Edmunds and Shand, 2009](#); [Kelly and Panno, 2008](#)). Furthermore, the assumption that pre-1950s samples are free from any anthropogenic inputs may not be true in some areas depending on the land use history (e.g. impacts of mining

120 activities, domestic effluents, World Wars). Therefore, historical data are unlikely to provide reliable background values for most dissolved chemical parameters, although these data may be useful to gain insight into the temporal evolution of groundwater constituents and improve the conceptual hydrogeochemical model of the study area.

2.2. *Pre-selection of uncontaminated groundwater samples*

2.2.1. *Groundwater dating*

125 Pre-selection (PS) methods estimate natural background values using a subset of samples that are expected to have a natural composition (thereafter referred as the “pre-selected dataset”). Groundwater age-dating methods have been utilized to select pre-modern groundwater samples (recharged before 1950s) that are considered to be unaffected by anthropogenic inputs for the purpose of estimating natural background concentrations (Edmunds et al., 2003; Edmunds and Shand, 2009; Griffioen et al., 2008; Morgenstern and Daughney, 2012). Average groundwater residence times are estimated using
130 environmental tracers for dating relatively young groundwater (< 100 years old) such as tritium (^3H), chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6) (Edmunds and Shand, 2009; Griffioen et al., 2008; Morgenstern and Daughney, 2012). This pre-selection approach is based on the observation that the natural background is challenging to determine in young groundwater systems due to their widespread contamination by human activities, including industrialization, urbanization, and agriculture (Griffioen et al., 2008). However, the extrapolation of background concentrations as
135 determined in old groundwater to young groundwater may not be valid, as the chemical composition of old waters is generally different from that of young recharge waters due to the geochemical evolution along the flow path. In particular, differences in redox and pH conditions of young and recently recharged groundwater compared to geochemically more evolved and older groundwater are likely to influence the speciation of a variety of groundwater constituents, resulting in significantly different background concentrations (see section 3.1). This is a major limitation as natural background values
140 are particularly required for vulnerable shallow aquifers which generally contain modern groundwater. It is noteworthy that the use of groundwater age tracers has been limited by the cost and complexity of the methods (e.g. development of analytical methods, methodological uncertainties). Because of these limitations, only a few studies have applied pre-selection methods based on groundwater age-dating to determine natural background concentrations of groundwater constituents (e.g. Griffioen et al., 2008; Morgenstern and Daughney, 2012).

145 2.2.2. *Anthropogenic indicators*

Largely developed by the BRIDGE project (Müller et al., 2006), the pre-selection approach based on indicator substances of anthropogenic inputs is the most widely used approach for estimating natural background concentrations of groundwater constituents (Biddau et al., 2017; Bulut et al., 2020; Coetsiers et al., 2009; Cruz and Andrade, 2015; De Caro et al., 2017; Ducci et al., 2016; Ducci and Sellerino, 2012; Gemitzi, 2012; Hinsby et al., 2008; Marandi and Karro, 2008;

150 Molinari et al., 2019, 2012; Parrone et al., 2019; Preziosi et al., 2014, 2010; Sajil Kumar, 2017; Sellerino et al., 2019; Serianz et al., 2020; Zabala et al., 2016). In this approach, natural background values are estimated based on a pre-selected dataset that is obtained by excluding groundwater samples impacted by anthropogenic inputs (Fig. 1). The pre-selection process is generally based on the concentration of common anthropogenic contaminants (selection criteria), primarily NO_3 and NH_4 , but also K, Cl and SO_4 (Molinari et al., 2012; Müller et al., 2006; Sellerino et al., 2019). In order to apply
155 appropriate selection criteria, the PS method requires the separation of 1) fresh and brackish/saline waters based on Cl and/or Na concentrations (Coetsiers et al., 2009; Cruz and Andrade, 2015; Ducci and Sellerino, 2012), and (2) aerobic and anaerobic waters based on the oxidation-reduction potential, dissolved O_2 measurements or redox-sensitive species (e.g. Fe, Mn) (De Caro et al., 2017; Parrone et al., 2019; Rotiroti et al., 2015) (Fig. 1). For example, elevated NO_3 and NH_4 concentrations are typically used as selection criteria to exclude samples affected by anthropogenic inputs, respectively in
160 oxidizing and mildly reducing groundwater (Ducci et al., 2016). Following the BRIDGE methodology, threshold values are mainly determined using selected percentiles (Müller et al., 2006). The 90th percentile is usually used for small datasets (< 60 samples), poorly-documented groundwater systems and/or groundwater systems affected by significant anthropogenic pressure (Cruz and Andrade, 2015; De Caro et al., 2017; Sellerino et al., 2019; Serianz et al., 2020). In contrast, the 97.7th percentile is used for large datasets (> 60 samples), well-documented groundwater systems and/or groundwater systems
165 with little anthropogenic influence (Gemitzi, 2012).

The main advantage of the PS approach based on anthropogenic indicators is its easy application without any thorough statistical knowledge and with scarce data (Preziosi et al., 2010; Rotiroti et al., 2015). However, it is questionable whether natural background values should be established without appropriate statistical treatment and with a limited number of data. Moreover, there are a number of important limitations related to the simplified PS procedure. First, the pre-selected dataset
170 may include a number of contaminated samples that show no evidence of anthropogenic contamination based on common indicator substances (De Caro et al., 2017; Serianz et al., 2020). For example, the pre-selected dataset obtained using NO_3 concentration as selection criteria is likely to consist of groundwater samples that are not affected by agricultural and domestic inputs, but may include samples that are affected by industrial inputs. Additional selection criteria such as synthetic organic substances may be required to detect contaminated samples in industrialized and urban areas (De Caro et
175 al., 2017; Ducci et al., 2016). However, hydrochemical datasets often include a limited number of anthropogenic indicators, some of them being inadequate under specific settings such as NH_4 in organic-rich aquifers (Molinari et al., 2012). In addition, these anthropogenic indicators may undergo changes in concentration associated with a variety of biogeochemical and physical processes (e.g. reduction, adsorption, precipitation) (Kelly and Panno, 2008). The inadvertent inclusion of contaminated samples may also be related to the application of arbitrary selection criteria exceeding the true local threshold
180 (e.g. 10 or 50 mg/L NO_3). Thorough investigations should be conducted to determine a proper threshold for the separation

of natural and anthropogenically influenced samples before conducting pre-selection (Parrone et al., 2019). Appropriate selection criteria can also be derived from previous studies in areas where the natural background of anthropogenic indicators has been investigated (e.g. NO₃; Kim et al., 2015; Limbrick, 2003; Panno et al., 2006).

