DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE **RAPPORT 2022/24**

Natural Background Levels for Barium and Phosphorus in Groundwater

Denitza D. Voutchkova & Lærke Thorling

GEOLOGICAL SURVEY OF DENMARK AND GREENLAND
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G E U S

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Udarbejdet af GEUS for Miljøstyrelsen, 2022

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GEUS

Indholdsfortegnelse

Resume (Dansk)

Denne rapport redegør for det arbejde, som er udført som en del af projektopgaven defineret af Miljøstyrelsen *"Opgavebeskrivelse – Fastsættelse af naturlige baggrundsværdier for fosfor og barium i de danske grundvandsforekomster"* (se Appendiks 1). Formålet med projektet er at foreslå naturlige baggrundsværdier (NBV) for barium (Ba) og totalfosfor (P_{tot}) for dansk grundvand. Der er ikke tidligere fastsat NBV for Ba og P i Danmark, så det var nødvendigt at fastlægge kriterierne for at gøre dette, hvilket krævede en vurdering af hvilke geologiske, geografiske og geokemiske parametre, der ville være relevante.

Den naturlige baggrundsværdi, NBV, er defineret som et koncentrationsniveau, for et kemisk stof i en grundvandsforekomst, hvorunder der kan forventes at være ingen eller meget lidt antropogen påvirkning. NBV'er bruges til at fastsætte tærskelværdier (TV'er) i forhold til de kemiske tilstandsvurderinger af grundvandsforekomster i EU, som fastsat i EU's vandrammedirektiv og grundvandsdirektivet. Den endelige fastlæggelse af tærskelværdier og vurderinger af grundvandsforekomsternes kemiske tilstand for Ba og P_{tot} ligger uden for denne rapports rammer.

Datagrundlaget, der blev brugt til at beregne NBV'erne, omfatter kemiske analyser for Ba, P_{tot}, pH og NO_3^- i grundvandsprøver fra perioden 2000-2021. Der er alene anvendt data fra det nationale grundvandsovervågningsprogram (GRUMO-indtag) og aktive vandværks boringer (BK). pH og NO_3^- blev inddraget, da det viste sig at være betydende geokemiske parametre for koncentrationsniveauerne baseret på den indledende litteraturgennemgang. Derudover indgik forskellige metadata for indtagene, fx lithologi, grundvandsforekomst, geografiske koordinater osv. Datasættet blev kvalitetssikret, og værdier under detektionsgrænsen blev håndteret hensigtsmæssigt, se kapitel 1. Data fra indtag med flere prøver i perioden blev aggregeret, så hvert indtag er repræsenteret af en enkelt værdi for perioden. Aggregeringen var baseret på et gennemsnit beregnet ud fra de årlige gennemsnit for hvert element og indtag. Der er anvendt de samme databehandlingsprocedurer her som i GEUS's tidligere arbejde med NBV'er for spormetaller til Vandplan III, således som det fremgår af opgavebeskrivelsen, se Appendiks 1.

De endelige datasæt brugt til NBV-beregningen omfattede 6.558 indtag (6.181 boringer) for Ba og 8.088 indtag (7348 boringer) for P_{tot}. Disse indtag er knyttet til henholdsvis 453 (22%) og 525 (26%) af de 2.050 grundvandsforekomster i Danmark og dækker hele landet og de hydrogeologiske enheder i DK-modellen.

De naturlige baggrundsværdier er beregnet som 90 % percentilen af de aggregerede data for hver af de definerede grundvandsmagasintyper, hvor der indgår mindst 50 indtag. 90 % percentilen blev derefter afrundet efter regler, der tager udgangspunkt i den relative analytiske usikkerhed på 15-20 % for Ba og P_{tot}. Disse afrundede værdier er de resulterende forslag til NBV'er for Ba og P_{tot}. Grundvandsmagasintyperne blev fastlagt ved at kombinere de forskellige klasser for geologi, geografisk beliggenhed, redox- og pH-forhold (pH var kun relevant for Ba):

• Beliggenhed: 1) Jylland, 2) Fyn, 3) Sjælland, 4) Bornholm, og 5) de små øer tæt på Jylland

• Geologiklasser: 1) opsprækket kalk, 2) kvartært sand, 3) prækvartært sand, 4) alle geologiske enheder på Bornholm

• Redox-klasser: 1) reduceret (NO_3^- ≤ 2 mg/l), oxisk (NO_3^- > 2 mg/l)

• pH-klasser: 1) Høj (pH > 7), 2) lav (pH ≤ 7)

NBV'er blev også beregnet alene for en kombination af geografisk beliggenhed og geologi, for de tilfælde, hvor der ikke er geokemiske oplysninger for indtagene i en specifik grundvandsforekomst eller for de tilfælde, hvor NBV'er for en specifik geokemisk tilstand ikke kunne beregnes på grund af lavt antal indtag.

Seks forskellige NBV'er blev bestemt for Ba i intervallet 40-250 µg/l for de forskellige grundvandsmagasintyper. Alle disse var over det generelle kvalitetskrav for fersk overfladevand (EQS = 19 µg/l), og nogle er endda over den maksimalt acceptable koncentration (MAC = 145 µg/l). Den laveste NBV for Ba er for kalkforekomster i Jylland (40 µg/l), mens den højeste er for det kvartære sand med reducerede forhold og høj pH (250 µg/l). De kvartære sandlag på Fyn og Sjælland har også høje NBV'er (150 eller 200 µg/l). Disse høje NBV'er kan blandt andet forklares med udbredelsen af tertiære lerlag i Danmark.

Otte forskellige NBV'er blev bestemt for P_{tot} i intervallet 0,04-0,3 mg/l. Sandmagasiner (både kvartære og prækvartære) har højere NBV'er for P_{tot} end kalkmagasinerne. Alle reducerede grundvandsmagasiner (NO_3^- ≤ 2 mg/l) har konsekvent højere NBV'er end de oxiske. I øjeblikket er der ingen miljø-, drikkevands- eller grundvandsstandard for P_{tot}. Grundvandsmagasiner med NBV'er, der overstiger det tidligere drikkevandskvalitetskrav på 0,15 mg/l er: Kvartært og prækvartært sand med reducerede forhold, grundvandsmagasiner med reducerede forhold på Bornholm og endelig det kvartære sand på Læsø, Samsø og Anholt. Mens kalkmagasiner generelt set har lave NBV'er for P_{tot}, skal det bemærkes, at et relativt stort område i Nordsjælland har systematisk høje P_{tot}-koncentrationer i kalken. Dette bør overvejes, når de her beregnede NBV'erne anvendes til fastlæggelse af tærskelværdier mm.

Endelig skal det bemærkes, at fosfor i overfladevand er reguleret i forhold til den årlige samlede stoftransport dvs. kg-P/år og ikke koncentrationer dvs. mg/l som for grundvand.

Summary (English)

The work reported here was done as part of the project task defined by the Miljøstyrelsen *"Opgavebeskrivelse – Fastsættelse af naturlige baggrundsværdier for fosfor og barium i de danske grundvandsforekomster"* (see Appendix 1). The purpose was to propose natural background levels (NBLs) for barium (Ba) and total phosphorus (P_{tot}) for Danish groundwaters. NBLs for Ba and P have not been set previously in Denmark, so it was necessary to establish criteria for doing this, which required assessing what geological, geographical, and geochemical parameters would be relevant.

NBL is defined as a concentration level, for a chemical element or parameter in a body of groundwater, corresponding to no or very minor anthropogenic influence. NBLs are used for setting threshold values (TVs) in relation to the chemical status assessments of groundwater bodies in EU, as stipulated in the EU Water Framework Directive and the Groundwater Directive. Setting TVs and assessing the chemical status of groundwater bodies for Ba and P_{tot} is beyond the scope of this report.

The data used for calculating NBLs included all chemical analyses for Ba, P_{tot}, pH, and NO_3^- of groundwater samples from the period 2000–2021 for only the well-screens (called further "intakes"), which are part of the national groundwater monitoring program (GRUMO) or the waterworks wells used for drinking water production (BK). Data for pH and NO_3^- were included, as those were found to be important geochemical parameters based on an initial literature review. In addition, different meta-data for the intakes were also available, e.g. lithology, groundwater body, location, etc. The dataset was quality assured and the values below the limit of detection were handled appropriately, se Chapter 1. The time-series were aggregated, so each intake is represented by a single value for the period. The aggregation was based on a mean calculated from the annual means for each element and intake. The data-processing procedures used here are similar those used in GEUS previous work on NBLs for trace metals for Vandplan III, as requested.

The final datasets used for the NBL calculation included 6558 intakes (6181 wells) for Ba and 8088 intakes (7348 wells) for P_{tot}. These intakes are associated respectively with 453 (22%) and 525 (26%) of the 2050 groundwater bodies in Denmark and cover the entire country.

NBLs are calculated here as the 90th percentile of the aggregated data for each of the defined aquifer types with at least 50 intakes. The 90th percentile was rounded following specific rules that account for the relative analytical uncertainty of 15-20% for Ba and P_{tot}. Those rounded values are the NBLs for Ba and P_{tot}. The aquifer types were defined by combining the different classes for geology, location, redox and pH states (pH was only relevant for Ba):

- Location: 1) Jutland, 2) Funen, 3) Zealand, 4) Bornholm, and 5) the small islands close to Jutland
- Geology classes: 1) fractured carbonate rocks, 2) Quaternary sand, 3) pre-Quaternary sand, 4) all geologically diverse units on Bornholm
- Redox classes: 1) reduced (NO_3^- ≤ 2 mg/l), oxic (NO_3^- > 2 mg/l)

- pH classes: 1) High (pH > 7), 2) low (pH ≤ 7)

NBLs were also calculated for the combination of only location and geology, to be used if there is no geochemical information for the groundwater samples from a specific groundwater body or for those cases when NBLs for specific geochemical condition could not be calculated due to low number of intakes.

Six different NBLs were determined for Ba in the range 40–250 µg/l for the different aquifer types. All these were above the general quality requirement for fresh surface waters (EQS = 19 µg/l) and some are even above the maximum acceptable concentration (MAC = 145 µg/l). The lowest NBL for Ba is for the carbonate aquifers in Jutland (40 µg/l), while the highest is for the Quaternary sand with reduced conditions and high pH (250 µg/l). The Quaternary sand aquifers on Funen and Zealand are also with high NBLs (150 or 200 µg/l). These high NBLs could be to some extent be explained by the spatial extend of Tertiary clay layers in Denmark.

Eight different NBLs were determined for P_{tot} in the range 0.04–0.3 mg/l. Sand aquifers (both Quaternary and pre-Quaternary) have higher NBLs for P_{tot} than the carbonate aquifers, and all reduced aquifers (NO_3^- ≤ 2 mg/l) have consistently higher NBLs than the oxic ones. Currently there is no environmental, drinking water, or groundwater standard for P_{tot}. The aquifer types with NBLs exceeding the previous drinking water standard (0.15 mg/l) are: Quaternary and pre-Quaternary sand aquifers with reduced conditions, aquifers with reduced conditions on Bornholm, and the Quaternary sand aquifers on Læsø, Samsø, and Anholt. While carbonate aquifers have low NBLs for P_{tot} in general, it should be noted that a relatively large area in North Zealand has consistently high P_{tot} concentrations in this type of aquifer. This should be considered when using the NBLs further.

Finally, it should be noted that phosphorus in surface water is regulated in relation to the annual total P transport, i.e. kg-P/year and not concentrations, i.e. mg/l as for groundwater.

Introduction

The EU Water Framework Directive (European Commission, 2000a) and the Groundwater Directive (European Commission, 2006) stipulate that the chemical status of groundwater bodies in the EU must be assessed and that a good status must be achieved to protect both human health and the groundwater-dependent or associated ecosystems (Hinsby et al. 2008).

The status assessment provisions only apply for anthropogenically altered conditions, so the chemical status of groundwater bodies is assessed against element-specific threshold values (TVs). To set these TVs, first the natural background levels (NBLs) for different aquifer types (i.e. hydrogeochemical conditions) must be determined.

