Marine Pollution Bulletin 174 (2022) 113303

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Assessment of chloride natural background levels by applying statistical approaches. Analyses of European coastal aquifers in different environments

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ARTICLE INFO

Keywords:
Natural background level
Chloride concentration
Saltwater intrusion
Coastal aquifers
European pilots

ABSTRACT

Estimated natural background levels (NBLs) are needed to assess groundwater chemical status according to the EU Groundwater Directive. They are commonly derived for different substances by applying statistical methodologies. Due to the complexity of the sea water intrusion process, some of those methods do not always provide appropriate assessment of chloride NBLs. This paper analyzes the applicability of different NBL estimation methods in five EU coastal aquifers with significant differences in available datasets and hydrogeological settings. A sensitivity analysis of results to different constraints was performed to remove samples with anthropogenic impacts. A novel statistical approach combining different methods to identify the range of chloride NBLs is proposed. In all pilots the estimated NBLs were below 85 mg/L and fitted well with previous studies and expert judgment, except Campina del Faro aquifer (the maximum being 167.5 mg/L). Although this approach is more time consuming, it provides a more robust solution.

1. Introduction

The prerequisite for appropriate assessment of anthropogenic impacts on groundwater quality and the advance of young potentially contaminated groundwater in aquifer systems (Hinsby et al., 2001) is identification of natural groundwater composition by establishment of natural background levels (NBLs) (Hinsby et al., 2008; Li et al., 2021; Menafoglio et al., 2021) and fingerprinting sources of contamination or elevated concentrations (Knudsen et al., 2021). This study defines NBL as "the concentration of substance or the value of an indicator in a body of groundwater corresponding to no, or only very minor, anthropogenic alterations to undisturbed conditions" according to the EU Groundwater Directive (GWD; EC, 2006). Even though the term "background" does not always have a coherent meaning across the studies (De Caro et al., 2017; Edmunds and Shand, 2008), the definition provided by Matschullat et al. (2000) as "relative measure to distinguish between natural and anthropogenically influenced concentrations" refers well to the general interpretation of the term.

As stated by Apello and Postma (2005), chemical composition of groundwater is a result of all the processes between water, minerals and gasses it has been in contact from recharge to discharge areas. Such natural factors as climate, rainfall composition and frequency,

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https://doi.org/10.1016/j.marpolbul.2021.113303
Received 13 May 2021; Received in revised form 9 December 2021; Accepted 25 December 2021
Available online 7 January 2022

biochemical processes in the vadose and unsaturated zone, evapo-concentration in the soil due to climatic factors, water-rock interaction and residence time, as well as water mixing contribute to the presence (or absence) of various inorganic compounds in groundwater (Edmunds and Shand, 2008; Hinsby and Rasmussen, 2008; Preziosi et al., 2010; Retike et al., 2016; Sellerino et al., 2019). In addition to natural factors, human activities may also affect the groundwater quality. For instance, significant groundwater pumping may modify the extension of the freshwater domain and initiate the water mixing (i.e., diffusion and dispersion of seawater intrusion into freshwater aquifers) (Bikše and Retike, 2018). The irrigation return flows with contaminants used in agriculture, the recharge coming from allochthonous water in floods, and any infiltrated water pollution due to industry and the pollution released from urban areas can modify natural conditions. While occurrence of some substances in groundwater such as pesticides is a direct indicator of human impact, inorganic components (i.e., trace metals) may originate from both natural and anthropogenic sources (Biddau et al., 2017). Urresti-Estala et al. (2013) highlight that the large number of factors responsible for the final groundwater composition means that differentiation between natural conditions and human introduced changes is a highly challenging task accompanied by many errors and uncertainties.

The EU Water Framework Directive (WFD; EC (European Commission), 2000) and the daughter GWD require Member States to evaluate the chemical status of groundwater bodies (GWBs) against threshold values (TVs) locally derived by individual Member States. Threshold values must be established for all pollutants that were identified as putting GWB at risk of failing environmental objectives and should not be exceeded to protect human health and dependent environment (Hinsby et al., 2008). The minimum list of parameters indicative for saline or other intrusions that should be considered in the TV derivation process includes electrical conductivity, sulfates, and chlorides (EC, 2006). Later TVs are used as criteria to test whether GWB is at good status (Bulut et al., 2020; De Caro et al., 2017) and may be used as part of criteria for identification of upward trends (worsening of the status) or the starting point for trend reversal (status improvement) (Hinsby et al., 2008). The provisions of GWD on the chemical status of a GWB only apply to anthropogenically altered conditions, thus a fundamental first step in establishing TVs is to derive NBLs. The NBLs should be derived for substances which can naturally occur in a range of concentrations at different hydrogeological conditions (Voutchkova et al., 2021a, 2021b) meaning that NBLs for synthetic substances are automatically set as zero (Müller et al., 2006).

In the last decade various EU research projects have focused on the development and testing of pre-selection methods (PS) to establish and assess NBLs and TVs, for example the EU BaSeLiNe or the BRIDGE projects (Müller et al., 2006). They were the EU-wide response to the identified need for scientific and rational approaches to define groundwater quality standards and evaluate the effectiveness of potential programs of measures. The BRIDGE project (Dahlstrom and Müller, 2006) proposed a methodology to derive groundwater TVs based on both NBLs and environmental quality standards (Müller et al., 2006). Pre-selection methods try to identify and remove the samples influenced by humans using high concentrations of substances (like nitrates) as indicators for contamination. This approach often leads to the significant reduction of the initial dataset (Masciale et al., 2021). Meanwhile, other NBL establishment approaches based on statistical and sample distribution analysis have been developed (Griffioen et al., 2008; Walter et al., 2012). Some statistical methods, also called Component Separation (CS) methods (De Caro et al., 2017), aim to identify and separate the natural and anthropogenic populations by application of statistical procedures. Efforts to automatize the applications of statistical methods for groundwater were made in 2005 by the working group 'groundwater background values' from the EU-WRRL (UAG EU-WRRL) task force of the Geological Surveys of the Federal States of Germany (SGD&BGR). An automated Excel-tool to determine geogenic background values using probability plots (PP) was developed (Walter, 2006). However, it is not possible to separate an anomaly from a given set of samples if the process that generated it has been integrated into the normal population (Kunkel et al., 2004). Both PS and CS methods have a certain degree of subjectivity, while the integration of the two methods is recommended to reinforce the validity of the assessment (Parrone et al., 2019; Preziosi et al., 2014). Nevertheless, the analysis of NBLs of chloride (Cl), whether based on PS or CS methods, is useful to study seawater intrusion (SWI) in coastal aquifers around the world (Custodio, 2010; García-Menéndez et al., 2016).

Different processes have caused aquifer salinization and have been discussed within the literature for both coastal and non-coastal aquifers (Burlakovs et al., 2020; Greene et al., 2016; Marandi and Karro, 2008). Salinization process has been commonly observed in coastal areas (typically observed as high chloride and/or sulfate content) with significant water demands due to large populations, intensive agricultural and/or industrial activities (Renau-Pruñonosa et al., 2016). In coastal areas where water supply partly or fully relies on the fresh groundwater resources, the saltwater intrusion may result in significant socio-economic impacts (Sola et al., 2013). The impacts may be exacerbated due to increase in drought events frequency, length, and severity as predicted climate change scenarios (Collados-Lara et al., 2018; Vera et al., 2012).

The NBL of Cl can vary significantly from one aquifer to another. For example, the NBL of Cl in aquifers of Finland or Latvia may be below 10 mg/L or 13.2 mg/L, whereas it may reach up to 200 mg/L in aquifers located in Portugal (Hinsby et al., 2008; Retike and Bikše, 2018). The spatio-temporal distribution of Cl or salinity can be approximated by different methods. Some studies apply simple interpolation/geo-statistical methods to generate salinity maps for specific time periods (Baena-Ruiz et al., 2018, 2020). Other studies use sharp interface solutions to simulate (Llopis-Albert and Pulido-Velazquez, 2014, 2015) the dynamics of the SWI. The use of density-dependent solutions for groundwater flow investigations is also common (Pulido-Velazquez et al., 2018).