Another major limitation of the PS approach is the reduction of the dataset and the associated loss of statistical significance. The PS process may lead to a drastic reduction of the dataset in areas affected by extensive human activities. For instance, a significant number of samples are likely to be discarded based on elevated NO₃ concentrations in intensive agricultural areas (Amiri et al., 2021; Preziosi et al., 2010). To overcome this drawback, some studies have adopted a less stringent selection criteria such as 50 mg/L NO₃ (e.g. Bulut et al., 2020; Ducci and Sellerino, 2012; Gemitzi, 2012; Preziosi et al., 2010). However, this strategy leads to the inclusion of anthropogenically influenced samples in the pre-selected dataset. It is noteworthy that the dataset may be further reduced owing to the separation into oxidizing/reducing and fresh/saline samples (Coetsiers et al., 2009; Ducci et al., 2016). Some authors suggested that a significant loss of information may result from the removal of anthropogenically influenced samples with high concentrations of constituents related to natural processes (Gao et al., 2020b; Preziosi et al., 2010; Urresti-Estala et al., 2013). This observation raises the question of whether PS methods are suitable for estimating background concentrations for natural constituents.

Statistical methods are usually applied to the pre-selected dataset for determining natural background concentrations, but a number of critical questions remain unanswered. In the absence of extreme positive natural values (geochemical anomalies), applying statistical techniques suggests that the upper tail of the pre-selected data is influenced by anthropogenic inputs, while the PS process is specifically designed to exclude anthropogenically-contaminated samples (Preziosi et al., 2014). Hence, the risk of applying statistical techniques to the pre-selected dataset is to exclude natural data that are potentially representative of the geochemical background (De Caro et al., 2017). Moreover, there is no scientific justification of using percentile-based thresholds, which corresponds to arbitrarily assuming a percentage of outliers in the distribution (Reimann et al., 2005). Specific percentiles may yield very different background values, in particular for highly skewed distributions and in presence of numerous outliers (Parrone et al., 2019; Preziosi et al., 2014).

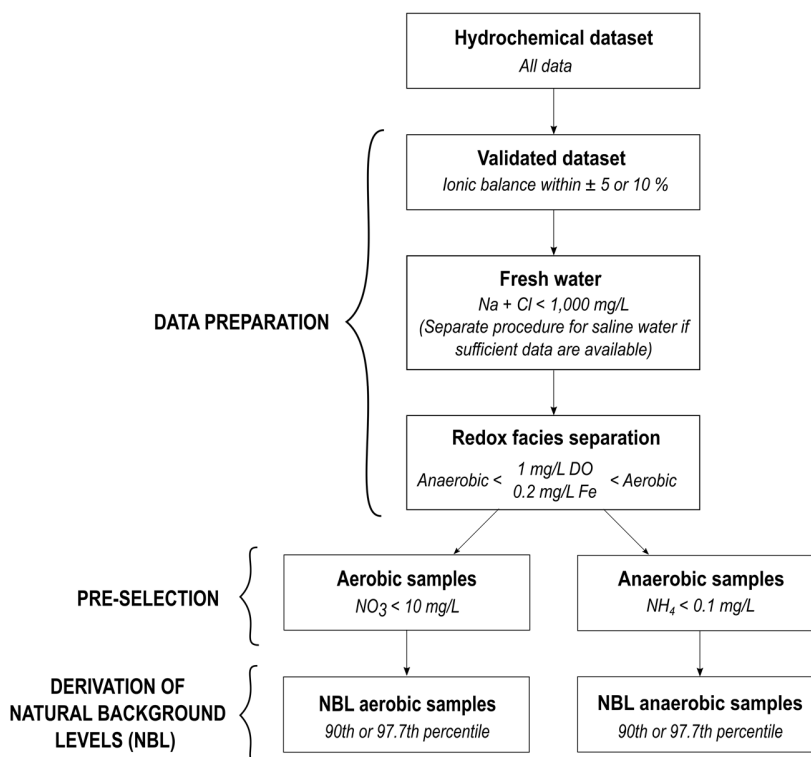


Fig. 1. Example flow chart of a PS procedure based on anthropogenic indicators.

2.3. Statistical approaches

2.3.1. Exploratory data analysis and robust statistics

A variety of exploratory data analysis (EDA) techniques have been applied to estimate the natural background values of groundwater constituents. EDA techniques explore the data distribution to identify a separation between the background population and anomalies (outliers), which may be indicative of anthropogenic inputs. The EDA approach is based on the principle that different geochemical sources produce different data populations that can be identified using appropriate graphical tools (Reimann et al., 2011). The most-widely used graphical technique to estimate threshold values is the cumulative probability (CP) plot (Koh et al., 2009; Panno et al., 2006; Preziosi et al., 2014; Rahman et al., 2020; Sellerino et al., 2019; Serianz et al., 2020) (Fig. 2B). The CP plot was originally designed to assess whether a dataset follows a given distribution, such as a normal or lognormal distribution (Sinclair, 1974; Tennant and White, 1959). In the CP plot, the sorted values are plotted against the cumulative probabilities of the theoretical distribution. For groundwater data, the theoretical distribution is generally the normal or lognormal distribution (Preziosi et al., 2014; Sellerino et al., 2019). Geochemical data following the theoretical distribution form a straight line, while slope changes and breaks in the curve indicate the presence of sub-populations (Panno et al., 2006; Reimann et al., 2005). The empirical cumulative distribution function (ECDF) plot has also been used to determine threshold concentrations (Edmunds and Shand, 2009; Kubier et al., 2020) (Fig. 2C). In the

ECDF plot, the sorted values are plotted against the probabilities of the empirical cumulative distribution. ECDF plots can be constructed using both the original and log-transformed data, but do not require any assumptions concerning the distribution. The threshold values are estimated by observation of inflection points and breaks in the curve, in a similar way to the CP plot. In contrast to the CP plot, the ECDF plot does not compress a portion of the data range but provides less detail at the extremes (Reimann et al., 2005). Both CP and ECDF plots provide a comprehensive insight into the data structure (i.e. range, extreme values, detection limits), each data value remaining visible in the plot (Figs. 2B and 2C). However, these graphical methods require a significant number of data to avoid attributing thresholds to slope changes reflecting only the incompleteness of the dataset (Panno et al., 2006). A major limitation of these methods is the subjective estimation of thresholds that depends on the user experience and expert knowledge on groundwater chemistry in the study area (Reimann et al., 2005; Sinclair, 1991). Previous knowledge is critical for the identification of the threshold between background and outliers, particularly when several inflection points are visible (see section 3). For this reason, the interpretation of probability graphs generally needs to be supported by other EDA methods including multivariate statistical, geospatial and hydrochemical techniques. A combination of EDA techniques is the best approach to explore the data distribution (Figs. 2A, 2B and 2C). In particular, statistical techniques can be associated with geochemical mapping to investigate the spatial distribution of data (Reimann et al., 2011) (see section 3). Geochemical maps provide crucial information about the relationship of dissolved constituents with spatially variable factors including the aquifer geology, groundwater flow conditions and land use. Geochemical mapping has been used in many studies of natural background concentrations in groundwater (e.g. Biddau et al., 2017; Gao et al., 2020b; Kubier et al., 2020; Preziosi et al., 2014).