NBL is defined as:

> *"…the concentration of a substance or the value of an indicator in a body of groundwater corresponding to no, or only very minor, anthropogenic alterations to undisturbed conditions." (Article 2.5, European Commission, 2006)*

In practice, NBL is a value representing the upper limit of the natural concentration distribution for a given chemical compound and aquifer type.

Figure 1 shows schematically how NBLs and TVs for groundwater can be determined. This methodology follows the recommendations provided in Guidance Document 18 (European Commission, 2000b) and in (Hinsby et al. 2008) and was used when NBLs for trace metals were set as part of the Vandplan III work (Mortensen et al. 2021).

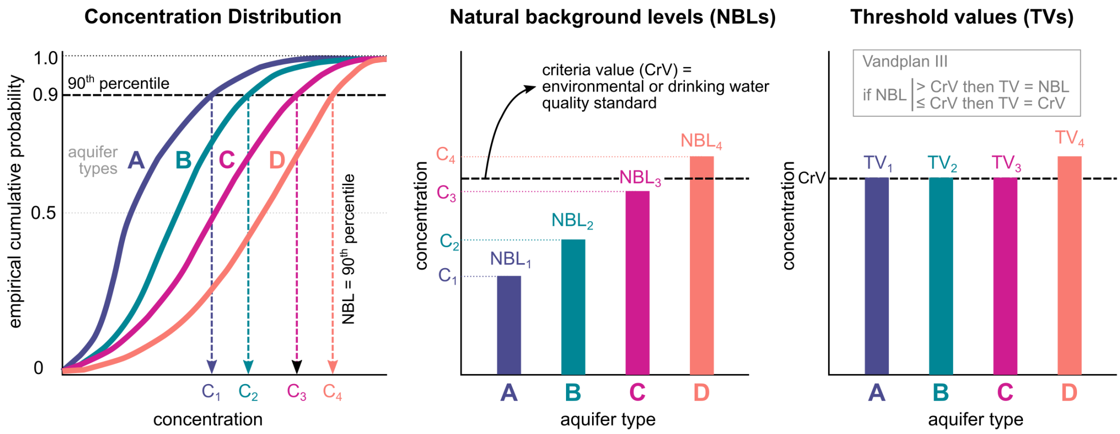


__Figure 1__. Conceptual figure showing how natural background levels (NBLs) for groundwater were determined and used for setting threshold values in Vandplan III (figure source: Voutchkova et al. (2022)).

Setting TVs is beyond the scope of this report, thus the work presented here ends with proposing NBLs for Barium (Ba) and Phosphorus (P) for different aquifer types. Nevertheless,

the calculated NBLs are put into context by comparing them to existing criteria values (i.e. environmental or drinking water quality standards).
The national environmental quality standard (EQS) for Ba for freshwaters, incl. streams, lakes, and associated artificial or heavily modified water bodies, according to Miljøministeriet (2017), are:

- 19 µg/l – general quality requirement (an annual average)
- 145 µg/l – maximum acceptable concentration (MAC)

The derivation of these values is explained in (Miljøstyrelsen Kemikalieenheden, 2009).

There is no EQS for P, as it is considered a nutrient. However, as part of the Vandplan work, a "need for action" is calculated, so the P input to lakes and coastal areas can be limited.

Currently there are no drinking water standards (dk: "drikkevandskvalitetskrav") for either Ba or P in Denmark, according to the Ministerial Order on drinking water (Miljøministeriet, 2022). However, previously there were drinking water standards for both Ba – 700 µg/l (health-based quality criterion, proposed by the Danish Environmental Protection Agency, DK EPA, (in dk: Miljøstyrelsen), (Nielsen & Ladefoged, 2013)) and total phosphorus (P_{tot}) – 0.15 mg/l (P was used as an indicator for wastewater pollution) (Miljøministeriet, 2016).

Next to the legally binding drinking water standards from Miljøministeriet (2022), there are additional drinking water quality criteria (dk: "drikkevandskvalitetskriterier"), provided in the Drinking water guidance (Miljøstyrelsen, 2022). These are recommended values, which can be used as indicative limits, and could become legally binding when/if the responsible municipality issues a decision that the parameter must be included in the drinking water quality control program of the specific waterworks (Miljøstyrelsen, 2022). They are set partially because of water safety requirements (for human consumption) and partially as indicators for good operation of the waterworks (Miljøstyrelsen, 2022). According to Miljøstyrelsen (2022), the drinking water quality criteria at the consumers' tap for:

- Ba is 700 µg/L
- P_{tot} is 0.15 mg/l, however higher content could be accepted, but the recommended maximum is 0.3 mg/l, if it can be documented that the P_{tot} is due to specific geology within the aquifer, or if it is not possible to improve the water quality at the consumer.

NBLs for Ba and P for Danish groundwater have not been set previously, as these elements were not included in the Vandplan II (2015-2021) status assessments (Nilsson et al., 2019).

The purpose of this report is, therefore, to:

1. Assess which parameters are significant for the NBLs of Ba and P in groundwater
2. Establish criteria for setting NBLs for Ba and P in groundwater
3. Propose (calculate) NBLs for Ba and P in Danish groundwater. This should be done for groundwater types, based on relevant groundwater chemistry and geology.

The work reported here addresses a project task defined by the Danish EPA (*"Opgavebeskrivelse – Fastsættelse af naturlige baggrundsværdier for fosfor og barium i de danske grundvandsforekomster"),* see Appendix 1 for details.

The report is structured in four chapters following the expected project task deliverables:

- **Chapter 1** provides information on the data sources, processing, and methods used in this report.
- **Chapter 2** examines the important factors for Ba and P distribution in Danish groundwater. This is based on a short literature review and data-exploration and allows for determining which parameters/factors are significant for setting NBLs for Ba and P.
- **Chapter 3** presents an overview of the criteria for determining Ba and P in groundwater, based on the results from Chapter 2.
- **Chapter 4** overviews the resulting 90^{th} percentiles and the NBLs for specific groundwater types.

In addition to these four chapters, the report includes also a Danish and English summary, and introduction, conclusion, complete list of references, and three Appendices.

Chapter 1: Data and data processing

All chemical data used here were extracted from the Jupiter database on 30 May 2022 for the annual Danish groundwater monitoring report (see the latest report: Thorling et al. (2021)). From these data, we used the subsets for only 1) the groundwater monitoring wells (GRUMO wells), and 2) the waterworks wells used for drinking water production (BK wells).

The original dataset comes in the form of an excel file with different sheets for the major and trace elements, field parameters, and well-characteristics for a specific datatype, i.e. the data for GRUMO and BK wells is in separate sheets. To be able to use this data for NBL calculation, it was exported as csv format, and then imported to R version 4.0.2 (2020-06-22). Only the relevant variables were kept, all the sub-sets were joined together using the combination of DGU nr and intake number (unique ID), the data was quality checked, and further processed, so it can be used for the data-exploration analyses, and finally for NBLs calculation (**Figure 2**).

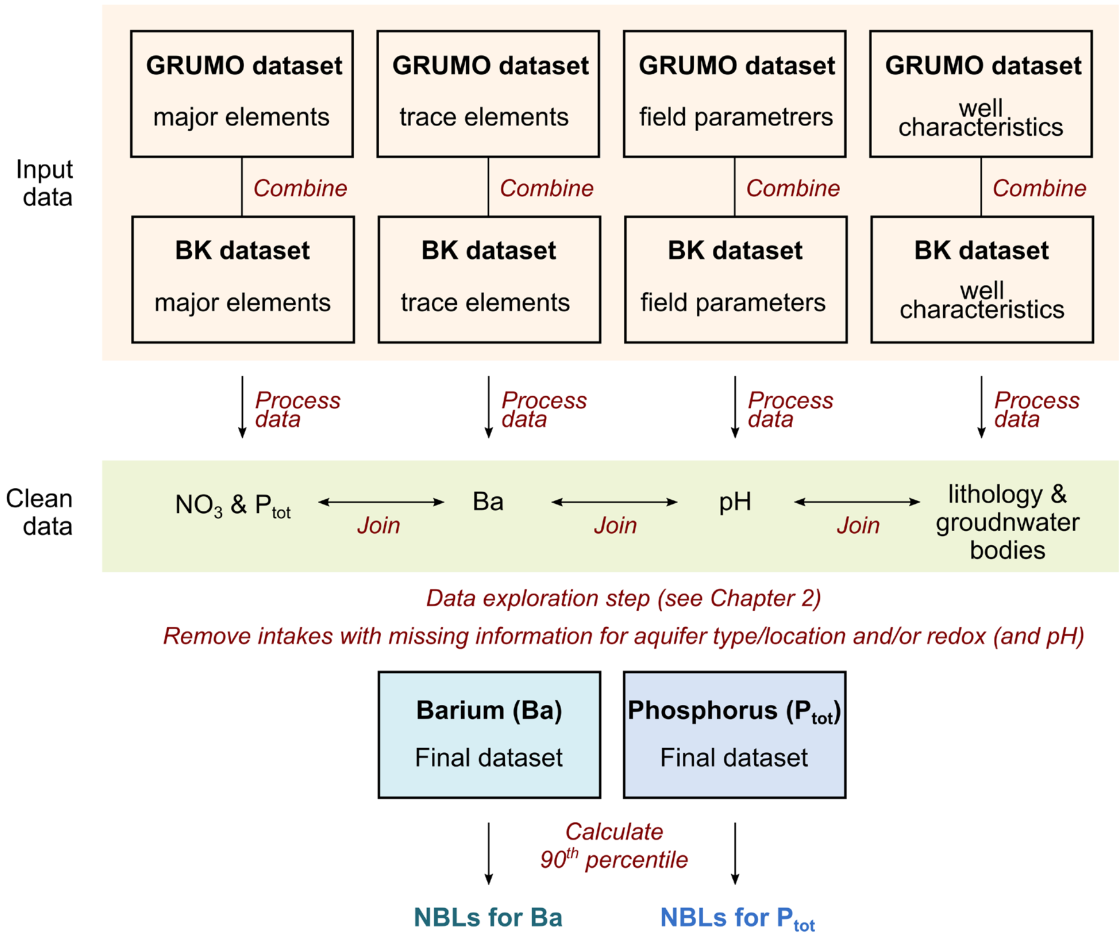


Figure 2. Overview of the data and data processing steps.

The commented R code is provided as an html file, which can be opened in any browser, so all data formatting, processing, and exploration steps can be followed. Below are summarised the most important data processing steps.

For all chemical parameters included in this work (Ba, P_{tot}, pH, NO_3^-), only the analyses for the period 2000-2021 (incl. both years) were used. Analyses taken before 2000 were also excluded in the NBL assessment for trace metals, that is a part of Vandplan III (Mortensen et al. 2021).

Duplicates and obvious reporting errors were excluded, i.e. analyses with 0 concentration and unit mistakes (obvious unit mistake would be if only one of the samples for a well was with few orders of magnitude different, e.g. instead 9-10 µg/l, it was reported as 1000 µg/l). This assessment was done manually by checking the time-series for the intakes with the highest reported values. It is possible that there are other unidentified reporting errors. For pH only analyses in the range between 3 and 10 were kept, which excluded obvious reporting errors.

Analyses below the limit of detection (< LOD) with high detection limits were excluded, where high LODs were:

- for Ba: > 1 µg/l
- for P_{tot} > 0.01 mg/l
- for NO_3^- > 1 mg/l

The values < LOD were substituted with half of the limit of quantification (LOQ = 3*LOD, i.e. < LOD = 1.5 LOD). This follows the methodology used in the NBL assessment for trace metals, that is a part of Vandplan III (Mortensen et al. 2021).

The aggregation at intake level for Ba, P_{tot}, NO_3^-, and pH was based on mean of the annual means (MAM) calculated for each intake and element (same as in Mortensen et al. (2021)). The purpose of the aggregation is to assure that there is only one representative concentration per intake. It was based on MAM, so each year would have equal influence on the calculated representative value. This is needed because the groundwater sampling has been irregular and, in some years, and some intakes (not all and always) there could be multiple measurements per year.

After the MAMs were calculated, all intakes with NO_3^- and/or pH data were classified, so later this classification can be used for assessing the Ba and P_{tot} variability (see **Chapter 2**) and to calculate the NBLs (see **Chapter 4**).