The aim of this paper is to improve the assessment of human induced saltwater intrusion by presenting and comparing different pre-selection and statistical approaches used for derivation of NBLs for Cl from available observations, and by discussing the application possibilities and limitations for various hydrogeological settings across Europe. This work is based on five case studies conducted in coastal aquifers of the Atlantic Sea, the Mediterranean Sea, The North Sea, and the Baltic Sea. A detailed sensitivity analysis of the NBLs for different hypotheses (constraints proposed to remove samples affected by anthropogenic impacts) was performed. Based on the results of this sensitivity analysis a novel approach, combining the results from modified statistical methods to identify in a consistent way a feasible range of NBLs for Cl, is proposed. Its applicability has been demonstrated in five coastal aquifers across Europe.

2. Method

The steps defined to apply the proposed method are summarized in Fig. 1 and explained below.

2.1. Cl data compilation and statistical analysis

A basic statistical analysis of the distribution of Cl samples was performed. Box-whiskers plots were generated for two variables: (1) the Cl concentration measurements available for each pilot and (2) the number of chemical analyses in each sampling point that is employed to assess the reference value in each observation well. Frequency distribution of the median Cl concentration at the sampling points (mg/L) for each pilot was plotted. Later this initial data-analysis helped to explain the differences in the NBLs for Cl obtained with different approaches in the selected pilots.

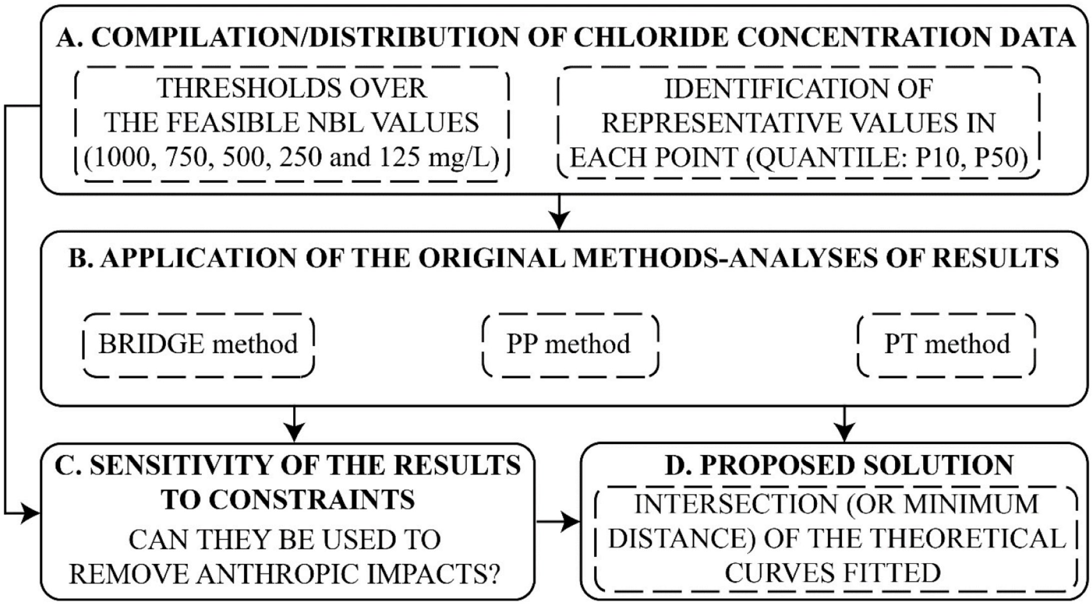

Fig. 1. Flowchart of the methodology.

2.2. Application of the selected original methods

Three common statistical approaches for deriving NBLs were applied in each pilot: the PS based BRIDGE method (Coetsiers and Walraevens, 2006) and two CS based methods, the PP based approach (Walter, 2011) and the method used in Portugal (PT method) (Fernandes and Almeida, 2018). These methods were not specifically designed for Cl concentrations, but they have been widely used to identify uncontaminated samples in a mixed population of trace elements (Tobías et al., 1997) and nitrates (Albo and Blarasin, 2014; Panno et al., 2006).

The BRIDGE method has been extensively applied (Dalla Libera et al., 2017; Ducci and Sellerino, 2012; Gemitzi, 2012; Hinsby et al., 2008; Marandi and Karro, 2008). Two major drawbacks have been reported. First, the nitrate and salinity data constraints (removing samples with nitrates above 10 mg/L or Na + Cl > 1000 mg/L) that might significantly reduce the number of observations in dataset and limit further application of the BRIDGE method (Hinsby et al., 2008). Second, the subjectivity in which percentile (90th or 97th has been adapted to establish NBLs (Griffioen et al., 2008). In addition, some BRIDGE applications have determined too high NBLs that do not correspond to the background values. Other research projects (e.g., HOVER WP3 project) recently made extra efforts to define and analyse NBLs and TVs (HOVER Report, 2020, Lions et al., 2021, Voutchkova et al., 2021a, 2021b).

The steps to apply the simplified BRIDGE method are as following:

Step 1: Pre-selection criteria to remove samples with incorrect ionic balance error (± 10%), taken from unknown depth and/or unknown aquifer type. Data from monitoring points with median nitrate concentration above 10 mg/L should be considered as polluted and excluded.

Step 2: Derivation of the NBL as the 90th or 97th percentile depending on the amount and quality of data. For small datasets ($n < 60$) or datasets where human impact cannot be excluded the 90th percentile is suggested.

The PP method may be used to partition or segregate a set of samples into its constituent populations by eliminating extreme values which could be considered as "anomalous" (Walter, 2011). Fig. 2 shows a hypothetical mixed population of samples with background and anomalous values. These are supposed to be affected by processes that modify natural conditions. In saltwater intrusion environments two populations are typically present; one corresponding to clean and uncontaminated fresh groundwater samples and the other corresponding to contaminated or saltwater intrusion affected samples at different degrees.

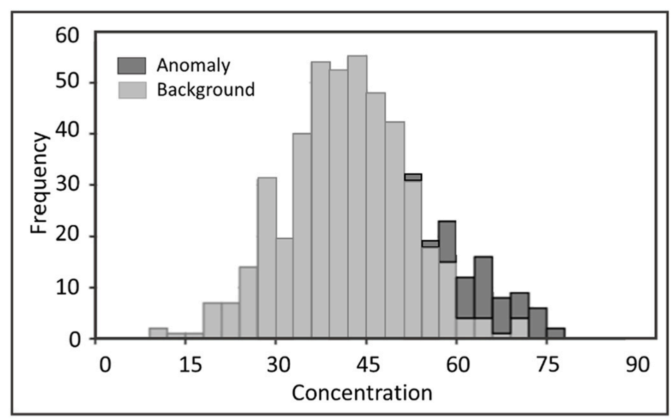

Fig. 2. Hypothetical mixed population of samples with background and anomalous values (Modified from Walter, 2011).

The PP is a simple graphical procedure to determine the distribution form of a random variable. To determine NBL, an iterative statistical process of exclusion of samples with anomalous values of the parameter (i.e., Cl) is performed until the normal distribution is achieved. The initial step uses all the available samples within the pilot area. To ensure that the time series at each sampling point do not bias the results and that all sampling sites contribute equally to the NBL calculation, time series are represented by median values (Hinsby et al., 2008). The steps for the PP method are:

Step 1: Histograms of frequency and cumulative probability plots are made. For the first iterative process, the 90th percentile is calculated and the data that exceed this value are excluded.

Step 2: Normality of the remaining samples is verified using the Shapiro-Wilk Test. Normal distribution is achieved when the *p*-value is ≥0.05.

Step 3: For p-value <0.05 normal distribution has not been achieved. Therefore, histograms of frequency and cumulative probability plots for the remaining samples are made and again samples above the 90th percentile are removed.

The iterative process stops when the distribution of the data has been normalized. The NBL is obtained from the samples that have remained by calculating the median of the parameter considered (i.e., Cl).