Robust statistical methods have also been used to calculate natural background values for groundwater, primarily the Tukey boxplot and the $MED \pm 2 \cdot MAD$ methods (Biddau et al., 2017; Edmunds and Shand, 2009; Gao et al., 2020b; Koh et al., 2009; Parrone et al., 2019). Robust estimators are less influenced by extreme values than classical statistical methods (e.g. $MEAN \pm 2 \cdot SD$), which allow for a better identification of outliers relative to the main body of data (Reimann et al., 2011). The Tukey boxplot identifies data outliers as the values lying beyond the $[Q_{25} - 1.5 \cdot (Q_{75} - Q_{25}); Q_{75} + 1.5 \cdot (Q_{75} - Q_{25})]$ interval (i.e. lower inner fence to upper inner fence), with Q_{25} the 25th percentile, and Q_{75} the 75th percentile. Conversely, the background corresponds to the values ranging from the lower to the upper whiskers, which correspond to the minimum value above the lower inner fence and the maximum value below the upper inner fence, respectively. For the $MED \pm 2 \cdot MAD$ method, the background range corresponds to the $[Q_{50} - 2 \cdot MAD; Q_{50} + 2 \cdot MAD]$ interval, with MAD the median of the absolute deviations from the median calculated as $MAD = \text{median}(|X_i - Q_{50}|)$ (Biddau et al., 2017; Gao et al., 2020b; Reimann et al., 2005). The $MED \pm 2 \cdot MAD$ method generally yields conservative (low) threshold values compared to the Tukey boxplot method. It is important to note that both methods require a symmetrical distribution, which may be obtained

using appropriate data transformation. In contrast to percentile-based methods, outliers are identified based on the entire
 250 data distribution (location and spread).

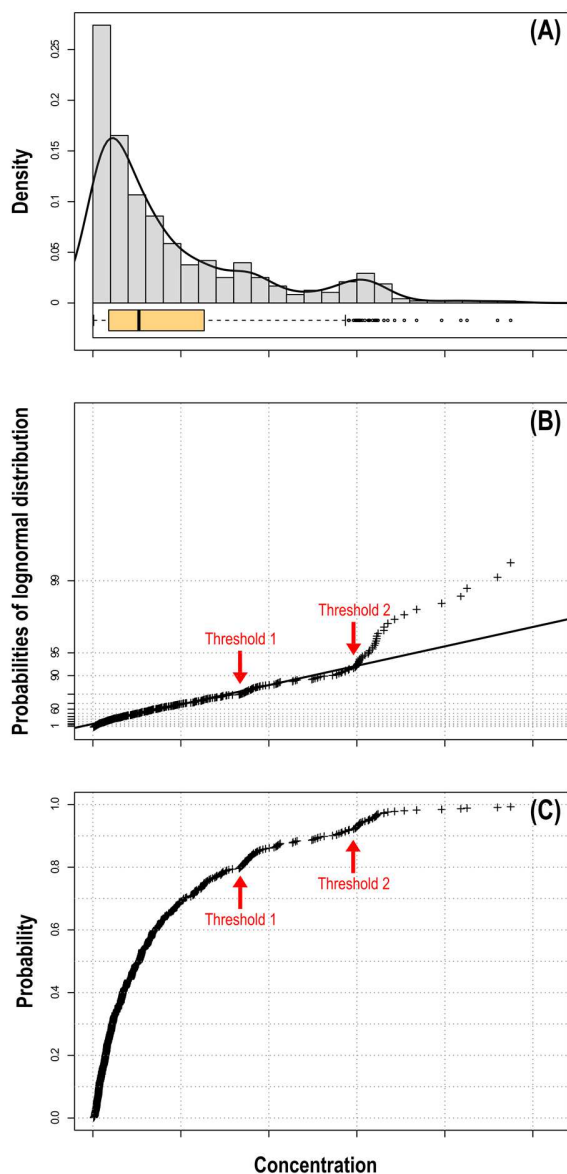


Fig. 2. Combination of (A) histogram, density trace and boxplot, (B) CP plot, and (C) ECDF plot for a randomly-generated dataset ($n = 500$) with a right-skewed distribution typical of geochemical variables.

2.3.2. Model-based methods

Model-based methods are based on the assumption that natural data follow an underlying theoretical distribution that is altered by anthropogenic influences. Natural data are assumed to correspond to the lowest values, whereas anthropogenically influenced data are expected to produce higher and more extreme values (right tail of the distribution)
 255 (Urresti-Estala et al., 2013; Wendland et al., 2005). The common objective of model-based methods is to model the shape of the natural distribution, from which background values can be calculated.

260 The component separation (CS) method assumes that the observed concentration distribution is a mixture of two overlapping populations representing the natural and anthropogenic contributions (Chidichimo et al., 2020; Molinari et al., 2012; Rotiroti et al., 2015; Wendland et al., 2005). In the CS method, the natural population is modeled by a log-normal distribution, while the anthropogenically influenced population is modeled by a normal distribution (Fig. 3A). As illustrated in Fig. 3A, different anthropogenic sources can theoretically produce distinct anthropogenically influenced populations, each modeled by a normal distribution. The forms of the theoretical distribution functions are not known *a priori*, and have to be fitted to the observed data distribution using appropriate statistical techniques (e.g. maximum likelihood estimation; Molinari et al., 2012; Rotiroti et al., 2015). The natural background values are calculated based on the modeled distribution of the natural contribution as the concentration range defined by the 10% and the 90% percentiles (Rotiroti et al., 2015; Wendland et al., 2005). A fundamental limitation of this approach is that there is no *a priori* reason that natural geochemical data follow a log-normal distribution (Reimann and Filzmoser, 2000). In addition, fitting the observed distribution can be subject to significant uncertainty, in particular with a limited number of data and when the natural and anthropogenic contributions largely overlap.

270 The iterative 2σ technique and the calculated distribution function both reduce the original dataset to approach a normal range (Amiri et al., 2021; Gao et al., 2020a; Koh et al., 2009; Matschullat et al., 2000; Nakić et al., 2007; Urresti-Estala et al., 2013). The iterative 2σ technique constructs an approximated normal distribution around the mode of the original dataset (Matschullat et al., 2000). The normal distribution is approached by iteratively removing the values lying outside the mean $\pm 2\sigma$ interval. The background range is determined as the mean $\pm 2\sigma$ range once all residual values lie within this interval. The iterative 2σ technique tends to yield conservative threshold values, particularly for right-skewed data (Fig. 3B). This technique is not valid for data following a polymodal distribution (Nakić et al., 2007). The calculated distribution function constructs an approximated normal distribution around the median of the original dataset. For this purpose, the values above the median are removed and all remaining values are being mirrored against the original median value by adding the distance from the individual value to the median (Matschullat et al., 2000; Nakić et al., 2007). The mean $\pm 2\sigma$ is taken as the natural background. The obtained distribution will be approximately normal if the original distribution is close to symmetry. However, for right-skewed data, the modeled distribution shows an inappropriate bimodal character (Fig. 3C). This method requires that the majority of data are unaffected by human influence (Nakić et al., 2007; Urresti-Estala et al., 2013). For both the iterative 2σ and calculated distribution function methods, statistical tests can be performed to evaluate the goodness of fit to a normal distribution (Nakić et al., 2007; Urresti-Estala et al., 2013). Here again, a fundamental limitation of these methods is that there is no *a priori* reason that natural geochemical data follow a normal distribution (Reimann and Filzmoser, 2000). Moreover, these methods provide background values without consideration of the original data distribution and should not be applied without a critical evaluation of the results.