Like in the NBL assessment for trace metals (Mortensen et al. 2021), NO_3^- was used as a proxy for the redox conditions, allowing to classify the intakes in reduced or oxic state. This decision was taken because NO_3^- had a better spatial coverage than O_2, and because the NO_3^- measurements are more robust to sampling errors than O_2 (Mortensen et al. 2021). The threshold of 2 mg/l was used considering potential sampling issues, thus:

- **reduced** intakes had mean annual mean of NO_3^- **≤ 2 mg/l**
- **oxic** intakes had a mean annual mean of NO_3^- **> 2 mg/l**

pH was a relevant parameter for Ba (see **Chapter 2** for details), so the intakes were also classified based on the pH into:

- intakes with **low pH** – mean annual mean of **pH ≤ 7**
- intakes with **high pH** – mean annual mean of **pH > 7**

The threshold for pH (=7) differs from the one used for the trace metals assessment (pH = 6) (Mortensen et al. 2021), because it was selected based on the observed relation between pH and Ba in this dataset (see **Chapter 2**).

The NBLs should be calculated for different groundwater types, considering not only the geochemical conditions, but also the geology/lithology of the aquifer. This could be done in different ways. In Chapter 2 (the data-exploration phase) we used three different options to get a better understanding about Ba and P_{tot} distribution in Danish groundwaters.

The first option was to use the same classification as in the National Water Resources Model for Denmark, the DK-model (https://vandmodel.dk/), where the 2050 Danish groundwater bodies are classified into four types:

- fractured carbonate rocks ("kalk")
- Quaternary sand ("ks")
- pre-Quaternary sand ("ps")
- all geologically diverse units on Bornholm ("uu")

A coupling between intakes and groundwater bodies was made (Troldborg, 2020), which allows using the same classification for the individual intakes.

The second option is to also consider the location of the aquifer (Jutland, Funen, Zealand, Bornholm, or the small islands near Jutland). For this purpose, we also used the coupling between intakes and groundwater bodies from the DK-model (Troldborg, 2020). A combination between the five locations and the four aquifer geology classes results in 9 classes:

- fractured carbonate rocks ("kalk") in Jutland, Funen, or Zealand (3 classes)
- Quaternary sand ("ks") in Jutland, Funen, Zealand, or the small islands (4 classes)
- pre-Quaternary sand ("ps") – only found in Jutland (1 class)
- all geologically diverse units on Bornholm ("uu") (1 class)

The third option is to classify the intakes based on the lithological descriptions of the wells, which is available in Jupiter database and in the dataset used here. In this option, since there could be multiple different lithologies within the intake, only the dominating one is used.

"Dominating lithology" is defined here as the lithology with the largest proportion within the intake. This is represented in the dataset as field in the format "ds 70%, dl 20%, di 10%", where the mnemonic codes ("ds", "dl", "di") represent specific lithology types, while the percentages provide information on what fraction of the intake is with each specific lithology. The dominating lithology in this example would be "ds" (Glacial melt water sand, dk: Glacial smeltevandssand), as it takes 70% of the intake length.

There were more than 70 different mnemonic codes for the lithology, present in this dataset, which were further grouped in the 11 categories defined previously by expert geologist from GRUK (PSA) (**Appendix 2**).

In the cases when there were two equally dominating lithologies (e.g. "ds 40%, dl 40%, di 20%"), additional assessment was needed in order to determine in which of the 11 groups it should fall. There were 63 different combinations where there were two equally dominating lithologies. Those were evaluated manually to determine which group they belong to. The cases when the two lithologies belonged to two different groups, they were recoded to be “mixed” (“M”). In most cases both lithologies fell into the same group. In few cases, one of the lithologies was unspecific (e.g. “s” for sand), while the other was more specific (e.g. “ds”). The specific lithology was used for the grouping in these cases.

The classification based on dominating lithology within the intake was used in the data-exploration phase only (see Chapter 2). For the NBLs calculation we used the second option (combination between location and aquifer type) as during the exploration phase it was found to be more appropriate.

The data-visualization types used in this report are:

- **scatter plot** – two variables plotted against each other, e.g. Ba vs NO_3^-; log10 axis transformation is used on most plots, as it better represents the variability of the data.
- **boxplot** – it summarizes the data-distribution for a specific class/type; the median is shown with a thicker horizontal line and the notches around the median help comparing groups. If the notches of two boxes overlap, this suggests that the medians are not significantly different. The notches extend 1.58 * IQR / sqrt(n), where IQR is the interquartile range (difference between the first and third quartiles). This gives roughly a 95% confidence interval for comparing medians. The lower and upper hinges (of the box) correspond to the first and third quartiles (the 25th and 75th percentiles, here denoted as q25 and q75). The upper and lower whiskers extend from the hinge (box) to the largest value no further than 1.5*IQR. The outliers are not shown as part of the boxplot, as all the data-points are plotted under the boxplot. The data-points are plotted as a cloud, where there is slight random horizontal displacement, so they are not all overlapping.
- **empirical cumulative distribution function (ECDF) plot** – it shows the distribution of the specific data-selection (it could be the entire dataset or specific subset). In this report it is used for visualising the 90^{th} percentiles and the difference between the Ba and P_{tot} distributions for different aquifer types (based on geology, location, and geochemical conditions).
- **maps** – the maps used in this report show the spatial distribution of MAMs for Ba and P_{tot} for the intakes included in the final dataset. The dataset was split in four parts, depending on the aquifer geology (carbonates, pre-Quaternary sand, Quaternary sand, and diverse units on Bornholm) and each part is plotted on top of the extend of the corresponding aquifer types. Higher concentrations are plotted on top.

All graphs were produced in R v. 4.0.2 (R Core Team, 2020) (see html file for code) and all maps were produced in QGIS 3.22 (QGIS Development Team, 2021).

All summary statistics accompanying the boxplots for the different classes discussed in Chapter 2, including number of intakes, min, max, median ± median absolute deviation (MAD), mean ± standard deviation (SD), first and third quartiles (q25 and q75) can be found in **Appendix 3**.

The NBLs were calculated as the 90th percentile based on a subset of the Ba and P_{tot} datasets (i.e. the final datasets), which included only the intakes that could be classified by the element-relevant parameters (see **Chapter 3**).

Chapter 2: Barium and Phosphorus distribution in Danish groundwater and governing factors

Barium

Barium (Ba) is an alkaline earth metal naturally present at low to moderate concentrations in the environment. Worldwide, natural environments rich in Ba are found where there are (Kravchenko et al., 2014):

- Volcanic terrains or areas with deposition of volcanic by-products (e.g. black shales)
- Sedimentary evaporites (containing barite)
- Sedimentary basins with depositional rates of volcanic clasts (e.g. plagioclase feld-spar)
- Restricted, highly evaporative shallow ocean basins (e.g. shallow gulfs)
-

None of these environments are typical for present day Denmark, where most of the land-scape is formed during the last glaciation (Weichselian glaciation), but most of them are rep-resented by sediments in the Danish underground.

The most common minerals associated with Ba include barite ($BaSO_4$), carbonates (e.g. $Ca(Ba)CO_3$), heavily weathered clay minerals (e.g. $Al(Ba)_2Si_2O_5(OH)_4$), iron oxyhydroxides ($FeO(OH)nH_2O$), and plagioclase feldspar silicates (e.g. $Ca(Ba)Al_2Si_2O_8$) (Kravchenko et al., 2014).

In most natural waters, Ba occurs in salt compounds, e.g. barite ($BaSO_4$), witherite ($BaCO_3$), and rarely barium chloride ($BaCl_2$) (Kravchenko et al., 2014).

In the natural aquatic systems, the concentration of Ba depends on the mineral matrix of the aquifer lithologies (e.g. sulfates, carbonates, granodiorite, and shale), as well as the physi-cochemical conditions (e.g. pH, temperature, and redox state) of the groundwater (Kravchenko et al., 2014). The long-term stability of Ba in groundwater is controlled by its adsorption onto metal oxides, colloidal particles, organic matter, and/or aluminosilicate clays, and the relative saturation of Ba ligand pairs (Kravchenko et al., 2014). Therefore, **pH and redox state are important factors that control the solubility of Ba compounds in natural waters**.

Changes in oxidation state do not affect Ba valence state or its solubility in natural waters directly but can impact the sulphur species (Kravchenko et al., 2014). For example, if SO_4^{2-} is reduced to H_2S, the concentration of SO_4^{2-} decreases, thus the solubility of Ba^{2+} will in-crease (Kravchenko et al., 2014). This will result in higher Ba in groundwater over time (Kravchenko et al., 2014). Therefore, Ba can accumulate in waters which are low in SO_4 and it can be used as an indicator of **groundwaters with highly/strongly reducing conditions** where SO_4 reduction is occurring (Reimann & Birke, 2010). Sulphate reduction could be an indicator for risk of high Ba concentrations, as well.

Ba solubility increases with decreasing pH (i.e. in **more acidic conditions**), however the scale of solubility would depend on the ligand pair and/or type of Ba salt. For example, $BaCl_2$ is less dependent on pH than $BaSO_4$ or $BaCO_3$ (Kravchenko et al., 2014). Ba sorption is also pH-dependent (Reimann & Birke, 2010).

Research focused on Ba distribution in Danish groundwaters is limited. Nilsson et al. (2019) observed an association between Ba in Danish groundwater and the presence of **Tertiary clay** (**East Jutland, Funen, Zealand**, except Southeast Zealand) or **Cretaceous chalk** aquifers (dk: skrivekridt; on **Møn and Lolland Falster**).

To support the decisions on which parameters are important enough to be included in the calculation of NBLs, here we explore the clean dataset with respect to the groundwater redox state (based on NO3- concentration), pH, and aquifer type/location or dominating lithology.

Figure 3 shows the relation between Ba and NO3- concentrations and the distribution of Ba in reduced (red color) or oxic (greenblue color) groundwaters. Overall, at the national scale, higher concentrations of Ba are observed in reduced groundwaters irrespective of the geology. The nationwide median (± median absolute deviation, MAD) for Ba for reduced waters is 69 ± 44 µg/l (n = 6020), while for oxic waters is 35 ± 23 µg/l (n = 1397) (***Appendix 3***). It should also be noted that the dataset is biased towards reduced groundwaters, as there are about four times more reduced vs oxidized intakes.

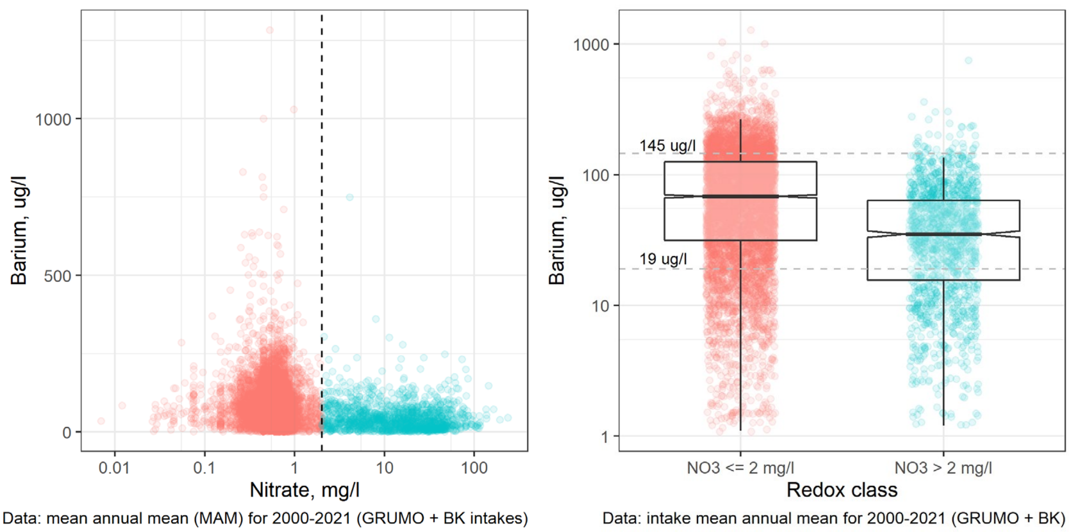


***Figure 3**. Ba concentrations and redox – left: Ba vs NO_3^- right: boxplot with Ba for reduced or oxic groundwaters; each point is an intake, log10 scale is used for both Ba and NO_3^-.*

Figure 4 shows the relation between Ba concentrations and pH and the distribution of Ba in groundwaters with low or high pH. Overall, at the national scale, most of the intakes with high Ba concentrations have pH > 7 (**Figure 4**). As mentioned previously, the pH threshold used for trace elements (Mortensen et al. 2021) was pH = 6, however by examining the scatter plot on **Figure 4**, it becomes clear that this is not appropriate for Ba. The elevated Ba concentrations start to appear near pH = 7 and are most pronounced at pH > 7. Therefore, here we chose pH = 7 to be the threshold for the two pH classes (low vs high pH). The nationwide median (± MAD) for Ba for groundwaters with low pH is 48 ± 22 µg/l (n = 703), while for high pH is 66 ± 44 µg/l (n = 6101) (***Appendix 3***). The dataset is strongly biased towards groundwaters with higher pH – there are 8-9 times more intakes with pH >7 than with pH ≤ 7. It must be noted also that there are fewer intakes that could be classified for pH (n = 6804) than for redox (n = 7417). Most likely, the observed relation is due to different type of geology, e.g. carbonates (with higher pH) vs the sandy aquifers (outwash plains) in western Jutland (with low pH).