The PT method also relies on selection of a non-anomalous subset, based on 50% of the data centered on the median, eliminating high or low anomalous values to achieve the normal distribution. The NBL corresponds to the 95th percentile and not the median, admitting slightly higher values. The Q-Q plot, or quantile-quantile plot, is a graphical tool to help assess if a set of data has some theoretical distribution such as normal distribution. A scatterplot is created by plotting two sets of quantiles against each other: the quantiles of a sample against the theoretical quantiles of the normal distribution. If both sets of quantiles came from the same distribution, the points should form a straight 1:1 line. Although the visual check is somewhat subjective, it allows us to see which data points are not aligned and easily remove one by one until our variable is normally distributed. To check if the normal distribution model fits the observations, a normality test should be applied.

The steps for the PT method are:

Step 1: From the initial dataset, an interquartile sample (Q1-Q3) is extracted, and a normality test is applied, for instance Shapiro-Wilk test, Lilliefors test or Probability Plot Correlation Coefficient.
Step 2: If the samples do not follow normal distribution, iteratively, with the help of a histogram and a quantile-quantile plot, the points should be removed until the normal distribution is reached.
Step 3: When the normal distribution is reached, the NBLs is calculated as 95th percentile.

This methodology has been successfully applied by the Geological Survey of Portugal, particularly in the Iberian Pyrite Belt, to assess mining contamination (Fernandes and Almeida, 2018).

The NBL results obtained with these three methods in each of the five pilots were compared with the range of values identified as plausible based on previous works and/or the expert judgment.

2.3. Sensitivity analysis

We assessed the sensitivity of the NBLs to (1) define the representative value in each sampling point and (2) test different salinity constraints to remove human influenced samples.

To define a representative Cl value in each sampling point, each of the three original methods used quantiles of the data distribution (e.g., the median). These representative values were then used to determine NBLs for each pilot area. In this sensitivity analysis, we tested the effect of adopting the 10th or the 50th percentiles (P10 or P50, i.e., median) as representative values on the estimated NBLs.

The second sensitivity analysis examines how the NBLs resulting from the three methods change when different Cl constraints (e.g., 1000, 750, 500, 250, 125 mg/L) are imposed to remove influenced samples. These thresholds were chosen as clearly higher than the maximum feasible NBLs in the pilots. Finally, the representative value for each sampling point (P10 and P50) was calculated based on the remaining data set (after applying the salinity constraints).

2.4. Proposed solution

According to the proposed sensitivity analyses, the three approaches should provide NBLs equal or smaller than the values obtained with the original methods, when the maximum values of Cl thresholds are decreased. Therefore, these NBL values tend to converge to similar values. Following that, we propose the next steps to estimate NBL ranges:

Step 1: To find the regression curve (linear or logarithmic) that fits best with the NBLs for Cl vs Cl thresholds for each method in each pilot.
Step 2: To identify different NBL values in each pilot as the intersection of the curves fitted to the solutions based on a PS method (the BRIDGE method) with the other two approaches (PP and PT methods), which are based on the identification of different populations within the sample distribution (CS methods).
Step 3: To define the NBL ranges in the aquifer with the minimum and maximum values defined by the intersection points. Its amplitude will depend on the pilot.

3. Pilots description

The described methodology was tested in five pilots located in different environments: two Mediterranean pilots (Plana de Oropesa-Torreblanca, and Fluvia and La Muga Delta Plain aquifers); an Atlantic ocean pilot (Campina de Faro aquifer system); a Baltic sea pilot (Liepaja aquifer), and a North Sea pilot (Tønder aquifer). The locations and geological cross-sections of the selected pilot areas are shown in Fig. 3.

3.1. Mediterranean sea pilots

Plana de Oropesa-Torreblanca aquifer (Spain) is a detrital aquifer that extends over 75 km^2 in the province of Castellón, within the Mediterranean coast of Spain. The aquifer has a length of 21 km and a width between 2.5 and 6 km. It is an unconfined, heterogeneous, Plio-Quaternary aquifer composed of a silty clay matrix with gravel and sand layers. The increasing population since 1970, especially in summer periods, and the transformation from dry to irrigated croplands led to an increase of groundwater pumping that extended for nearly two decades (1980–1995, especially in the period 1985–1995). It produced a drop in groundwater level and SWI problems (Baena-Ruiz et al., 2018). From 1995 to 2010 there was a progressive reduction in pumping due to the abandonment of certain crops and irrigated areas. In this pilot data comes from the Júcar River Basin Authority and they are available on https://www.chj.es/es-es/medioambiente/redescontrol/Paginas/IntrusionMarina.aspx. The chloride analysis method is not specified in this dataset but the most frequently applied is the ion chromatography.

The aquifer system of the Fluvià and la Muga rivers delta plain (Catalonia) is in the Northeast of the Iberian Peninsula. It is a porous media which consists of Quaternary detrital deposits overlapping the Neogene detrital sediments of the Empordà basin. It is a typical Mediterranean fluviodeltaic aquifer system with an unconfined upper aquifer and a discontinuous confined deep aquifer. Between them, a clay and silt sediments layer acts as an aquitard. The study area had been mainly agricultural until the end of the 1960s and early 1970s, when (like in other Mediterranean areas) the construction of tourist infrastructures was intensified. The paradigm of this situation is found in the inland harbors of Empuriabrava and Santa Margarida constructed between the 1960 and 1975 in the north of the study area. With more than 30 km of inland navigable channels, it is one of the biggest marine urban areas in the world. Consequently, as a result of significant overexploitation of aquifers a SWI was initiated. Opposite to this, in an area adjacent to the coastline and surrounding the Empuriabrava harbor there is a natural protected area “the Natural Park of the Empordà Wetlands” recognized by the International Treaty of RAMSAR (site No. 592 of RAMSAR Convention Bureau, 1990) where mixed saline and fresh water coexists. In this pilot data comes from the hydrogeological databases of the Catalan Water Agency (SDIM-ACA) and the ICGC (BDSIMHCat). Catalonian data from SDIM-ACA is available on https://aca-web.gencat.cat/sdim21/ while data from the BDSIMHCat has no public access. The analytical method for Cl is not reported in the databases. Nevertheless, the analyses from both ACA and ICGC are carried out in officially accredited laboratories which follows the specifications of the “Accreditation office for collaborating entities – OAEC” of the Catalan