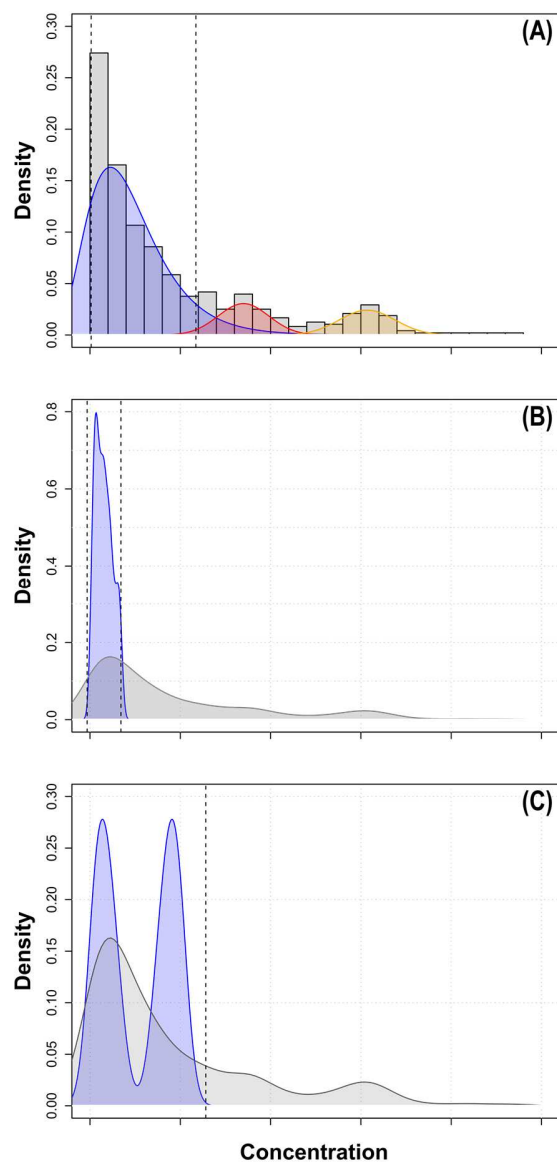


Fig. 3. Application of the (A) component separation, (B) iterative 2σ and (C) calculated distribution function techniques to a random distribution (see Fig. 2). Gray curve = random distribution, blue curve = background population, red and orange curves = anthropogenic populations, dashed lines = lower and upper thresholds.

3. Case studies

To illustrate the estimation of background concentrations for natural groundwater constituents, two case studies were conducted using exploratory data analysis techniques for geogenic fluoride in aquifers located in Alberta and Quebec, Canada.

3.1. Aquifers in south-central Alberta

3.1.1. BWWT database

The Baseline Water Well Testing (BWWT) database contains baseline groundwater chemistry data collected between 2006 and 2020 (mainly in 2011) in coalbed methane (CBM) production areas in south-central Alberta, Canada. In Alberta, CBM companies are required to test shallow groundwater (<150 m) obtained from water wells adjacent to future CBM wells that are to be completed above the base of groundwater protection (i.e. the base of non-saline groundwater with <4000 mg/L total dissolved solids) (Alberta Energy Regulator, 2006a). The BWWT groundwater samples were mostly obtained from domestic and agricultural wells located in the Edmonton-Calgary corridor (Humez et al., 2019) (Fig. 4). Central and south-central Alberta is underlain by Upper Cretaceous to late Paleogene sedimentary formations of the Western Canada Sedimentary Basin (Dawson et al., 1994). In the study area, the majority of groundwater wells produce from fractured bedrock aquifers formed by the Scollard-Paskapoo and Horseshoe Canyon Formations. The Horseshoe Canyon, Scollard and Paskapoo Formations consist of siliciclastic rocks composed mainly of sandstone, siltstone, mudstone and shale that are frequently associated with coal beds. A number of sampled groundwater wells are also completed in Quaternary glacial and glaciofluvial deposits composed of silt, sand and gravel. More information about the geological formations and aquifer units of the region can be found in Cheung et al. (2010), Dawson et al. (1994) and Grasby et al. (2008). Groundwater sampling and analysis were performed following a standard protocol established by the government of Alberta (Alberta Energy Regulator, 2006b, 2006c). The BWWT data were subject to quality control procedures that included 1) database queries for the identification and removal of duplicate samples, and 2) the calculation of charge balances and the selection of samples within $\pm 10\%$. In addition, groundwater samples collected outside the Calgary-Edmonton corridor were excluded ($n = 565$), as the sampling sites were too sparse to provide statistically representative data. The validated database includes field measurements of temperature, pH, electrical conductivity and dissolved oxygen, and dissolved concentrations of HCO_3 , CO_3 , Cl, SO_4 , F, $\text{NO}_3+\text{NO}_2\text{-N}$, Ca, Mg, Na, K, Fe and Mn for 13,357 groundwater samples (Table S1). HCO_3 and CO_3 concentrations were calculated from alkalinity and pH using the llnl database in PHREEQC (Parkhurst and Appelo, 1999). A statistical summary of the BWWT data is provided as supplementary material (Table S1).

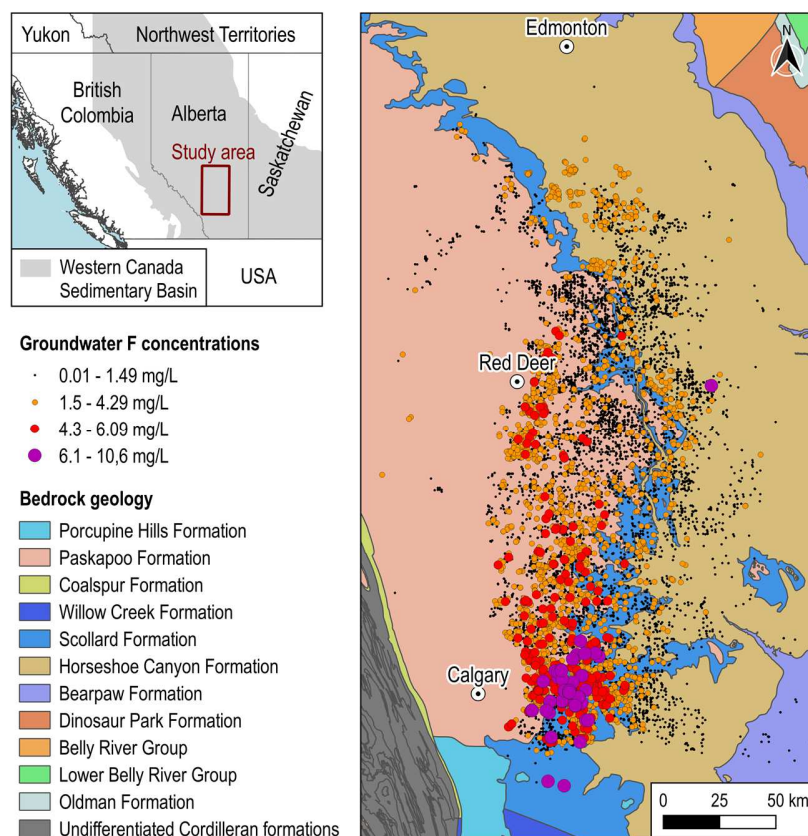


Fig. 4. Geochemical map showing the distribution of F concentrations in groundwater of south-central Alberta.