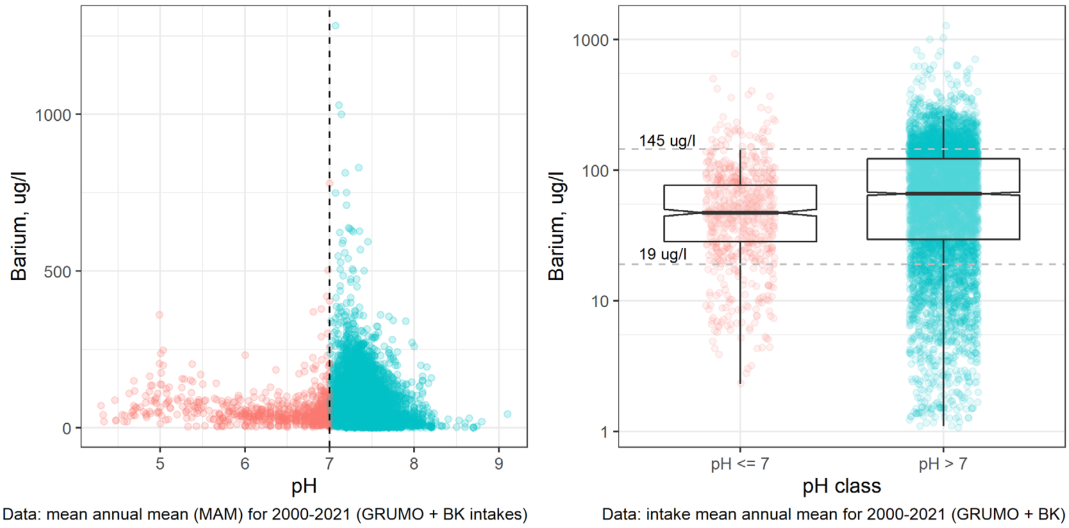


Figure 4. *Ba concentrations and pH – left: Ba vs pH, right: boxplot with Ba for groundwaters with low or high pH; each point is an intake, log10 scale is used for both Ba and* NO_3^-.

Figure 5 shows the distribution of Ba concentrations for the four aquifer types (kalk – Carbonate aquifers; ks – Quaternary sand aquifers; ps – pre-Quaternary sand aquifers; uu – Diverse units on Bornholm). Overall, at the national scale, higher Ba concentrations are observed in the Quaternary sand aquifers (**Figure 5**), which had the highest median Ba (82 ± 45 µg/l). However, if we distinguish between those aquifers located in different parts of the country, it becomes clear that there are regional differences (***Figure 6***). Of all Quaternary sand aquifers, those with the highest Ba median (133 ± 27 µg/l) are on Funen, followed by Zealand (84 ± 31 µg/l), and those in Jutland (58 ± 36 µg/l) and the small islands near Jutland (53 ± 47µg/l).

Regional difference can be observed also for the carbonate aquifers. The nationwide Ba median was 38 ± 27 µg/l (***Appendix 3***). When the location is considered, the carbonate aquifers on Zealand have the highest median Ba (58 ± 28 µg/l), followed by Funen (22 ± 18 µg/l), and the lowest is for Jutland (10 ± 7 µg/l).

Overall, the highest number of intakes with Ba data are tapping into Quaternary sand aquifers (n = 3915), followed by those for carbonate aquifers (n = 2382) and pre-Quaternary sand aquifers (n = 730). Bornholm is represented by only 100 intakes for Ba. The Quaternary sand aquifers in Jutland are represented by 2438 intakes with Ba data, while the next class with highest representation is the carbonate aquifers on Zealand (n = 1594).

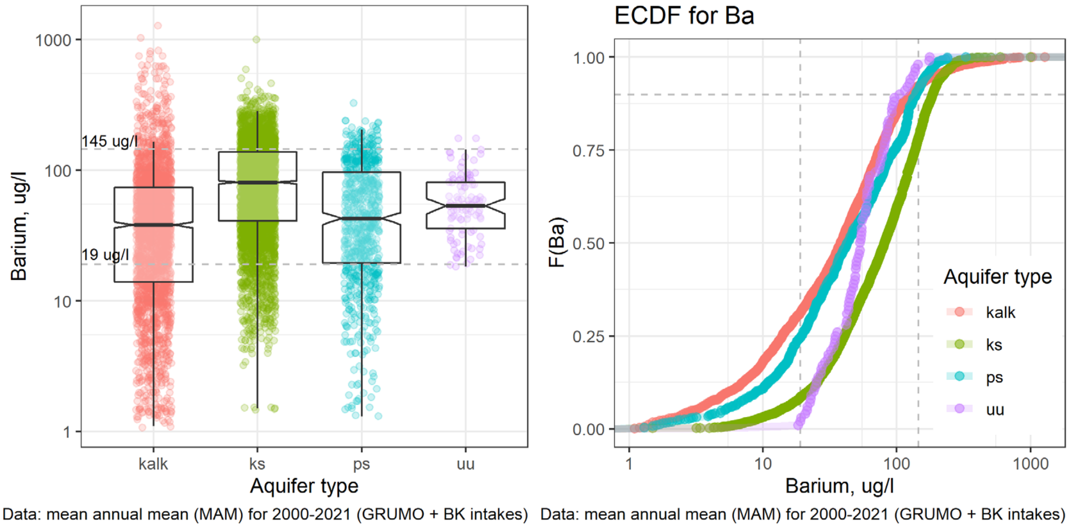


Figure 5. *Ba concentrations and aquifer type, where: "kalk" – Carbonate aquifers; "ks" – Quaternary sand aquifers; "ps" – pre-Quaternary sand aquifers; "uu" – Diverse units on Bornholm. left: boxplot, right: ECDF plot; log10 used for Ba.*

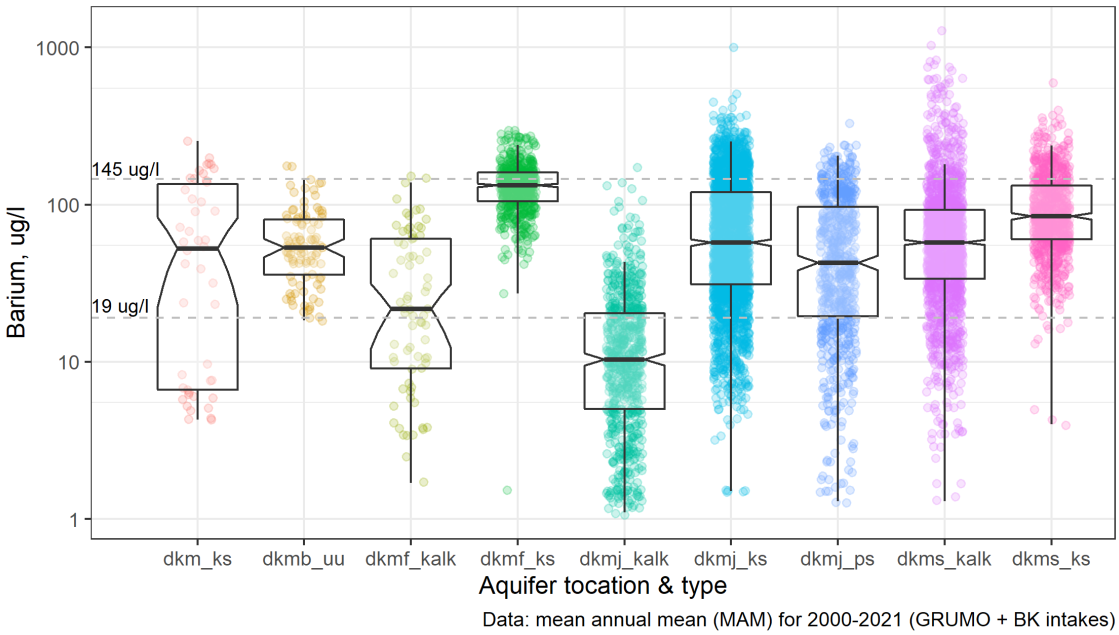


Figure 6*. Ba concentrations for different location and aquifer types, where: "dkm_ks" – Quaternary sand on the small islands near Jutland; "dkmb_uu" – Diverse units on Bornholm; "dkmf_kalk" – carbonate aquifers on Funen; "dkmf_ks" – Quaternary sand aquifers on Funen; "dkmj_kalk" – Carbonate aquifers in Jutland; "dkmj_ks" – Quaternary sand aquifers in Jutland; "dkmj_ps" – pre-Quaternary sand aquifers in Jutland; "dkms_kalk" –carbonate aquifers on Zealand; "dkms_ks" – Quaternary sand aquifers on Zealand.*

The dominating lithology within the intake was also used here, as it could provide more insight into the Ba distribution. Only the categories with more than 20 intakes are shown on ***Figure 7***. The categories with most intakes are Quaternary sand, gravel, or alternating beds

(G2, n = 2875), pre-Quaternary limestone and chalk (G6, n = 2117), unspecified sand or gravel (G11, n = 935), and pre-Quaternary sand and gravel (G8, n = 563). Except for G11, the other three categories (G2, G6, G8) are similar to the aquifer types discussed previously. The differences with the DK-model classes are in the presence of clay/silt categories (G1, G5, G7, G10), the category for marine sand/gravel/silt (G4), and the mixed category (M).

The dominating lithology with the highest Ba median and enough data is the Quaternary sand, gravel, or thin alternating beds (G2, 84 ± 45 µg/l). This result is similar to the nationwide Ba median for the Quaternary sand aquifer type (ks, 81 ± 45 µg/l). The Ba median for pre-Quaternary limestone and chalk (G6) is the same as the nationwide Ba median for the carbonate aquifer type (kalk, 38 ± 27 µg/l). The lowest median (11 ± µg/l) is for the Quaternary marine sand, gravel, and silt category (G4), but there were only 76 intakes in this category.

According to Nilsson et al. (2019), higher Ba concentrations were observed for Campanian-Maastrichtian chalk ("sk", dk: Campanien-maastrichtien skrivekridt). The information about dominating lithology within the intake allows for assessing the Ba distribution for the different types of carbonates present in Denmark (**Figure 8**). Overall, the medians for the different carbonates are not vastly different, however the data distributions differ (**Figure 8**). Even though the median for the Campanian-Maastrichtian chalk ("sk") is similar to the rest of the medians, it has the highest mean Ba (87 ± 141 µg/l) and highest q75 (93 µg/l). There are clay-rich marl layers in this type of chalk, which could be a possible explanation for the higher Ba concentrations. The carbonate type with the lowest median Ba is the Danian calcilutite or chalk ("lk", dk: Danien slamkalk, skrivekridt; 24 ± 21 µg/l).