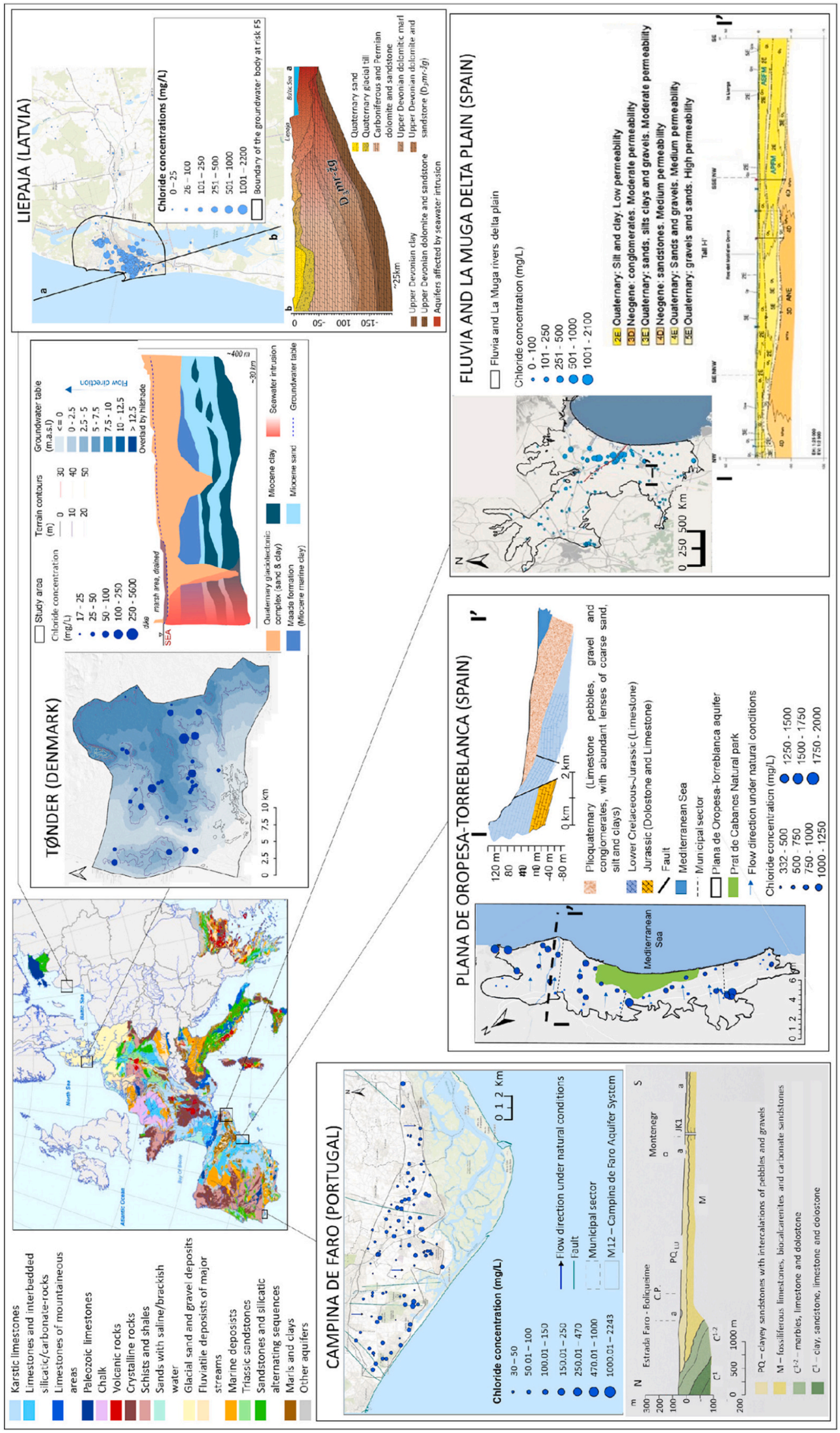

Fig. 3. Location of the case studies, aquifer typologies, representative cross-sections and median Cl concentration in the studied period. Aquifer typologies adapted from Wendland et al., 2008.

Government.

3.2. Atlantic Ocean pilot

The Campina de Faro aquifer system (M12) is a coastal aquifer along the Algarve coast (south coast of Portugal) in the Atlantic Ocean. The aquifer system is used for agricultural supply. However, over the last years, the extraction for the tourism sector has intensified with the irrigation of golf courses located in Vale de Lobo and Quinta do Lago (in the western sector), causing declining groundwater levels. Sands and gravels of the Plio-Quaternary deposits (30–60 m thick) form a shallow phreatic aquifer, which covers a confined multi-layered aquifer composed of Miocene sandy limestones (300 m thick). Evaporites are injected through faults at 90 to 120 m depth and a saline dome outcrops in the Faro city. In the past, there was evidence of artesian water levels in some areas, showing the hydraulic difference of the two aquifers. Nowadays, poor drilling practices caused hydraulic connection between them, increasing the vulnerability to contamination of the deeper aquifer. Downstream, the rivers and streams have an effluent behavior and maintain sensitive ecosystems dependent on groundwater discharge. In the western sector of the aquifer system, time-series show that water levels have been persistently lower than the sea level since 1995. Since 2010, this trend has been followed by a constant increase of Cl, which may indicate an ongoing SWI process. In this pilot data comes from the SNIRH- Sistema Nacional de Informação de Recursos Hídricos (hydrogeological database of the Portuguese Environment Agency-APA), and from LNEG, available online on snirh.pt. and geoportal.lneg.pt. The analytical method for Cl analysis is not reported in the databases, but in general the titration method was a common approach in the past century while in the recent decades ion chromatography is the most frequently used method. APA Lab is an officially accredited laboratory and a reference Lab of Portugal.

3.3. Baltic Sea pilot

Seawater intrusion in Liepaja (Latvia) takes place in a freshwater aquifer located at the Baltic Sea coast of Latvia, in the vicinity of the third most populated city in Latvia. It is an Upper Devonian Mūru-Žagares (D_3*mr-žg*) partly confined aquifer which is formed of weakly cemented sandstones, siltstones and dolomites. Deposits of Mūru-Žagares aquifer outcrops at the bottom of the Baltic Sea, approximately 5 km from the coast. Consequences of the intensive groundwater abstraction from Mūru-Žagares aquifer in the form of an increased salinity have been observed already since the 1930's. In 1986 groundwater levels in the exploited aquifer were reported as 14 m below sea level. Depression cone started to decline only in the beginning of the 1990's when groundwater demand significantly dropped due to the collapse of the Soviet Union (Bikše and Retike, 2018). The groundwater level in Mūru-Žagares aquifer has significantly increased since then and currently is above the Baltic Sea level. While Cl concentrations have decreased in the marginal zone of the affected area, the central part of the area still contains high Cl concentrations (~2000 mg/L) (Retike and Bikše, 2018). In Liepaja data comes from database "Wells" (limited access) that is maintained by Latvian Environment, Geology and Meteorology Centre and contains data from monitoring and groundwater abstraction wells since 1960's. The analytical method is not reported in the database, and it can vary over time, but in general the titration method was a common approach in the past century while in the recent decades ion chromatography is the most frequently used method. Analyses have been performed by accredited laboratories to the standards at that time.

3.4. North Sea pilot

The Tønder study site is in the southwesternmost part of Denmark, characterized by flat topography (max 62 m a.s.l.), coastal temperate climate, and intensive agriculture (~80% of the area). The largest town is Tønder with a population of 7600 inhabitants. The subsurface geology is highly complex, characterized by glaciotectonic deformation, at least 3 generations of deep buried tunnel valleys and a deep-seated graben structure crossing the area southwest to northwest bounded by faults and/or flexures (Jørgensen et al., 2015). The primary aquifer in the area used for drinking water purposes is Quaternary sand within the Glaciotectonic complex. The partially confined aquifer due to overlying clay layers is composed of heavily deformed sediments with varying sand-clay ratios, extending to depths of 40–150 m (Jørgensen et al., 2015). The other aquifers in this area are unusable for drinking water either due to naturally high dissolved organic content, high salinity (mainly in the deeper Miocene sand layers) or due to contamination with nitrate and other anthropogenic pollutants (upper shallow sandy glacial meltwater deposits) (Hansen et al., 2016; Voutchkova et al., 2021a, 2021b). The saltwater interface in the southwest corner of the area reaches up to 20 km inland and it has been described well through 3D modeling based on high density geophysical and lithological data (Aagaard, 2016; Meyer et al., 2019; Rasmussen and Sonnenborg, 2015). Meyer et al. (2019) showed that the salt water originates from a combination of lateral SWI and vertical infiltration of transgression water. The main features controlling the SWI into the coastal aquifers are the highly permeable deep Miocene sands and the buried valleys that provide preferential flow paths in combination with the extensive Miocene clay layers that delay the saltwater intrusion (Meyer et al., 2019). Our assessment focuses only on the sandy Quaternary aquifer dominated by glaciotectonic with primary drinking interest in the area, so only sampling points (well screens) associated with it were included. The data set includes Cl analyses of groundwater samples from 2013 to 2019 ($n = 214$) from 77 sampling points. None of these sampling points are located within the SWI zone, however Cl concentrations could be elevated at some of the wells due to influence from the deeper marine Miocene layers. In Tønder data comes from our Jupiter database, IC (ion chromatography) is the most frequently used method. The method/instrumentation is not always recorded in the database. Sometimes, the method is given by ISO or Danish Standard number. It is safe to state that the Cl measurements were done according to standard methods, including ion chromatography.