3.1.2. Natural background concentrations of fluoride in south-central Alberta groundwater

In the BWWT database, groundwater F concentrations range from below detection limits (as low as 0.01 mg/L) to 10.6 mg/L (Table S2). Dissolved F concentrations exceed the Canadian drinking water guideline and provincial standard of 1.5 mg/L in 3,169 of 13,357 groundwater samples (23.7%). The distribution of F concentration data is presented using a combination of histogram, density trace and boxplot in Fig. 5A, and a CP plot in Fig. 5B. As shown in Figs. 5A and 5B, F concentrations approximately follow a log-normal distribution below a concentration of 4.3 mg/L. The CP plot shows two major inflection points at F = 4.3 mg/L and F = 6.1 mg/L, suggesting the existence of three data populations (Fig. 5B). Geochemical mapping shows groundwater F concentrations in the range of 1) 0.01-4.3 mg/L in the Horseshoe Canyon aquifer (excluding the extreme value of 10.6 mg/L), 2) 0.01-6.1 mg/L in the Paskapoo-Scollard aquifer, and 3) 0.01-10.2 mg/L in a limited area of the Paskapoo-Scollard aquifer east of Calgary (Strathmore area) (Fig. 4). This spatial pattern is likely related to lithological characteristics of the aquifer units, although further investigations would be required to identify the mineralogical sources of F in groundwater. Moreover, there is a good relationship between groundwater F concentrations and most major dissolved constituents. As shown in Fig. 6, F is positively correlated with Na, HCO₃ and Cl, and negatively correlated with Ca, Mg and Mn. These correlations and the calculation of saturation indices for fluorite

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suggest that groundwater F concentrations are largely controlled by the solubility of fluorite (CaF_2) (Fig. 6 and Fig. S1), which is a well-documented process in groundwater (Chae et al., 2007; Edmunds and Smedley, 2013; Hitchon, 1995). In alkaline groundwater, the desorption of F from mineral surfaces is likely to be an additional mechanism resulting in increasing F concentrations. Hence, F concentrations were found to be closely related to the groundwater type, which is largely determined by the geochemical evolution of groundwater. In south-central Alberta, shallow groundwater typically evolves from near-neutral Ca-Mg- HCO_3 - SO_4 waters to alkaline Na- HCO_3 and Na-Cl waters, mostly as a result of cation exchange of Ca for Na, silicate weathering and mixing with saline formation waters (Cheung et al., 2010; Humez et al., 2016). Therefore, dissolved F concentrations are low in poorly to moderately evolved Ca-rich groundwaters due to fluorite precipitation, and increase in more geochemically evolved Ca-depleted alkaline groundwaters that are undersaturated with

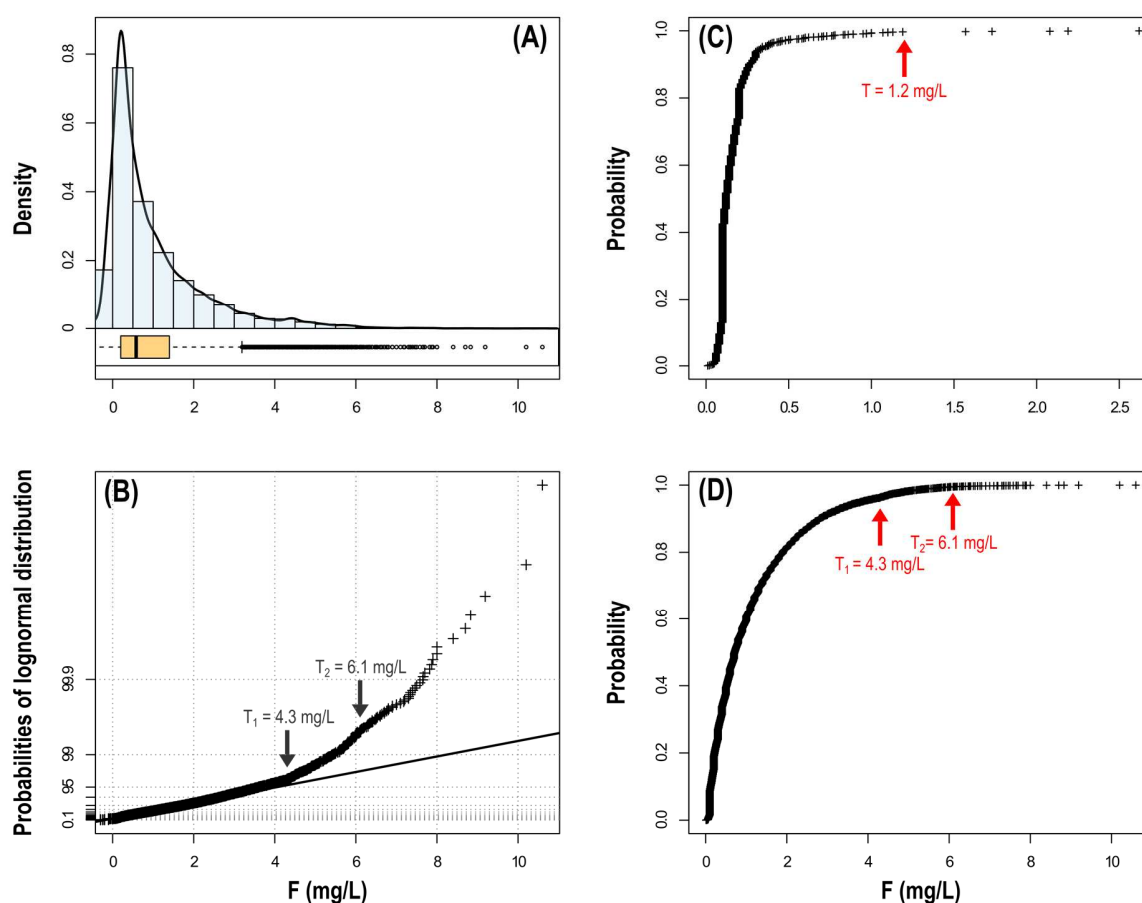


Fig. 5. A) Combination of histogram, density trace and boxplot and B) CP plot for the whole BWWT data (n = 13,357), C) ECDF plot for poorly to moderately evolved Ca-rich groundwater (n = 1,668), and D) ECDF plot for evolved to highly evolved Ca-depleted groundwater (n = 11,689).