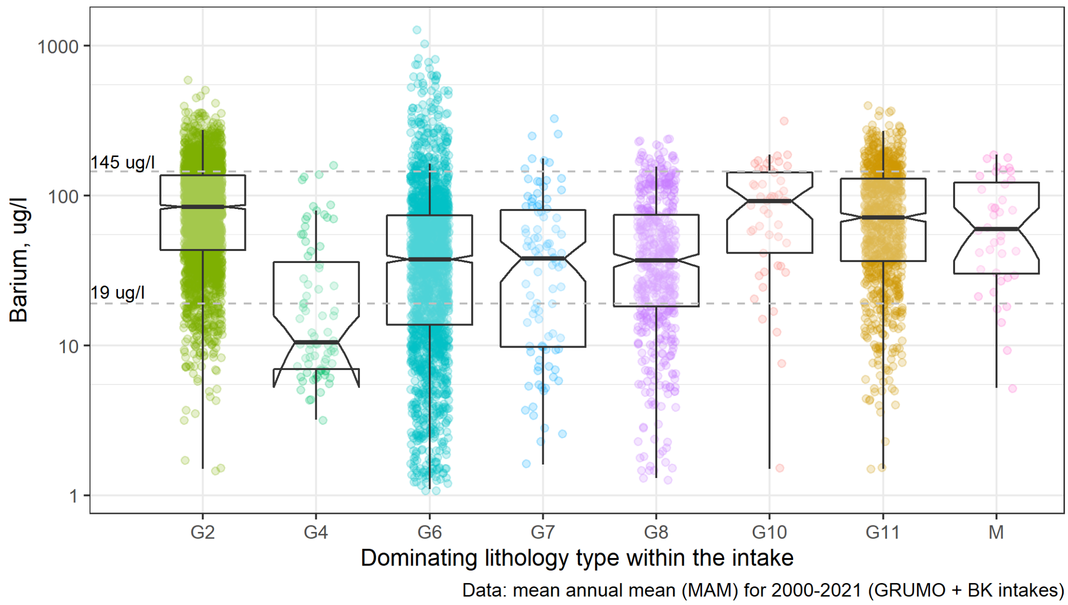


__Figure 7__. Ba concentrations for different groups of dominating lithology type within the intake, where: G2 – Quaternary sand, gravel, or thin alternating beds; G4 – Quaternary marine sand, gravel, and silt; G6 – Pre-Quaternary limestone and chalk; G7 – Pre-Quaternary clay, silt, and brown coal; G8 – Pre-quaternary sand and gravel; G10 – Unspecified clay or silt; G11 – Unspecified sand or gravel; M – mixed (two diff. types equally represented). Log10 is used for Ba

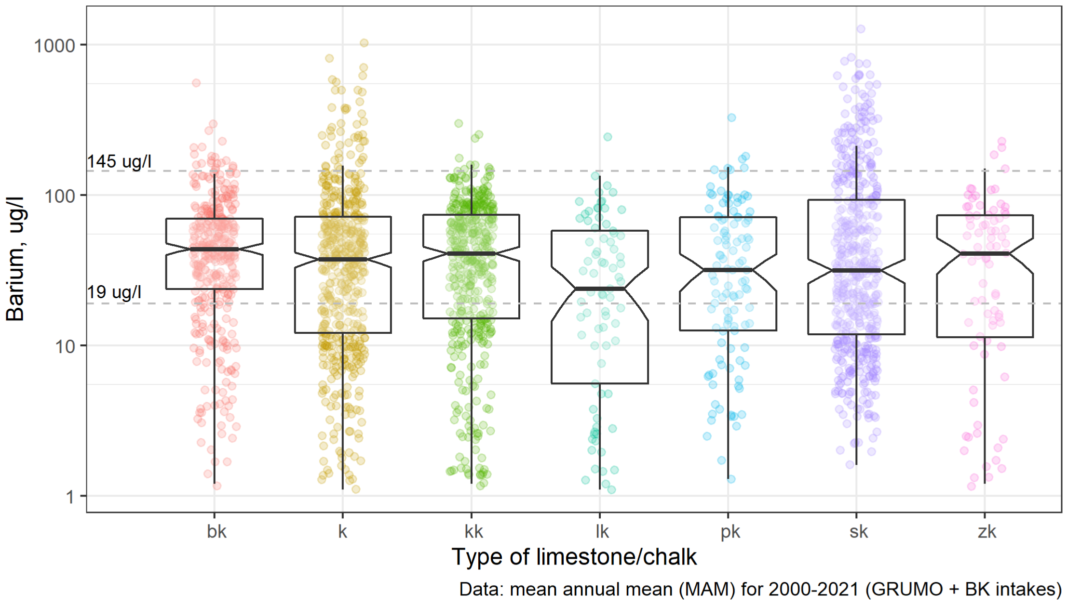


***Figure 8**. Ba concentrations for different types of carbonates (limestone/chalk), where: "bk" – Danian bryozoan limestone, corallian limestone; "k" – limestone, chalk (unspecified); "kk" – Danian calcarenite; "lk" – Danian calcilutite, chalk; "pk" – Selandian sandstone, Palaeocene greensand stone; "sk" – Campanian-Maastrichtian chalk; "zk" – Danian limestone, limestone, and chert.*

To conclude the data-exploration for Ba, the results presented in this Chapter showed that the following factors are important for setting meaningful NBLs for Ba:

- aquifer type and location
- redox state of the groundwater
- groundwater pH.

Phosphorus

Phosphorus (P) is an essential element for all living organisms and a major nutrient for plants, and it is the eleventh most abundant element in the Earth's crust (Reimann & Birke , 2010). Important phosphate minerals include apatite ($Ca5(PO_4,CO_3)c(F,OH,Cl)$), monazite ($(Ce,La,Nd,Gd,Th)PO_4$), and xenotime (YPO_4), but P is also occurring in many of the common rock-forming minerals: olivines, garnets, pyroxenes, amphiboles, and micas (Reimann & Birke, 2010).

Soluble P-compounds in soils are readily taken up by plants and bacteria can immobilize P in soils as calcium hydroxyapatite (Reimann & Birke, 2010). It is poorly mobile in groundwater, because of 1) microbiological mineralization, 2) sorption, and 3) low solubility of P-containing minerals (Reimann & Birke, 2010). High P concentrations in groundwater are usually indication for pollution, especially from wastewater or sewage (Reimann & Birke, 2010).

According to Nilsson et al. (2019), the P content in Danish groundwater is primarily geologically determined. Usually, the source of P is decomposing organic matter. For example, high content of P is found in **marine deposits**, incl. **postglacial** deposits as those found in **North Jutland**. Mobilisation of P from the sediments could occur under **iron-reducing conditions when** P desorption from iron oxides is possible (Nilsson et al., 2019).

It has also been observed previously that P content in Danish groundwater is usually **low in areas with carbonate pre-quaternary geology** (Nilsson et al., 2019). This was explained by the strong affinity of carbonate rocks (chalk and limestone) to bind P; thus, P is not easily released to groundwater.

Nilsson et al. (2019) suggested that it is appropriate to distinguish groundwater types for P based on:

- Areas with carbonate (low P) vs. non-carbonate geology (higher P)
- Areas with interglacial marine layers or Tertiary marine sands (higher P)
- Oxic groundwater, e.g. type A (low P) vs reduced, e.g. type C (high P)

To support the decisions on which parameters are important enough to be included in the calculation of NBLs, here we explore the clean dataset with respect to the groundwater redox state (based on NO_3^- concentration), and aquifer type/location or dominating lithology.

In this assessment there is only focus on total phosphorus (P_{tot}), as there was better data-coverage in the Jupiter database than for ortho-phosphate.

Figure 9 shows the relation between P_{tot} and NO_3^- concentrations and the distribution of P_{tot} in reduced (red color) or oxic (greenblue color) groundwaters. Overall, at the national scale, higher concentrations of P_{tot} are observed in reduced groundwaters (**Figure 9**) irrespective of the geology. The nationwide median (±MAD) for P_{tot} for reduced waters is 0.082 ± 0.056 mg/l (n = 6554), while for oxic waters is 0.025 ± 0.014 mg/l (n = 1906) (**Appendix 3**). As with Ba, the dataset is biased towards reduced groundwaters.

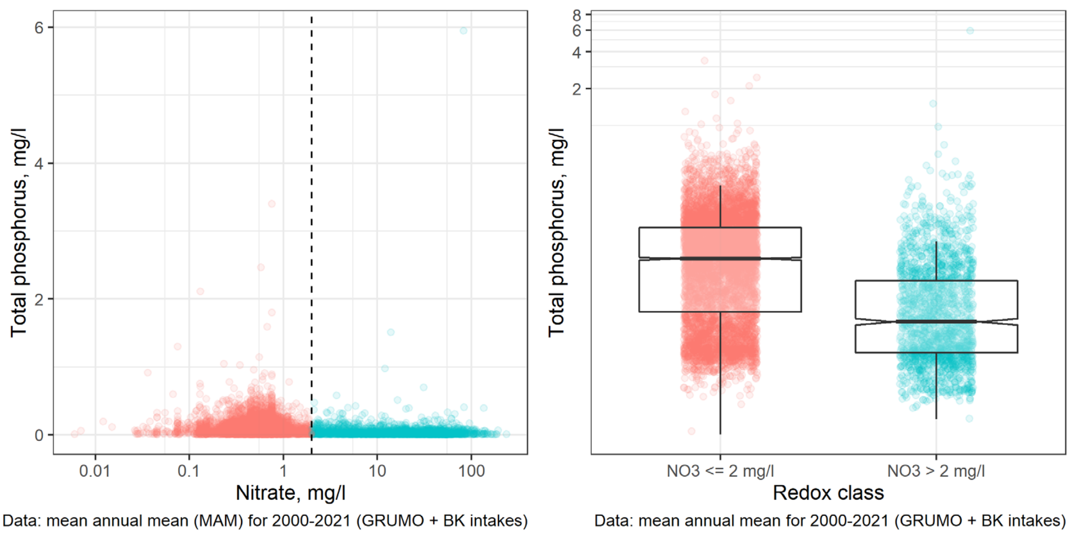


__Figure 9__. Total phosphorus (P_{tot}) concentrations and redox – left: P_{tot} vs NO_3^-, right: boxplot with Ptot for reduced or oxic groundwaters; each point is an intake, log10 scale for P_{tot} is used only on the boxplot.

Figure 10 shows the distribution of P_{tot} for the four aquifer types ("kalk" – Carbonate aquifers; "ks" – Quaternary sand aquifers; "ps" – pre-Quaternary sand aquifers; "uu" – Diverse units on Bornholm). Overall, at the national scale, higher P_{tot} concentrations are observed for the sandy aquifers (both "ks" and "ps"), where the median ± MAD for the Quaternary sand is 0.094 ± 0.054 mg/l (n = 4668) and for pre-Quaternary sand is 0.103 ± 0.044 mg/l (n = 820). As suggested by Nilsson et al. (2019), nationwide, the carbonate aquifers have lower P_{tot} concentrations than the sandy aquifers. The median ± MAD for carbonate aquifers is 0.020 ± 0.007 mg/l (n = 2489). Bornholm is also characterised with low P_{tot} concentrations, like those for carbonate aquifers.

When the location of the aquifers is also considered (**Figure 11**), the carbonate aquifers in Jutland have overall lower concentrations (median ± MAD = 0.016 ± 0.004 mg/l, n = 768) than those on Funen and Zealand, respectively (0.024 ± 0.008 and 0.023 ± 0.010). Of the Quaternary sand aquifers, those on Zealand have slightly higher median ± MAD (0.115 ± 0.066 mg/l, n = 995).

Figure 12 shows the P_{tot} cocnentrations for the different dominating lithologies within the intake length. As suggested in (Nilsson et al., 2019), the Quaternary marine sand, gravel, and silts (G4) have the highest concentrations, with median ± MAD of 0.197 ± 0.138 mg/l (n = 96). The rest of the results are similar to those from **Figure 11**.