4. Results and discussion

4.1. compilation and analyses of the Cl data

In all five pilots (Fluvia and La Muga Delta Plain, Tønder, Liepaja and Campina de Faro), except for Plana de Oropesa-Torreblanca, most of the samples had low Cl concentrations, and only a few high values were observed (Fig. 4a). Majority of samples in the Plana de Oropesa-Torreblanca aquifer had high Cl concentrations (more than 50% of samples above 800 mg/L) and this dataset had the highest interquartile range, Q_3-Q_1, (near 800 mg/L). On the contrary, Liepaja aquifer showed the smallest interquartile range (near 20 mg/L) and 82% of the sampling points had a median value below 25 mg/L.

The number of samples in each sampling point varied a lot (Fig. 4b). The pilots Plana de Oropesa-Torreblanca and Campina de Faro had longer time-series whereas other pilots had less Cl measurements in each sampling point (Table 1).

There were also significant differences in the distribution of the median Cl concentrations at the sampling points within the pilots (Fig. 5).

4.2. Application of the selected original methods

In all the studied pilots, the NBLs obtained by applying the simplified BRIDGE method were significantly higher than those obtained with the other two methods (Fig. 6), except for Plana Oropesa-Torreblanca, where the NBL is smaller obtained by the BRIDGE method. This might

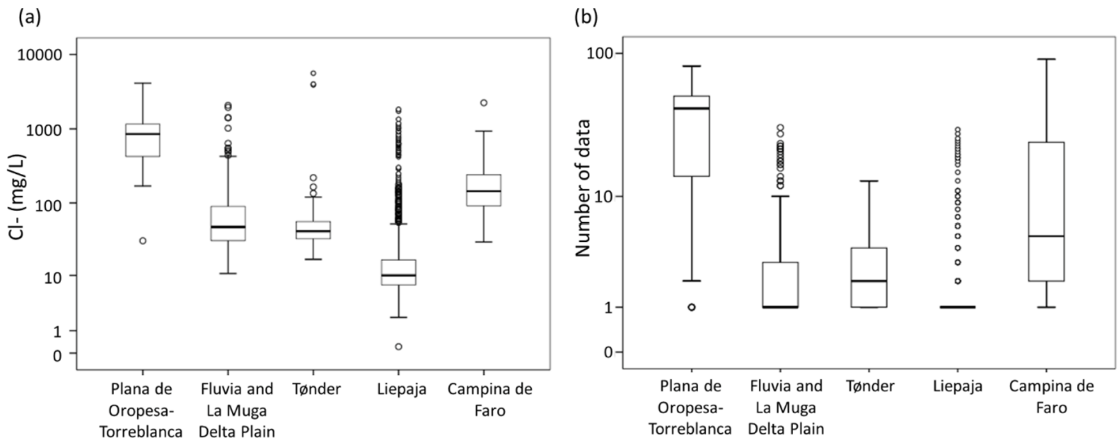

Fig. 4. Box-whiskers plots of (a) Cl concentrations at each pilot and (b) the number of samples for each sampling point.

Table 1
Summary of data statistics for Cl in five pilots.

Pilot	Number of observation points	Number of samples in each observation point (range)	Minimum Cl value (mg/L)	Maximum Cl value (mg/L)	Mean and median Cl value (mg/L) for all samples in the aquifer	Standard deviation of Cl (mg/L) for all samples in the aquifer
Plana de Oropesa-Torreblanca	53	1–82	31.0	8600.0	1039.5/ 895.0	929.7
Fluvia and La Muga Delta Plain	151	1–24	10.6	13,164.2	181.0 / 56.5	615.0
Tønder	77	1–13	11.0	5600.0	112.3 / 44.0	533.4
Liepaja	804	1–30	0.2	3670.0	139.4 / 12.0	386.5
Campina de Faro	103	1–91	23.0	2242.4	195.6 / 134.9	185.6

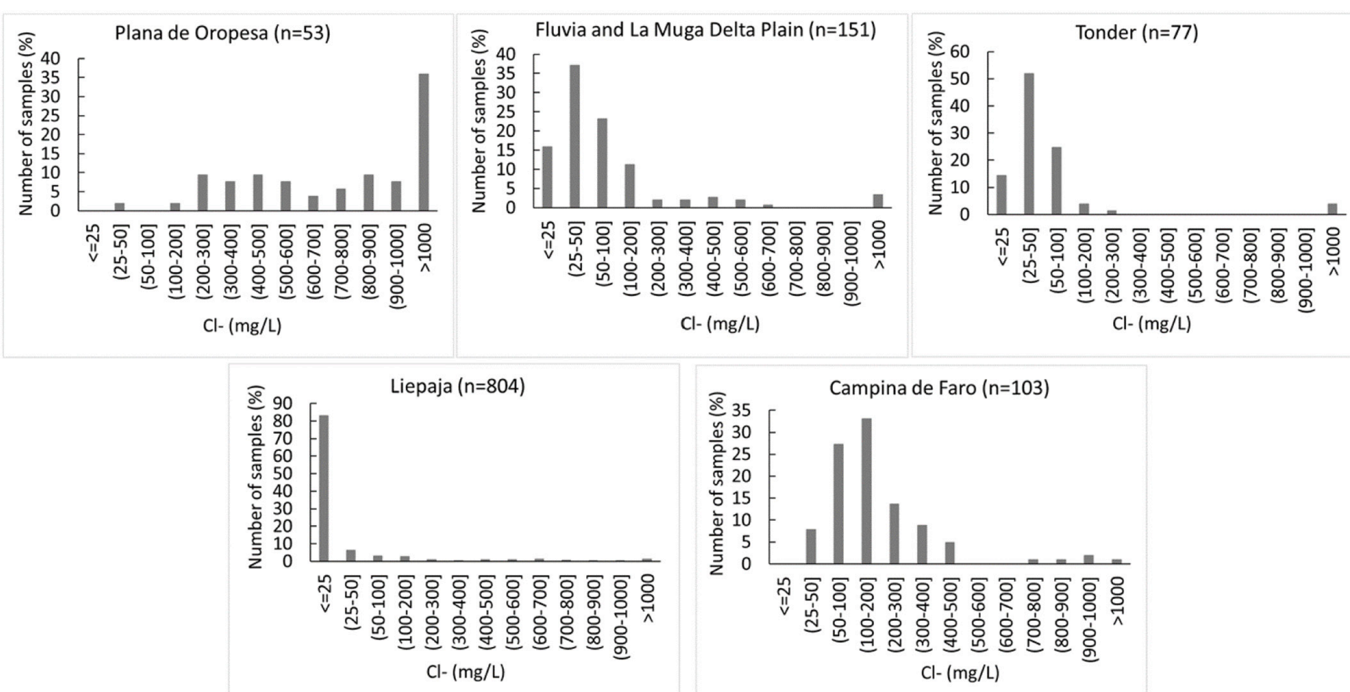

Fig. 5. Frequency distribution plots of the median Cl concentrations in the sampling points (mg/L) for the selected pilots (n - number of sampling points in each pilot).

be a result of the different Cl distribution observed in this pilot as most of the sampling points had median Cl values over 1000 mg/L (Fig. 5).

The PP and the PT methods resulted in very similar NBLs for Cl in three pilots. While for Campina de Faro the difference between the NBLs was 34.8 (mg/L), and in Plana Oropesa-Torreblanca the difference was 150.6 (mg/L).

When determining NBLs with purely statistical methods, the results need to be validated. Table 2 shows the range of likely Cl concentrations

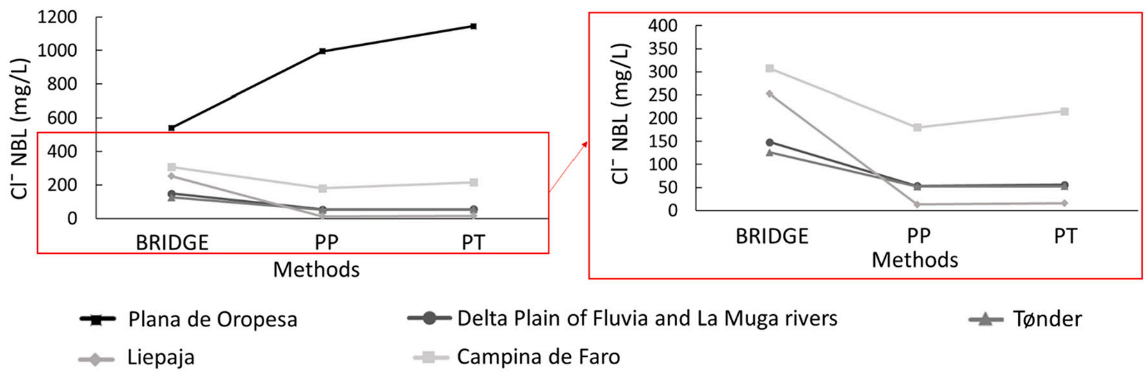

Fig. 6. Estimated Cl natural background levels by the BRIDGE, PP and PT methods.