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respect to fluorite.

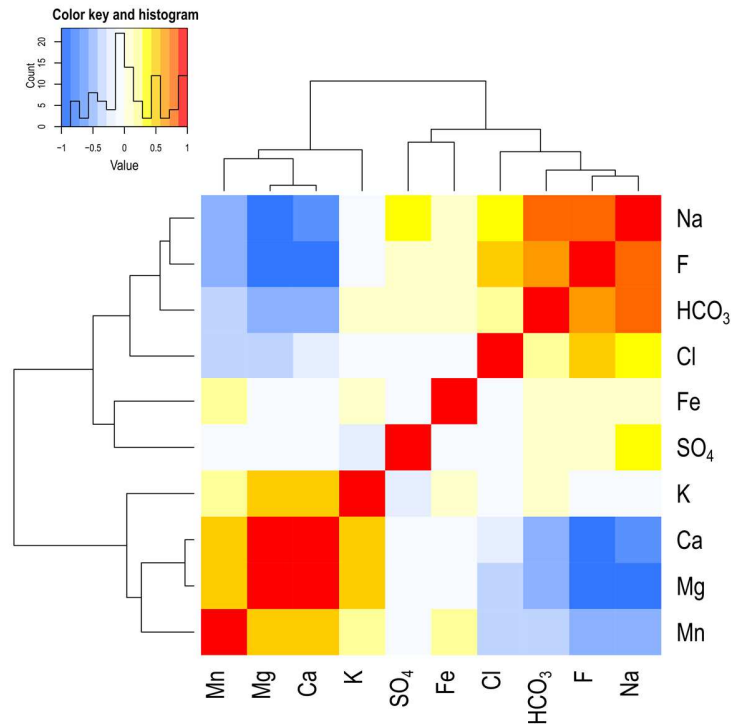


Fig. 6. Correlation heat-map for BWWT samples ($n = 13,357$). The heat-map shows the Spearman correlation coefficients for symmetric coordinates, as described in Bondu et al. (2020). Only hydrochemical variables with less than a third of non-detects are presented to avoid artifacts associated with a high proportion of data with an identical value (DL/2).

Threshold F concentrations were estimated for different groundwater bodies, as determined based on major groundwater types and aquifer units:

1) *Poorly to moderately evolved Ca-rich groundwater of the Horseshoe Canyon, Scollard-Paskapoo and surficial aquifers.*

345 This category includes 1,668 samples, mainly of Ca-Mg-HCO₃, Ca-HCO₃, Ca-Mg-HCO₃-SO₄, Ca-Mg-Na-HCO₃, Ca-Mg-Na-HCO₃-SO₄, Ca-Mg-Na-SO₄, Ca-Na-HCO₃, Ca-Na-HCO₃-SO₄ and Ca-Na-SO₄ water types. The ECDF plot of F concentration for poorly to moderately Ca-rich groundwater is presented in Fig. 5C. The distribution of F concentrations shows a threshold at $F = 1.2$ mg/L, separating five extreme outliers from the main body of data.

2) *Evolved to highly evolved Ca-depleted groundwater*, including 11,689 samples of Na-SO₄, Na-HCO₃-SO₄, Na-HCO₃, 350 Na-HCO₃-SO₄-Cl, Na-HCO₃-Cl and Na-Cl types.

a. Horseshoe Canyon aquifer. The ECDF plot of F concentration for evolved to highly evolved Ca-depleted groundwater is shown in Fig. 5D. In agreement with the geochemical map (Fig. 4), the upper limit of groundwater F concentrations in the Horseshoe Canyon aquifer corresponds to the threshold of 4.3 mg/L (Fig. 5D).

b. Scollard-Paskapoo aquifer. The upper limit of groundwater F concentrations in the Scollard-Paskapoo aquifer 355 corresponds to the threshold of 6.1 mg/L, with the exception of the Strathmore area (Fig. 4 and Fig. 5D). For the Strathmore

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area, a threshold value of 8.0 mg/L was derived after the exclusion of 5 extreme outliers, although additional data would be necessary to confirm the relevance of excluding these extreme values.

c. Surficial aquifers. Only 70 samples containing evolved Ca-depleted groundwater were identified as originating from surficial aquifers. Additional samples from surficial aquifers are needed to estimate natural background values, in particular above a range of bedrock formations.

Table 1
Natural background values of fluoride concentrations for selected groundwater bodies in south-central Alberta

Groundwater composition	Aquifer units		
	Horseshoe Canyon	Scollard-Paskapoo	Surficial deposits
Poorly to moderately evolved Ca-rich groundwater		0.01-1.2 mg/L	
Evolved to highly evolved Ca-depleted groundwater	0.01-4.3 mg/L	0.01-6.1 mg/L (0.01-8.0 mg/L; Strathmore area)	Insufficient data

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The estimated background values indicate a geogenic fluoride contamination in groundwater from bedrock aquifers of south-central Alberta resulting in a number of cases in F concentrations above the drinking water guideline. Considering the occasionally elevated F levels, further investigations would be required to better understand the sources and distribution of fluoride in groundwater, particularly in the Paskapoo-Scollard aquifer. Groundwater F concentrations are a potential public health concern, particularly for the rural population relying on unregulated private water supplies. This case study demonstrates the relevance of combining EDA techniques to derive natural background concentrations using an extensive groundwater chemistry database. The EDA approach provides a simultaneous evaluation of F sources, groundwater body delineation and natural background values. However, there is no justification to exclude anthropogenically-contaminated samples while F is thought to be only of natural origin. In absence of other selection criteria, applying the PS method using NO₃ concentrations would have led to the exclusion of a number of Ca-rich oxidizing water samples and a bias in the estimation of F threshold values. In the region, establishing natural background concentrations for groundwater constituents is valuable for assessing the potential impacts of hydrocarbon exploitation on groundwater quality.

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3.2. Aquifers in western Quebec

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3.2.1. BADGEQ database

The Quebec Geochemical database (BADGEQ) contains groundwater chemistry data collected to guide exploration for economic mineral deposits in several areas of the Province of Quebec, Canada. In this case study, we used the BADGEQ data collected between 1974 and 1976 in an area of about 20,000 km² in the Abitibi region (western Quebec), which is one of the most important areas for precious and base metal mining in Canada (Lalonde et al., 1980; Lalonde and Chouinard,

1983). Geologically, the study area is mainly underlain by Archean volcanic and metasedimentary rocks intruded by granitoids of the Abitibi Greenstone Belt (Abitibi Subprovince), in the southern part of the Superior Province of the Canadian Shield (Hocq, 1994) (Fig. 7). The extreme southern part of the study area lies on the Pontiac Subprovince, which is dominated by Archean metasedimentary rocks intruded by granitoids and gneiss (Hocq, 1994) (Fig. 7). The bedrock is covered by discontinuous Quaternary deposits consisting mostly of glaciolacustrine clay-silt and glaciofluvial sand-gravel sediments. More information on the hydrogeological context of the Abitibi region can be found in Cloutier et al. (2016), Nadeau et al. (2018) and Rey et al. (2018). The BADGEQ database is the most extensive database related to groundwater quality in the Abitibi region with more than 4,700 groundwater samples. Groundwater samples were mainly obtained from private domestic wells and to a lesser extent from exploratory drill holes and natural springs, in both bedrock formations and Quaternary deposits. Details on the sampling protocol and analytical methods are provided in Lalonde (1983) and Lalonde and Chouinard (1983). Quality control procedures included the removal of samples collected without well purging (n = 198) and from sampling sites outside the study area (n = 5). The validated database includes temperature and pH measurements, and dissolved concentrations of Cl, Si, F, B, PO₄-P, Ca, Mg, Na, K, Sr, Fe, Mn, Al, As, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, U and Zn for 4,561 samples (Table S2). A statistical summary of the BADGEQ data is provided as supplementary material (Table S2).