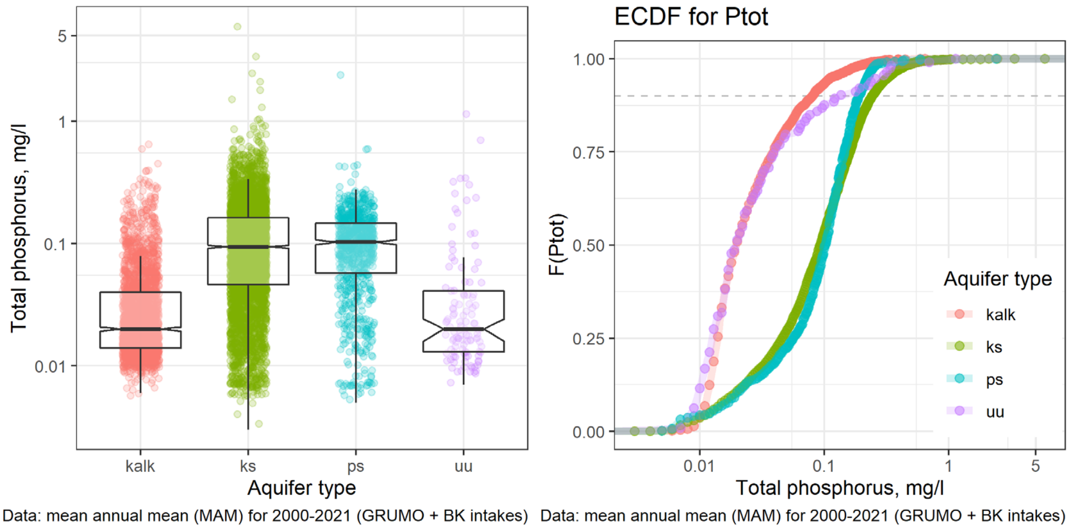


Figure 10. P_{tot} concentrations and aquifer type, where: "kalk" – Carbonate aquifers; "ks" – Quaternary sand aquifers; "ps" – pre-Quaternary sand aquifers; "uu" – Diverse units on Bornholm. left: boxplot, right: ECDF plot; log10 used for P_{tot}.

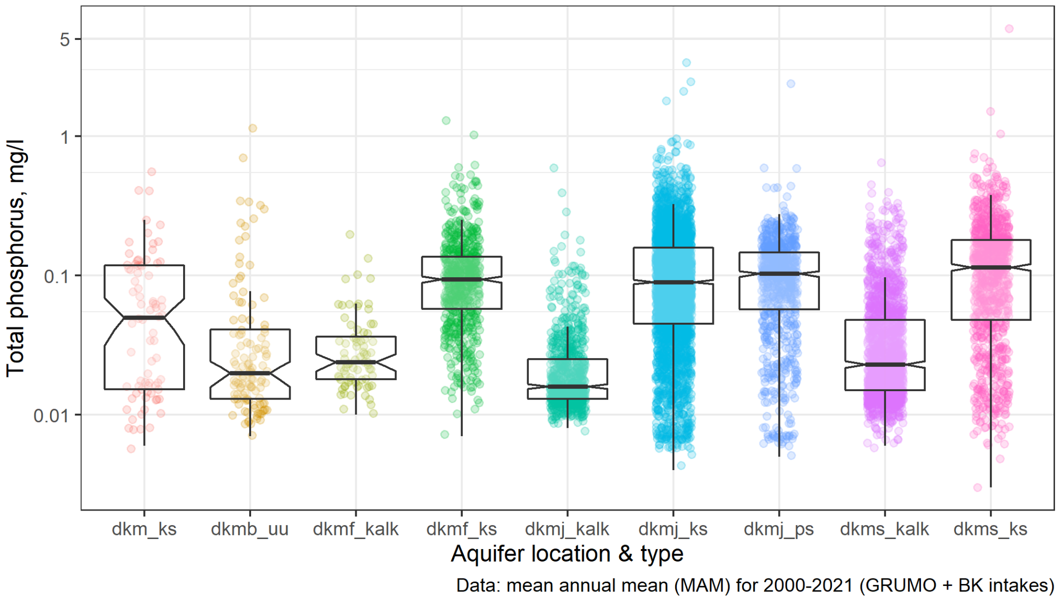


***Figure 11**. P_{tot} concentrations for different location and aquifer types, where: "dkm_ks" – Quaternary sand on the small islands near Jutland; "dkmb_uu" – Diverse units on Bornholm; "dkmf_kalk" – carbonate aquifers on Funen; "dkmf_ks" – Quaternary sand aquifers on Funen; "dkmj_kalk" – Carbonate aquifers in Jutland; "dkmj_ks" – Quaternary sand aquifers in Jutland; "dkmj_ps" – pre-Quaternary sand aquifers in Jutland; "dkms_kalk" – carbonate aquifers on Zealand; "dkms_ks" – Quaternary sand aquifers on Zealand. log10 used for P_{tot}.*

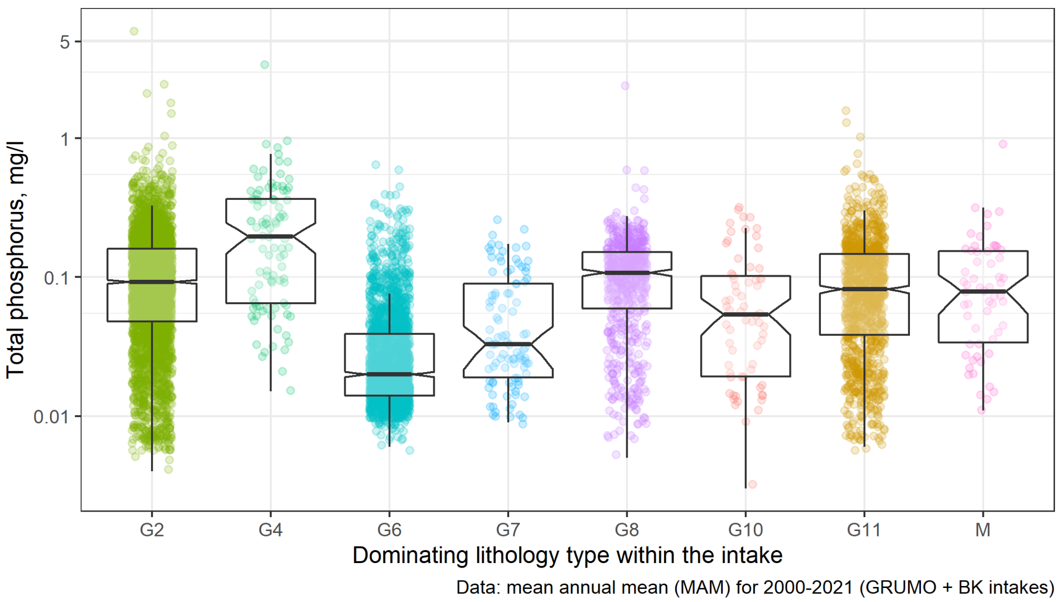


***Figure 12**. P_{tot} concentrations for different groups of dominating lithology type within the intake, where: G2 – Quaternary sand, gravel, or thin alternating beds; G4 – Quaternary marine sand, gravel, and silt; G6 – Pre-Quaternary limestone and chalk; G7 – Pre-Quaternary clay, silt, and brown coal; G8 – Pre-quaternary sand and gravel; G10 – Unspecified clay or silt; G11 – Unspecified sand or gravel; M – mixed (two diff. types equally represented). Log10 is used for P_{tot}.*

To conclude the data-exploration for P_{tot}, the results presented in this Chapter showed that the following factors are important for setting meaningful NBLs for P_{tot} :

- aquifer type and location
- redox state of the groundwater

In general, for both Ba and P_{tot}, it was decided to use the aquifer location and type based on the coupling of the intakes with the DK-model instead of the dominating lithology type within the intake. This was done, as the results were not significantly different between these two classifications. It was found more important to consider the location of the aquifer, as there are some regional differences.

Chapter 3: Criteria for determining natural background levels (NBLs)

Natural background levels (NBLs) for barium (Ba) and phosphorus (P) are determined here for different groundwater types. These groundwater types are defined by combining the classes for the parameters listed in **Table 1**. The relevance of the parameters was assessed and reported in **Chapter 2**.

Table 1. *Parameters and classes, and relevance for calculating NBLs for barium (Ba) and phosphorus (P).*

Parameter	Classes	Relevance
Geography	Jutland ("dkmj"), Funen ("dkmf"), Zealand ("dkms"), Bornholm "dkmb", small islands ("dkm")	Ba, P
Aquifer type	Fractured carbonate rocks ("kalk"), Quaternary sand ("ks"), pre-Quaternary sand ("ps"), all geologically diverse units on Bornholm ("uu")	Ba, P
Redox	Reduced ($NO_3^- \leq 2$ mg/l), oxic ($NO_3^- > 2$ mg/l)	Ba, P
pH	High (pH > 7), low (pH ≤ 7)	Ba

To supplement this, NBLs was calculated for groundwater types defined by combining only the two parameters "geography" and "aquifer type". These can be used in the cases when:

- the geochemical parameters (redox and/or pH) are not known for a specific groundwater body; or
- for the cases when NBLs could not be calculated including the geochemical parameters, because of low number of intakes (low representativity).

NBLs considering the geochemical parameters were calculated only for the classes with at least 50 intakes, as in Mortensen et al. (2021).

NBLs are calculated as the 90th percentile of the mean annual means for Ba and P_{tot} for the different groundwater types (**Table 1** and Chapter 2 for details), rounded based on the rounding rules used by Mortensen et al. (2021). Those rounding rules accounted for the relative uncertainty for the specific elements. According to Miljøministeriet (2021), all analyses for P_{tot} and Ba should have maximum relative uncertainty of 15-20% (P_{tot} - 15%, Ba - 20%). This relative uncertainty is similar for the trace metals (Mortensen et al., 2021), so it was decided to keep the same rounding rules (**Table 2**).

The rounding rules from **Table 2** apply for both lower and higher concentrations than the shown ones; for lower concentrations – divided by 10, 100, etc., while for higher concentrations – multiplied by 10, 100, etc. Both the calculated 90th percentile (before rounding) and the NBLs (after rounding) are presented in the results-tables in **Chapter 4**. The resulting NBLs are summarised to facilitate future use (see **Conclusion)**.

Table 2. Rounding rules used for deriving NBLs (Mortensen et al., 2021).

Concentration interval	Rounded value
1–1.5	1.5
1.5–2	2
2–2.5	2.5
2.5–3	3
3–4	4
4–5	5
5–7.5	7.5
7.5–10	10

Accounting for the analytical uncertainty when calculating NBLs is a topic that needs further investigations, and because it was beyond the scope of this project, it could not be addressed here. By using the rounding from **Table 2** it is assumed that there is a 20% uncertainty on the 90th percentile, and thus round roughly to +20%. Another way to handle the issue of propagating uncertainty is to instead calculate 95% confidence intervals for the 90th percentile and use the upper boundary (see for example Voutchkova et al., 2021).

Another limitation of the used methodology is the assumption that the 90th percentile represents a clear boundary for concentrations that are considered "natural" (or with *"only very minor, anthropogenic alterations to undisturbed conditions."* Article 2.5, European Commission, 2006). Hinsby et al. 2008 suggested the 90th percentile when working with small datasets (<~60 sampling points) or with datasets where human impact cannot be excluded. Guidance Document No. 18 (European Commission, 2000b) also refers to the BRIDGE methodology (used in Hinsby er al. (2008)) and mentions the 90th percentile as a practical criterion for setting the NBLs. The 90th percentile has become a "standard" way of dealing with NBLs in many European countries, some examples can be found in:

- Lions et al. (2021), where six EU countries tested a methodology based on the 90th percentile for SO_4, As, Cd, Cr, Cu, Ni, Zn, and F,
- Pulido-Velazquez et al. (2022), where five EU countries tested different statistical approaches, incl. the 90th percentile for Cl

See also the rest of the peer-reviewed articles from the special issue on Natural Background Levels in Groundwater, published in the open access journal "Water" (available at: www.mdpi.com/journal/water/special_issues/Background_Levels_Groundwater).

Hinsby et al. (2008) suggested also the 97th percentile, but for groundwaters where all data points represent natural composition. The reasons why 97th percentile was not used here are that: 1) It can never be sure that all intakes represent (near) natural composition, even though only data from GRUMO and waterworks wells used for drinking water production are included, 2) some of the sub-sets for specific aquifer types are rather small (~60 intakes), 3) any percentile (90th, 95th, 97th) is an equally subjective choice differing in what is defined as *"very minor anthropogenic alteration"* (as used in Article 2.5, European Commission, 2006) – 10%, 5%, or 3% of the dataset or subset.