Table 2
Range of the natural Cl concentrations considered feasible in each pilot according to previous studies and/or expert judgment.

Pilot	Range of natural Cl concentrations (mg/L)
Plana de Oropesa-Torreblanca	30–90
Fluvia and La Muga Delta Plain	35–80
Tønder	5–60
Liepaja	10–20
Campina de Faro	100–200

considered natural in each pilot, in accordance with previous studies and/or expert judgment. When the maximum values from Table 2 were compared with those estimated with the three applied methods (Fig. 6), it could be observed that methods do not provide an appropriate assessment of the NBL in all the cases if applied directly. Therefore the sensitivity of the NBLs to different Cl constraints applied to remove the anthropic influence were analyzed. The purpose was to determine if introducing any of the constraints would improve the plausibility of the assessment.

4.3. Sensitivity analyses of the results to different constraints

We assessed the impacts of (1) the selected quantiles (P10, P50) defining the representative value in each sampling point, and (2) the salinity constraints used for removing the influenced samples due to anthropogenic impacts.

Each of the three methods used quantiles of the data distribution to define the representative Cl concentration in each sampling point. In Fig. 7 the estimated NBLs change is shown whether the 10th percentile (P10) or 50th percentile (P50) was used to define the representative value for each sampling point. The BRIDGE method was not sensitive to these changes. The sensitivity of the PP and PT methods was also low, except for the Plana de Oropesa-Torreblanca pilot, where the impact of this assumption was large. The Cl NBLs obtained for P10 with the PP and PT methods decreased for 38% and 33% respectively regarding the obtained for P50. This might be a result of Cl variation in each sampling point, which could be caused by periodic SWI during the data collection period. In those pilots in which the results were sensitive to the adopted quantile, P10 reduced the NBL values and the difference from the feasible values was noticeable (Table 2).

For each of the three statistical methods, the change in results (Fig. 8) due to the application of various Cl constraints (1000, 750, 500, 250 and 125 mg/L) to remove influenced samples was analyzed. Both P10 and P50 were used to define the representative value with the remaining data set (after applied constraints) in each observation point. Note that in Campina de Faro we did not impose the constraint of 125 mg/L, because it included the range of natural Cl concentrations (Table 2).

Obviously, when the percentile P10 was used, smaller NBLs were obtained in all pilots. Natural background levels derived by all three methods decreased when we applied more strict Cl concentration constraints to remove human influenced data. The only observed discrepancy was in Campina de Faro when the PP method was applied with P50 and the Cl constraint changed from 500 to 250 mg/L and where a small increment of the NBL was observed. However, differences were negligible and could be a result of the particularity of the data frequency distribution.

The PP and PT methods were not sensitive to the applied constraints in most cases (Tønder, Liepaja, Fluvia and La Muga Delta Plain), and a clear decreasing trend of the NBLs for these methods could not be

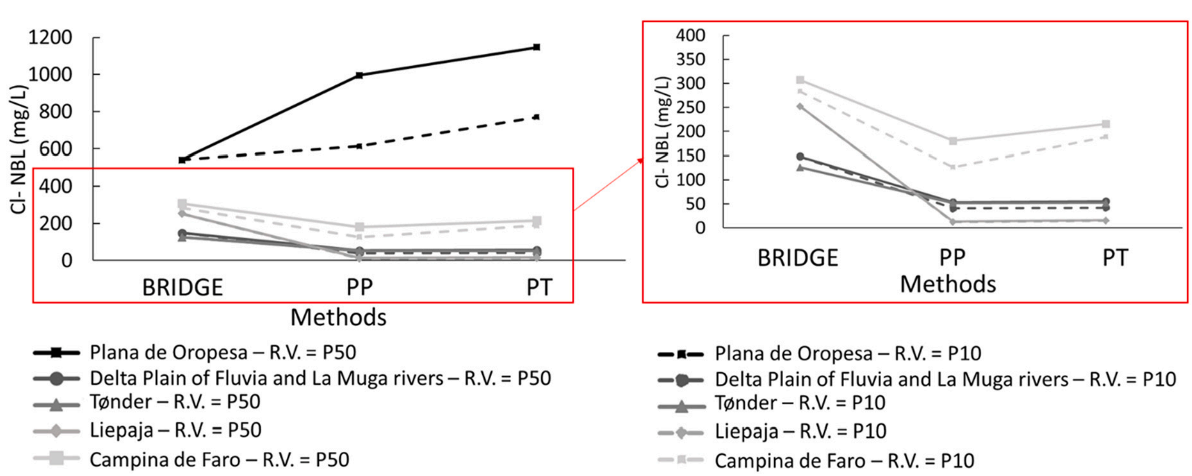

Fig. 7. Chloride NBLs (mg/L) obtained depending on the quantile (P10 or P50) used to define the representative value (R.V.) in the sampling points.

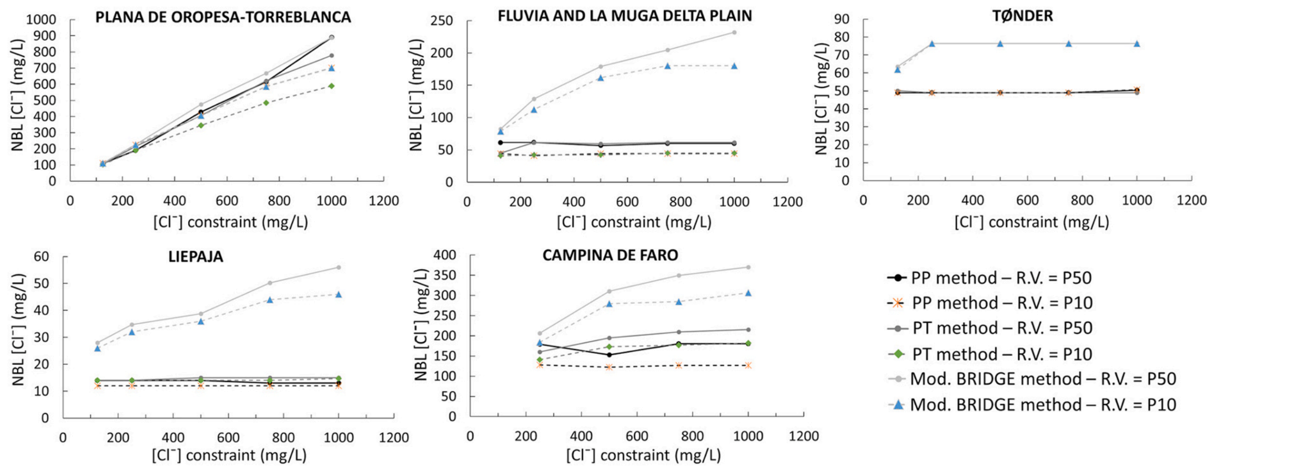

Fig. 8. Chloride NBLs obtained by the selected approaches with different salinity constraints applied. P10 and P50 are used to define the representative value (R.V.) in each sampling point.

concluded. The PP method showed some anomalies in Campina de Faro when P50 was used, but a reduction trend with the obtained results cannot be inferred. In Campina de Faro the PT method showed some sensitivity to the Cl constraint, especially when the threshold was below 500 mg/L and the NBL values decreased with a higher steepness. In Plana de Oropesa-Torreblanca all the methods showed a decreasing trend, which was likely due to high variability of the Cl concentrations in the observation points due to long periods of time having significant impact by SWI. Excluding the Plana de Oropesa-Torreblanca pilot, the results of sensitivity analyses allowed to conclude following:

- The PP method was not sensitive to the different Cl constraints in the other four pilots.
- The PT method was not sensitive to various Cl constraints in three pilots (Tønder, Liepaja, Fluvia and La Muga Delta Plain). It was only sensitive in Campina de Faro when the threshold was below 500 mg/L.
- The BRIDGE method showed a decrease in the NBLs as a function of the applied Cl constraint. It was observed in all pilots except for Tønder, where the decrease was only observed for Cl constraint values smaller than 250 mg/L. This was since there were few samples with Cl concentrations in the range 250–1000 mg/L (see Fig. 4).