3.2.2. Natural background concentrations of fluoride in Abitibi groundwater

In the BADGEQ database, groundwater F concentrations ranged from 0.013 to 1.76 mg/L, exceeding the Canadian drinking water guideline and provincial standard of 1.5 mg/L in only five out of 4,421 samples (Table S2). The distribution of log-transformed F data is presented using a combination of histogram, density trace and boxplot in Fig. 8A, and a CP plot in Fig. 8B. As shown in Fig. 8A, the log-transformed F concentration data show a near-symmetrical distribution around the median value of 0.11 mg/L. The CP plot shows the presence of two breaks followed by inflection points, a subtle break and inflection at F = 0.28 mg/L and a more obvious break and inflection at F = 0.65 mg/L (Fig. 8B). However, it is not clear which inflection point can be considered as a meaningful upper limit of the background.

Fig. 7 shows the spatial repartition of F concentrations in groundwater on a simplified map of the bedrock geology. Groundwater F concentrations above 0.28 mg/L were associated with bedrock groundwater within and immediately adjacent to intrusive bodies of magmatic rocks such as granodiorite, monzonite, monzodiorite and tonalite. In contrast, groundwater F concentrations were below 0.28 mg/L in surficial aquifers (i.e. glaciofluvial and glacial deposits) and bedrock aquifers distant from magmatic intrusions. In contrast to Alberta groundwater, dissolved F concentrations are not significantly correlated with the concentrations of major dissolved constituents and do not appear to be controlled by the solubility of fluorite. Elevated F concentrations generally occur in moderately mineralized Ca-Na-HCO₃ groundwater

410 typical of aquifers composed of felsic to intermediate intrusive rocks (Fig. S2). This suggests that groundwater F concentrations are primarily controlled by the mineralogical composition of the bedrock. Elevated F concentrations are thought to be derived from fluorite-bearing veins associated with magmatic intrusions, although F can also be derived from primary mineral sources such as hornblende and biotite (Chae et al., 2007; Edmunds and Smedley, 2013). The threshold of 0.65 mg/L F likely reflects the occurrence of fluorite mineralization, but further investigations are needed to identify precisely the mineralogical sources and mobilization mechanisms of F in groundwater. Therefore, the value of 0.28 mg/L would be a conservative threshold for regional groundwater, given the spatial extension of intrusive rocks. The value of 0.65 mg/L F is a more appropriate threshold at the regional scale, providing a clear indication of natural geochemical anomalies and potential future anthropogenic pollution (e.g. mining effluents, phosphate fertilizers; Fuge, 2019).

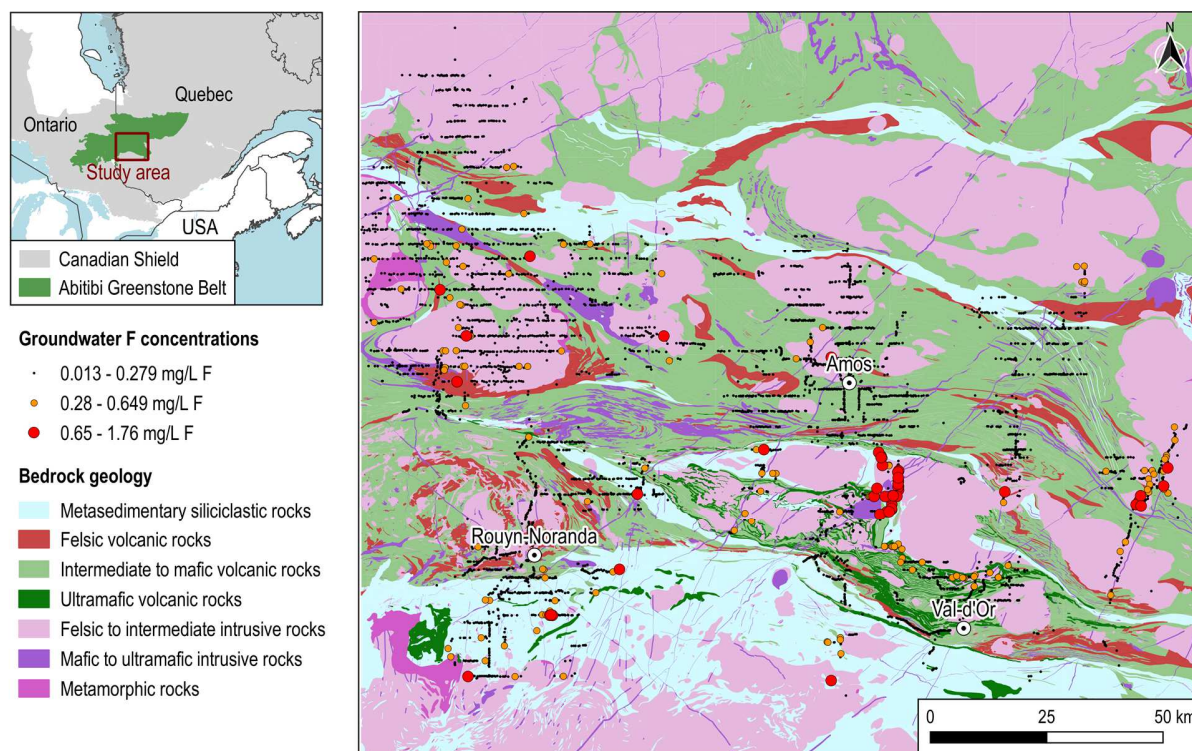


Fig. 7. Geochemical map showing the distribution of F concentrations in groundwater of the Abitibi region.