Chapter 4: Proposed natural background levels

Before presenting the resulting NBLs for Ba and P_{tot}, here we show first the spatial distribution of the final datasets, which include only the intakes that could be classified by the combination of relevant parameters (final datasets). **Figure 13** and **Figure 14** show respectively the mean annual mean concentrations (MAM) for Ba and P_{tot} over the period 2000–2021, by aquifer types. The class-breaks for Ba (**Figure 13**) were selected, so it is easier to compare the MAMs to the general EQS (19 µg/l) and the maximum acceptable concentration (MAC = 145 µg/l). However, since there were no EQS or drinking water standard set for P_{tot}, the class-breaks were selected so they represent best the data-variability and are rounded in appropriate way.

Table 3 summarises the number of intakes, wells, represented groundwater bodies (GVF), and the number of groundwater types in the final Ba and P_{tot} datasets. Overall, the final dataset for P_{tot} is larger than that for Ba.

Table 3*. Characteristics of the final datasets for barium (Ba) and total phosphorus (P_{tot}); GVF – groundwater body.*

Dataset	Intakes (n)	Wells (n)	GVF (n, %) *	Groundwater types (n/n) **
Ba	6558	6181	453 (22%)	9/17
P_{tot}	8088	7348	525 (26%)	9/14

* the percentage is calculated from the total number of delineated groundwater bodies in Denmark (n = 2050); it does not account for the volume or area of the groundwater bodies.

** the first number corresponds to the number of groundwater types if only the location and geology are considered, while the second number corresponds to the number of groundwater types when also the geochemical parameters are considered; for the latter only classes with at least 50 intakes are used

Figure 15 and **Figure 16** show the empirical cumulative distribution function (ECDF) plots for Ba and P_{tot}, respectively. On the plots it can be seen the distribution of the final datasets for the relevant combination of parameters. The 90th percentile is marked as well, so it is easier to compare the plots for the different groundwater types.

The 90th percentiles and the corresponding NBLs for Ba and P_{tot} are presented in **Table 4** and **Table 5**, respectively (see **Conclusion** for summary).

The 90th percentiles for Ba are all exceeding the EQS (19 µg/l), with the lowest for carbonate aquifers in Jutland (the oxic aquifers had slightly lower 90th percentile than the reduced ones). The highest 90th percentile (205 µg/l) was for the Quaternary sand aquifers in Jutland, which are reduced and with a high pH ("dkmj_ks & NO_3^- ≤ 2 mg/l & pH > 7").

The 90th percentiles for P_{tot} range from 0.032 mg/l for the oxic carbonate aquifers on Zealand ("dkms_kalk" & NO_3^- > 2 mg/l) to 0.289 mg/l for the reduced Quaternary sand aquifers on Zealand ("dkms_ks" & NO_3^- ≤ 2 mg/l).

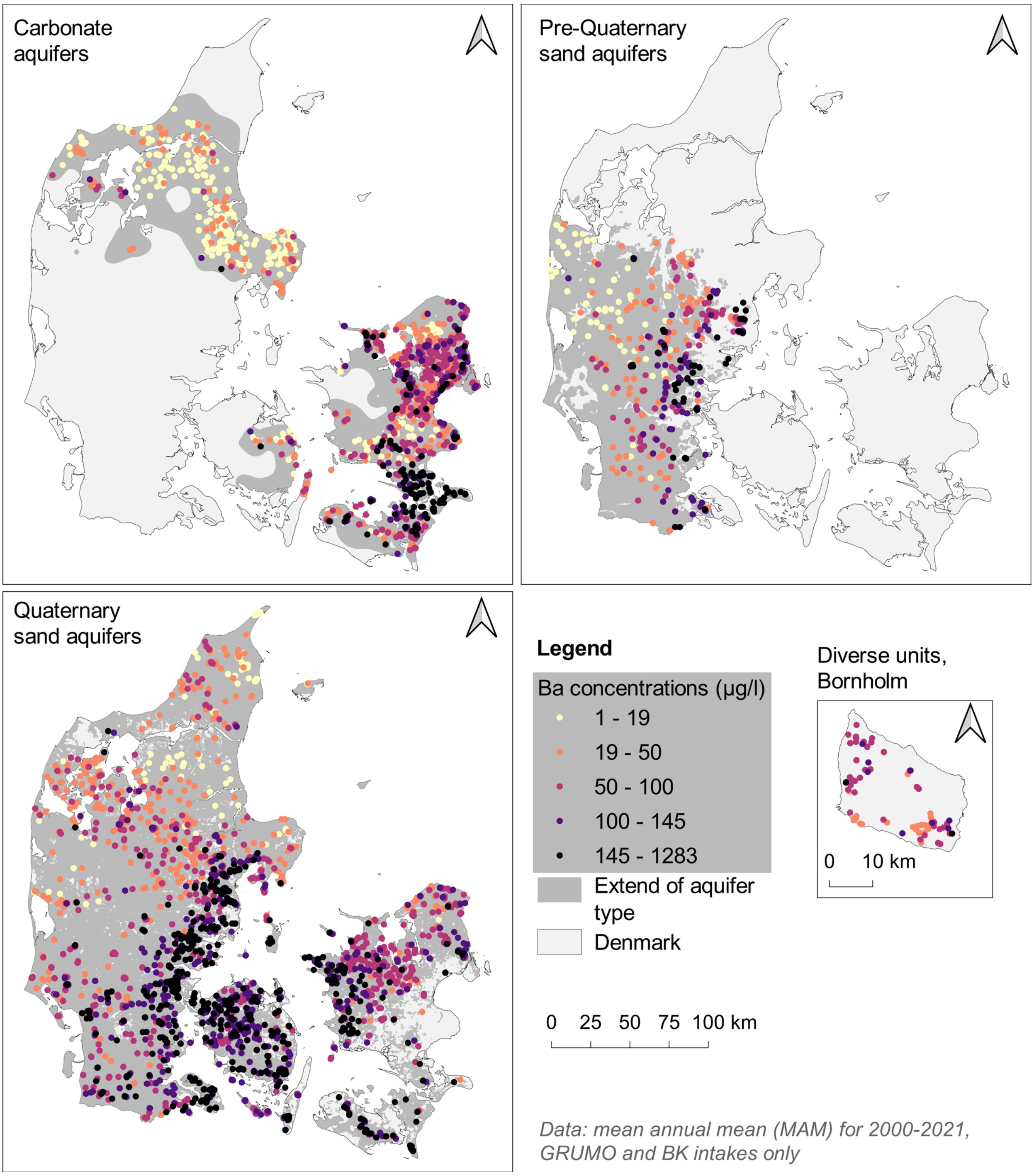


Figure 13. *Mean annual mean Ba concentration (2000-2021) at GRUMO and BK intakes included in the final dataset (n=6558) used for NBL calculation; on the different panels are shown only the intakes for the specific aquifer types from the DK-model coupling; the higher concentrations are plotted on top of those from lower class.*

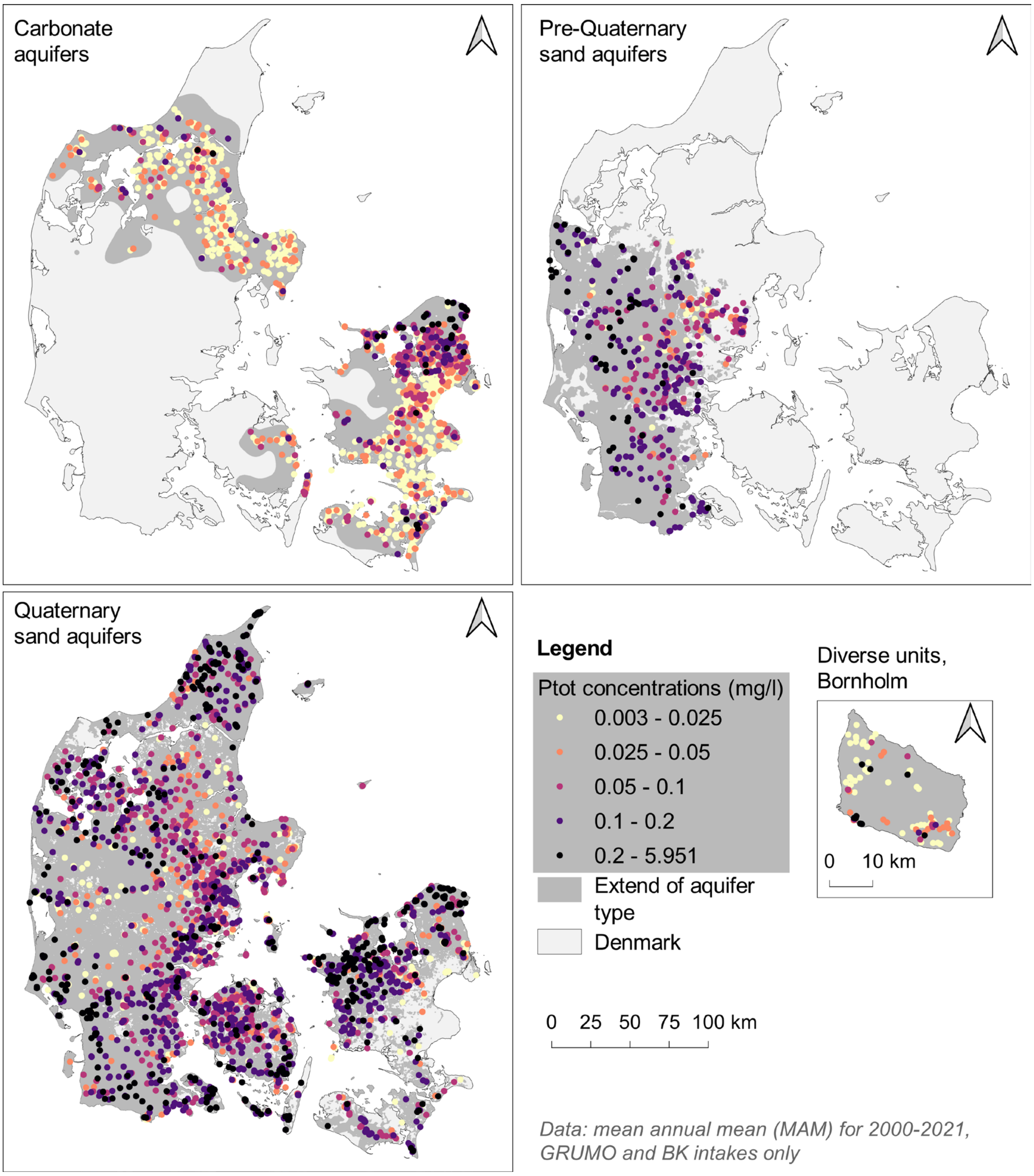
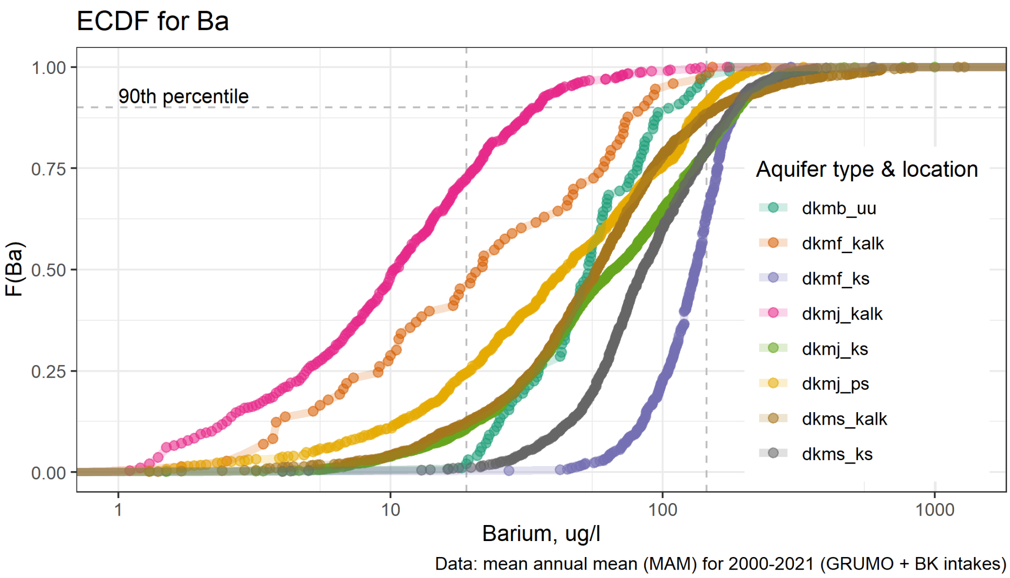