4.4. Proposed solution

In each pilot the best regression curves (linear or logarithmic) that fitted with the NBL vs Cl constraint values for each method were identified. The intersection of the curves fitted to the NBL solutions obtained by applying the PS method (the BRIDGE) with the CS methods (PP and PT) defined a range of NBLs for the aquifer, whose amplitude depends on the pilot (see Fig. 9). This range of NBLs was the proposed solution. It was obtained as the result of integrating different approaches (PS and CS methods) that allowed to establish a robust solution.

Note that, in Campina de Faro, the constraint 125 mg/L could not be considered to fit the regression curves, because this value was within the range of feasible NBL values for the pilot identified in previous studies.

Fig. 10 shows the range of NBLs obtained with the three methods (BRIDGE, PP and PT) with different Cl constraints. It also presents the range of NBLs obtained with the intersection of the regression curves (proposed solution) and the range of feasible NBL values from expert judgment (red lines). In Tønder, Liepaja, Fluvia and La Muga Delta Plain

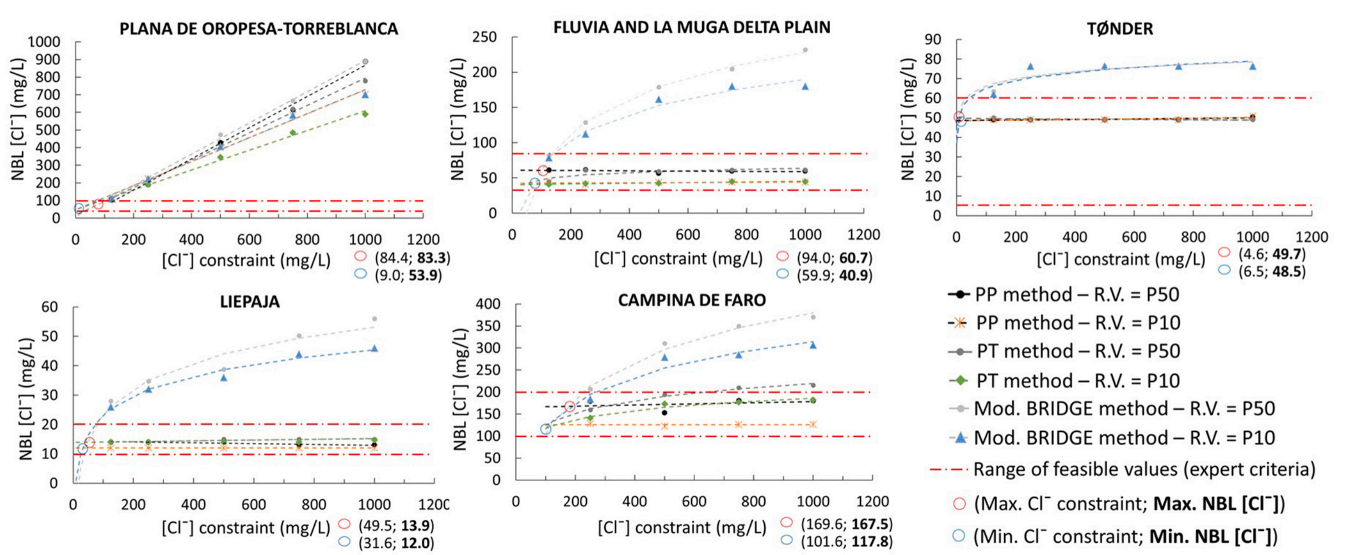

Fig. 9. Chloride NBLs (mg/L) calculated by applying three statistical methods and the regression curves with the best fit to the data. Red dashed lines indicate the range of feasible Cl values in each pilot (from Table 2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

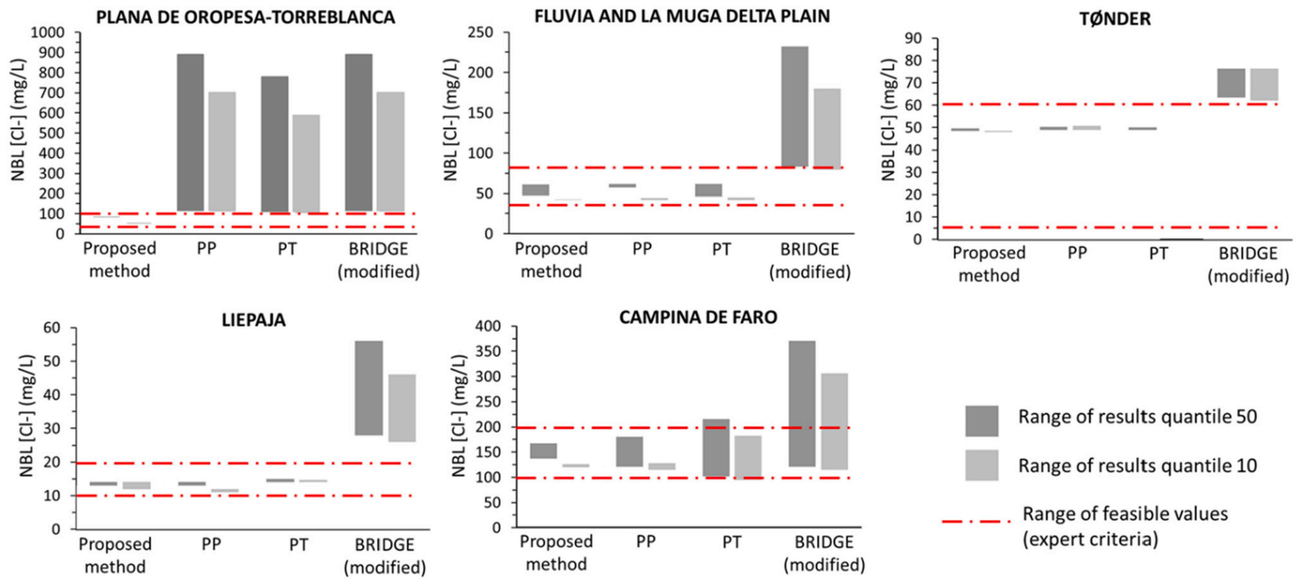

Fig. 10. Range of NBLs (mg/L) obtained by applying the proposed method and the three previous approaches.

the range of the NBLs estimated with the proposed approach was similar to that obtained when applying only the PP or the PT methods (Fig. 10). This is due to the low sensitivity of these two methods to the salinity constraint in those pilots where the assessment could be carried out without imposing any Cl constraint. In Campina de Faro the range of the NBLs estimated with this procedure showed differences with the range of NBL values obtained with the PP and PT methods with the different salinity constraints. Nevertheless, the PP and PT methods provided NBL values within the range of feasible values from Table 2. In Plana de Oropesa-Torreblanca, the results provided by any individual method were not reasonable (Table 2) if the salinity constraint was not applied, thus the proposed procedure to find a feasible approach for the establishment of NBL had to be applied.

The NBLs calculated in previous studies showed similar results. Chloride concentrations in aquifers in Denmark, which have been completely flushed since the latest glactions is around 20 mg/L (Hinsby and Rasmussen, 2008), however, partly flushed marine sediments are widespread in Danish aquifer systems and make the salinity highly variable even within short distances (Rasmussen et al., 2013) and the salinization sources difficult to locate and quantify (Knudsen et al., 2021). Hence, the average NBL for Danish aquifers using the 90th percentile, as proposed in the BRIDGE method (Hinsby et al., 2008), of thousands of samples is around 100 mg/L of Cl, which for practical work is similar to 85 mg/L of Cl obtained with the proposed methodology in this paper.