420 The natural background values indicate that naturally-high F concentrations are not a public-health concern in the region, in contrast to naturally-high As and Mn concentrations (Bondu et al., 2018, 2017). However, there is a risk of deficiency-related health problems, as background F concentrations are well below the optimal level in drinking water of 0.7 mg/L recommended by Health Canada (Health Canada, 2019). In that respect, it is important to inform the rural population relying on groundwater for drinking water so that people can ensure sufficient fluoride intake from other sources. This case study highlights the importance of investigating the spatial distribution of groundwater constituents for

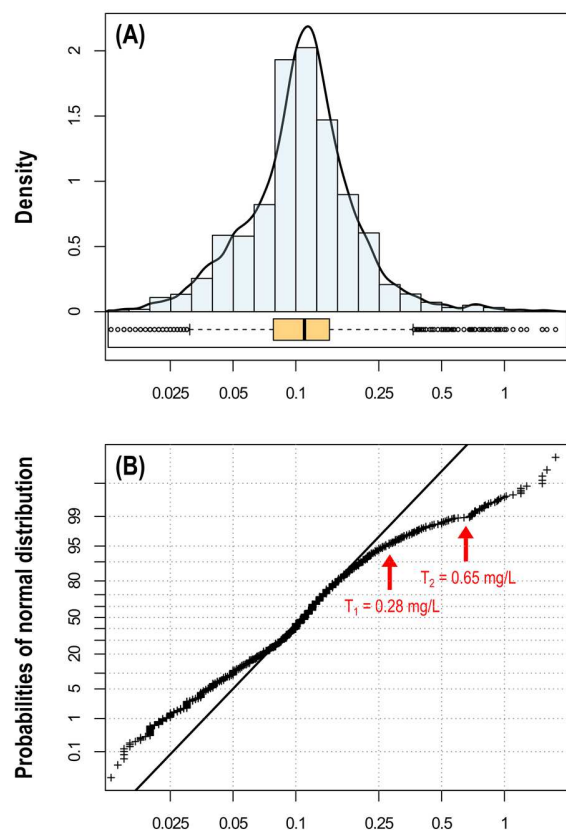


Fig. 8. A) Combination of histogram, density trace and boxplot and B) CP plot for the BADGEQ data ($n = 4421$).

estimating natural background values. If a threshold of 0.28 mg/L would probably be estimated for a small area dominated by volcanic-metasedimentary rocks and surficial deposits, a threshold of 0.65 mg/L is more appropriate at the regional scale. In the Abitibi region, determining natural background concentrations for groundwater constituents can be useful to set regulatory levels of contaminants in mining and hydrometallurgical effluents.

430 4. Concluding remarks

This critical review shows that there is no universal method to determine the natural background concentrations of groundwater constituents. Each method has its own advantages and limitations, and should be selected based on the available groundwater chemistry data and understanding of the groundwater system, but also on the sources of the constituents of interest in the studied area:

435 1) *Purely anthropogenic substances.* These substances are not present in the natural environment and occur only in anthropogenically-contaminated groundwater. Purely anthropogenic substances include a wide range of synthetic organic compounds such as industrial compounds, pharmaceuticals and pesticides. Their natural background concentrations are theoretically zero, but in practice the detection limit can be used as the threshold value.

2) *Substances from both natural and anthropogenic sources*. These substances are generally present at limited concentrations in natural groundwater, while elevated concentrations result usually in part from anthropogenic contamination. Typical examples of such groundwater constituents include nutrients such as NO₃ and PO₄, major inorganic constituents such as Cl, SO₄ and K, and trace elements such as Cr, Cu and Zn. Determining natural background values is important to assess the current contamination of groundwater, assess public-health risks and set realistic remediation goals. Different approaches can be applied to estimate the natural background for such constituents including pre-selection methods, model-based approaches and exploratory data analysis.

3) *Purely natural substances*. These groundwater constituents are derived exclusively from natural sources. This may particularly be the case for inorganic constituents such as F, As, Mn, Ba, B and radionuclides such as ²²²Rn and ²²⁶Ra. Estimating their natural background is useful to distinguish between natural anomalies and potential future anthropogenic contamination, assess public-health risks and establish realistic regulatory levels. The most suitable method for estimating threshold values for naturally-occurring constituents is exploratory data analysis, whereas pre-selection and model-based methods are not suitable for such purposes.

The determination of natural background concentrations should always be based on a solid understanding of the processes controlling groundwater quality. In that respect, previous knowledge of the geology (structure, lithology, mineralogy, geochemistry), hydrogeological settings, hydrometeorology, groundwater chemistry, anthropogenic activities and land use is of critical importance (Preziosi et al., 2010; Rotiroti et al., 2015). Moreover, natural background values should be established using a statistically representative number of samples, in the range of hundreds of samples for local-scale studies and thousands of samples for regional-scale studies. The compilation of existing groundwater data provides a good opportunity to obtain extensive hydrochemical datasets (e.g. Biddau et al., 2017; De Caro et al., 2017). In addition, groundwater data from monitoring programs can be valuable to take into account the temporal variability of groundwater constituents in the estimation of natural background concentrations (e.g. Guadagnini et al., 2020; Kim et al., 2015; Molinari et al., 2014). Natural background concentrations are to be estimated for well-defined groundwater bodies that should be delineated based on easily available parameters such as physical (e.g. geology, topography) and geochemical variables (e.g. major ion concentrations, physico-chemical parameters). In contrast, groundwater bodies should not be delineated using complex and costly analyses (e.g. age tracers), as well as hardly reproducible statistical methods (e.g. cluster analysis). This is important for ensuring that the method can be easily replicated by other researchers and practitioners. These findings may have implications for the determination of natural background values for a large range of groundwater constituents including common groundwater contaminants such as nitrate, fluoride and metals/metalloids as well as methane and higher hydrocarbon gases in areas of oil and natural gas development from unconventional hydrocarbon resources (Bondu et al., 2021; Humez et al., 2019). More studies are needed to estimate the background concentrations of different groundwater

470 constituents using a range of methodological approaches. In addition, further efforts should be made to predict the spatial distribution of natural background values in large-scale groundwater bodies (Guadagnini et al., 2020; Molinari et al., 2019). Geostatistical approaches have been recently developed to assess the spatial distribution of the probability that background values exceed a given threshold by including uncertainty quantification (Guadagnini et al., 2020; Menafoglio et al., 2021; Molinari et al., 2019). Moreover, future research needs to consider the compositional nature of groundwater chemistry data 475 in the calculation of natural background concentrations (Herms et al., 2021; Nisi et al., 2016). Finally, it is important to keep in mind that natural background concentrations are theoretical values, due to their spatio-temporal variability and scale dependence, and should be viewed as concentration values above which further investigation is required to determine the sources of groundwater constituents at a given site.

CRediT authorship contribution statement

480 **Raphaël Bondu:** Conceptualization, Formal analysis, Data curation and interpretation, Validation, Visualization, Writing - Original Draft, Writing - Review & Editing. **Pauline Humez:** Conceptualization, Data curation and interpretation, Validation, Writing - Review & Editing. **Bernhard Mayer:** Writing - Review & Editing, funding acquisition. **Emeline Chaste:** Software, Visualization, Writing - Review & Editing. **Maria O. Naumenko-Dèzes:** Writing - Review & Editing. **Vincent Cloutier:** Writing - Review & Editing. **Eric Rosa:** Writing - Review & Editing. **Wolfram Kloppmann:** Funding 485 acquisition, Project administration, Writing - Review & Editing.

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