For the Liepaja pilot, Cl natural background level of 13.2 mg/L was derived using locally adjusted BRIDGE methodology (Retike and Bikše, 2018) that contributed to the calculation of threshold value for the area and for the development of Latvian River Basin Management Plans. Moreover, a national-wide geochemical classification in Latvia (Retike et al., 2016) suggests that in typical carbonate freshwater (similar to pilot area) Cl concentrations for 25th and 75th percentiles are 5 and 12 mg/L respectively. These previous studies show similar results to the ones obtained by the PP, PT and the proposed solution for any of the chosen constraints in this study, however the modified BRIDGE method shows two to five times higher NBLs depending on the applied constraint.

In Catalonia, Cl is one of the indicators considered for the Groundwater quality standards assessment on the "Management plan for the river basin district of Catalonia" (ACA, 2017). The Cl NBL for this quality standard is established following the BRIDGE method and the "Guidance on groundwater status and trend assessment" (Grath and Ward, 2008). For the groundwater body corresponding to the aquifer system of the Fluvià and la Muga rivers delta plain a value of 338.5 mg/L is set for the period 2016–2021.

Regarding Algarve River Basin Management Plans, Cl natural background level of 257 mg/L was established to Campina de Faro Aquifer System by APA – Portuguese Environmental Agency. It's a simpler methodology than the one that is proposed in Guidance No. 18 – Groundwater Status and Trend Assessment of the European Commission (Grath and Ward, 2008). The methodology takes into account the 90th percentile of historical data recorded in the national quality surveillance network of the groundwater, after elimination of abnormal values. Previous studies focused on data from 1978 to 1981 showed a median Cl concentration of 225 mg/L for the upper aquifer and much lower Cl levels for the lower aquifer, with a median of 92.7 mg/L (Stigter, 2005). Silva (1988) presents a median of 268 mg/L for samples collected in May 1983 and 178 mg/L in September 1983.

In Plana de Oropesa-Torreblanca a hydrogeochemical characterization was performed in previous studies (Giménez-Forcada, 1994, 2019), although a CL NBL estimation was not included. The Plana de Oropesa-Torreblanca aquifer receives lateral inflows from a mesozoic aquifer, which is not affected by sea water intrusion and provides lateral inflows. The groundwater of this mesozoic aquifer is considered to be freshwater and its Cl concentration could be a good approximation of the NBL in both aquifers. The Cl concentration measured in wellsprings from the northern mesozoic aquifer is 48.3 mg/L, whereas in the southern the Cl concentration rises to 100 mg/L approximately.

The examples briefly described above demonstrate large variations across Europe both at local and regional scales, and for general assessments of the natural background levels we find the proposed methodology relevant and widely applicable.

For the proposed method in this paper, it was concluded that, in order to carry out a reliable NBL assessment, application of different methods instead of relying on only one method is strongly encouraged, and performance of sensitivity analyses to different Cl constraints can be suggested. The methods with low sensitivity to the Cl constraints might provide a higher confidence of the estimated NBLs and it was observed for the PP and PT methods in Tønder, Liepaja, Fluvia and La Muga Delta Plain, and even in Campina de Faro, where although a higher Cl range was observed, it fell in the range initially identified as feasible (Table 2). If the sensitivity of the chosen methods to the salinity constraint is high (as for example in the Plana de Oropesa-Torreblanca) and values far from the feasible are observed, we propose the application of the proposed solution by this paper (see Section 4.4.). It allows to obtain a NBL within the range of the feasible NBL values in the aquifer, which is more appropriate than to obtain a fixed NBL value (Amiri et al., 2021; Li et al., 2021).

If a certain confidence about the range of feasible chloride NBL in study area is already present and there is no possibility or willingness to perform the described sensitivity analyses, it is recommended to remove all the Cl samples over the feasible range of NBL to perform the assessment with any of the cited methods. This study showed that removing the samples with Cl values above the NBL in some pilots did not affect the results significantly but in case there was an influence we could avoid the risk to obtain significantly higher results than the feasible NBL for the pilot. Finally, as the BRIDGE method showed the highest discrepancies in NBL assessment, we suggest using the other two approaches instead.

Although the BRIDGE method applies pre-selection criteria to remove samples with anthropogenic impacts (typically $NO3 > 10$ mg/L and $Na + Cl > 1000$ mg/L), they might not be enough to remove all samples affected by anthropogenic SWI. The solution proposed in this paper proved to be robust to determine a range of Cl NBL in the five coastal aquifers although its applicability for other case studies should also be tested and further studies are encouraged.

5. Conclusions

In this paper we presented and compared different statistical approaches to derive chloride NBLs from the available measurements and discussed their applicability in different hydrogeological settings across Europe on the basis of five case studies conducted in coastal aquifers in of the Atlantic Sea, the Mediterranean Sea, The North Sea and the Baltic Sea. We performed a detailed sensitivity analysis of the results to different Cl constraints (1000, 750, 500, 250 and 125 mg/L) applied to remove samples affected by anthropogenic impacts. Based on the sensitivity analysis a novel approach that combined results from different statistical methods to identify in a consistent way a feasible range of values for the chloride NBL was proposed. Its applicability was demonstrated in coastal aquifers across Europe with significantly different distributions of Cl concentrations. However, its applicability testing should be extended to other case studies as well. If detailed assessments (of e.g. the advance of pollution plumes from landfills or saltwater intrusion toward specific water supply wells) are performed, more specific analyses of chloride distributions for a given setting may be needed (e.g. by the use of airborne geophysical measurements of resistivity in the subsurface).

To make a reliable NBL assessment the application of more than one method is strongly encouraged, we suggest carrying out sensitivity analyses for different Cl constraints. If the NBL derivation method shows low sensitivity to the Cl constraints defined with values over the feasible NBL range, a higher confidence of the estimated NBL values is expected. Therefore, the range of the NBL could be based on their results. If a high degree of confidence exists about the feasible range for chloride NBL in the study area, the described sensitivity analyses might be skipped but we would recommend removing all the Cl samples over the feasible range of NBL to perform the assessment with any of the proposed methods. Nevertheless, as the BRIDGE method shows the highest discrepancies in the assessment, therefore we would suggest using any of the other two approaches (PT and PP methods).

Funding

This research has been partially funded by the projects GeoE.171.008-TACTIC and GeoE.171.008-HOVER, funded by European Union's Horizon 2020 research and innovation program; SIGLO-AN (RTI2018-101397 -B-I00) project from the Spanish Ministry of Science, Innovation and Universities (Programa Estatal de I + D + I orientada a los Retos de la Sociedad); Innovation Fund Denmark under agreement no 8055-00073B; and by performance-based funding of University of Latvia Nr.AAP2016/B041 within the "Climate change and sustainable use of natural resources" program.

CRediT authorship contribution statement

D. Pulido-Velazquez: Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **L. Baena-Ruiz:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision, Software, Data curation, Visualization. **J. Fernandes:** Methodology, Writing – original draft, Writing – review & editing, Software, Data curation, Visualization. **G. Arnó:** Methodology, Writing – original draft, Writing – review & editing, Software, Data curation, Visualization. **K. Hinsby:** Methodology, Writing – original draft, Visualization, Funding acquisition. **D.D. Voutchkova:** Methodology, Writing – original draft, Writing – review & editing, Supervision, Data curation, Visualization. **B. Hansen:** Writing – original draft, Writing – review & editing, Supervision, Data curation. **I. Retike:** Methodology, Writing – original draft, Writing – review & editing, Data curation, Visualization. **J. Bikše:** Writing – review & editing, Supervision, Data curation. **A.J. Collados-Lara:** Methodology, Writing – original draft, Data curation, Visualization. **V. Camps:** Writing – original draft. **I. Morel:** Methodology, Writing – original draft. **J. Grima-Olmedo:** Writing – original draft, Data curation, Visualization. **J.A. Luque-Espinar:** Writing – original draft, Data curation, Visualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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