Figure 14. *Mean annual mean phosphorus (P_{tot}) concentration (2000-2021) at GRUMO and BK intakes included in the final dataset (n=8088) used for NBL calculation; on the different panels are shown only the intakes for the specific aquifer types from the DK-model coupling; the higher concentrations are plotted on top of those from lower class.*



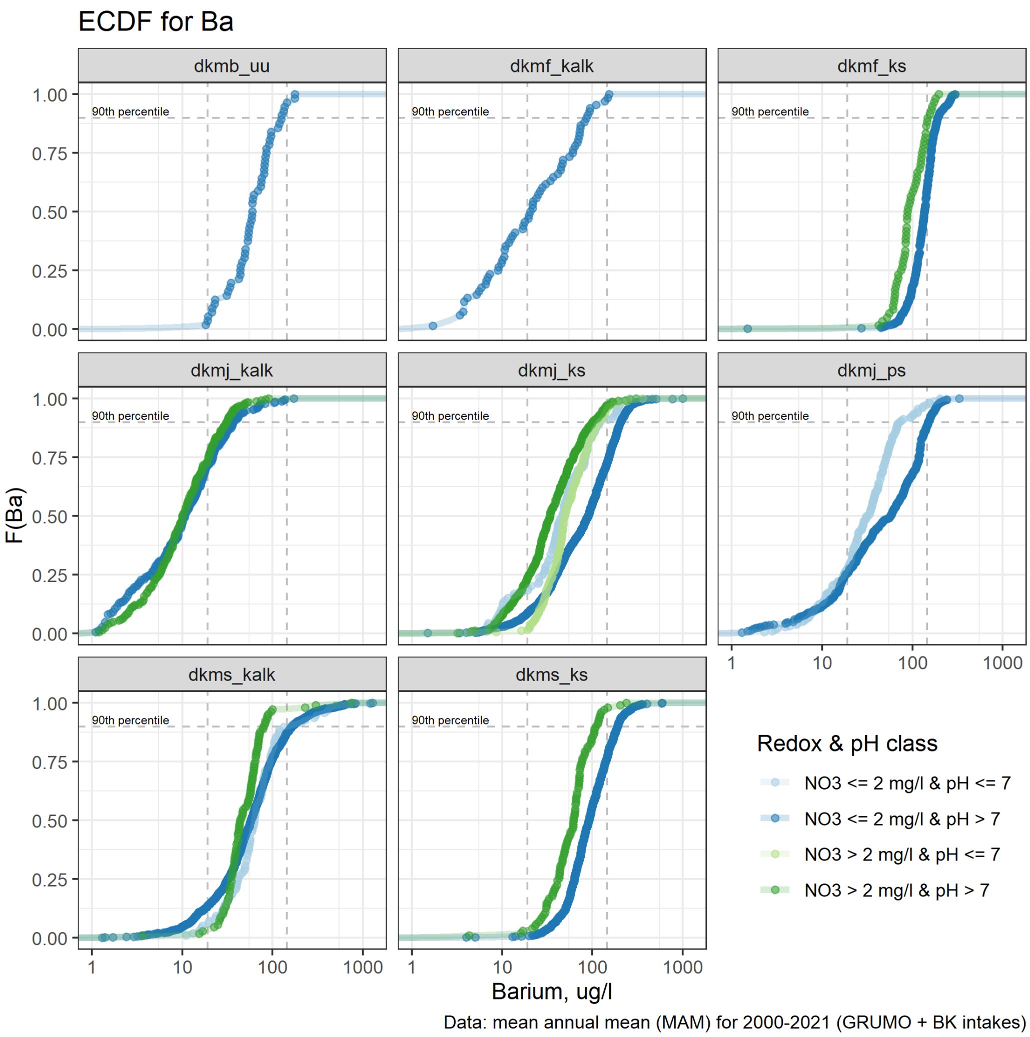


***Figure 15**. Empirical cumulative distribution function (ECDF) plot for the final dataset for Ba; top – only aquifer type and location considered; bottom – aquifer type, location (different panels) and redox & pH class combination (different colours); only groundwater types with 50 or more intakes are shown.*

Table 4. 90th percentile and NBLs for Ba [μg/l]. NBLs are rounded using the rules from Table 2.

Location	Aquifer type	Redox	pH	Code	n	q90	NBL
Bornholm	Diverse units	Reduced	High	dkmb_uu & NO_3^- ≤ 2 mg/l & pH > 7	56	126	150
		-	-	dkmb_uu	98	108	150
Funen	Carbonate	Reduced	High	dkmf_kalk & NO_3 ≤ 2 mg/l & pH > 7	68	86	100
		-	-	dkmf_kalk	73	85	100
	Quaternary sand	Reduced	High	dkmf_ks & NO_3 ≤ 2 mg/l & pH > 7	494	191	200
		Oxic	High	dkmf_ks & NO_3 > 2 mg/l & pH > 7	60	148	150
		-	-	dkmf_ks	563	188	200
Jutland	Carbonate	Reduced	High	dkmj_kalk & NO_3 ≤ 2 mg/l & pH > 7	294	37	40
		Oxic	High	dkmj_kalk & NO_3 > 2 mg/l & pH > 7	282	31	40
		-	-	dkmj_kalk	577	34	40
	Quaternary sand	Reduced	Low	dkmj_ks & NO_3 ≤ 2 mg/l & pH ≤ 7	113	120	150
		Reduced	High	dkmj_ks & NO_3 ≤ 2 mg/l & pH > 7	1470	205	250
		Oxic	Low	dkmj_ks & NO_3 > 2 mg/l & pH ≤ 7	177	116	150
		Oxic	High	dkmj_ks & NO_3 > 2 mg/l & pH > 7	326	101	150
		-	-	dkmj_ks	2086	190	200
	Pre-Quaternary sand	Reduced	Low	dkmj_ps & NO_3 ≤ 2 mg/l & pH ≤ 7	184	72	75
		Reduced	High	dkmj_ps & NO_3 ≤ 2 mg/l & pH > 7	464	150	150
		-	-	dkmj_ps	699	140	150
Zealand	Carbonate	Reduced	Low	dkms_kalk & NO_3 ≤ 2 mg/l & pH ≤ 7	97	146	150
		Reduced	High	dkms_kalk & NO_3 ≤ 2 mg/l & pH > 7	1364	163	200
		Oxic	High	dkms_kalk & NO_3 > 2 mg/l & pH > 7	108	80	100
		-	-	dkms_kalk	1577	160	200
	Quaternary sand	Reduced	High	dkms_ks & NO_3 ≤ 2 mg/l & pH > 7	727	190	200
		Oxic	High	dkms_ks & NO_3 > 2 mg/l & pH > 7	102	109	150
		-	-	dkms_ks	844	186	200
Islands	Quaternary sand	-	-	dkm_ks	41	170	200

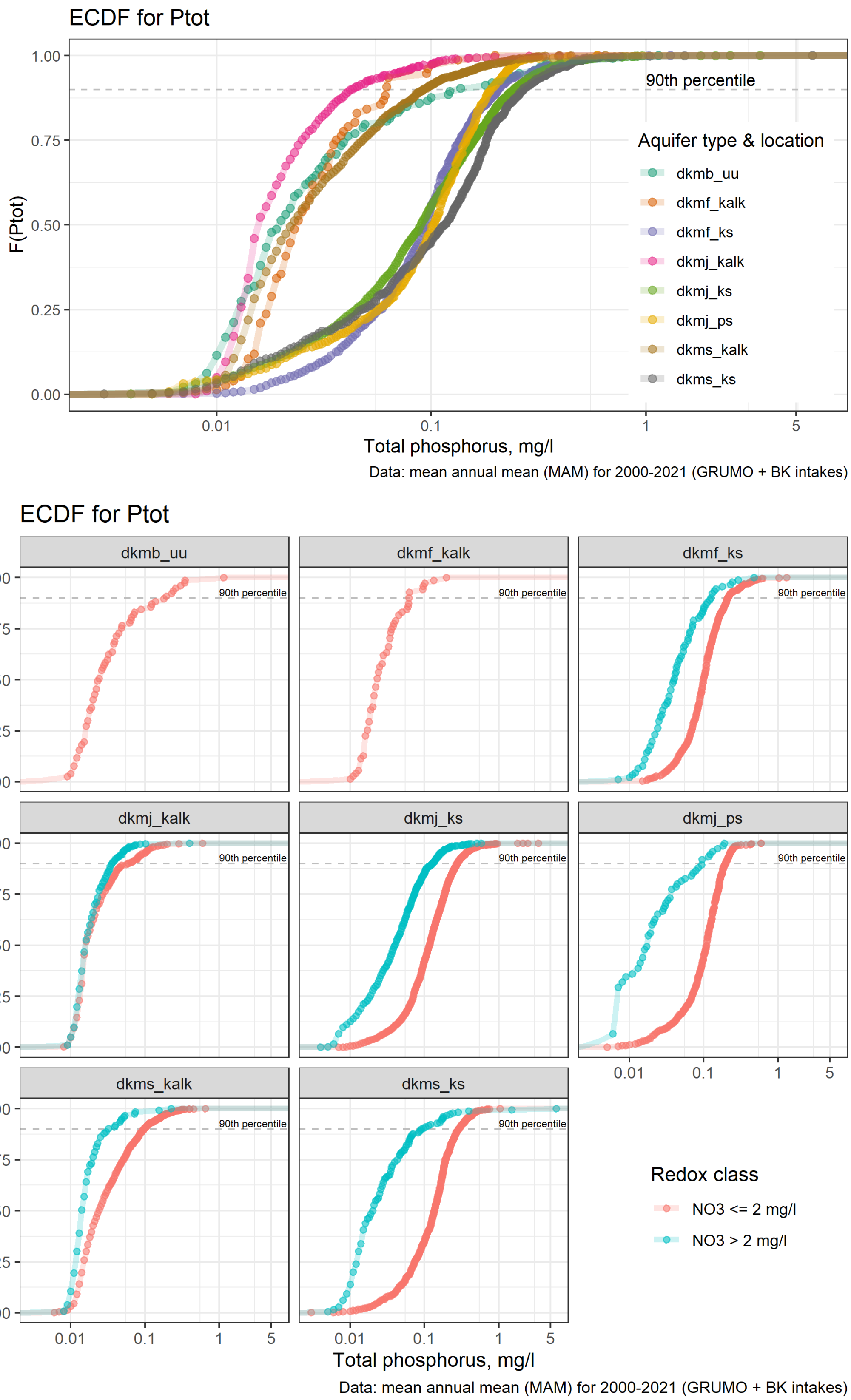


Figure 16. *Empirical cumulative distribution function (ECDF) plot for the final dataset for Ptot; top – only aquifer type and location considered; bottom – aquifer type, location (different panels) and redox class (different colours); only groundwater types with 50 or more intakes are shown.*

Table 5. 90th percentile and NBLs for P_{tot} [mg/l]; NBLs are rounded using the rules from Table 2.

Location	Aquifer type	Redox	Code	n	q90	NBL
Bornholm	Diverse units	Reduced	dkmb_uu & NO_3 ≤ 2 mg/l	77	0.184	0.200
		-	dkmb_uu	113	0.134	0.150
Funen	Carbonate	Reduced	dkmf_kalk & NO_3 ≤ 2 mg/l	71	0.062	0.075
		-	dkmf_kalk	76	0.062	0.075
	Quaternary sand	Reduced	dkmf_ks & NO_3 ≤ 2 mg/l	556	0.210	0.250
		Oxic	dkmf_ks & NO_3 > 2 mg/l	91	0.125	0.150
		-	dkmf_ks	647	0.206	0.250
Jutland	Carbonate	Reduced	dkmj_kalk & NO_3 ≤ 2 mg/l	391	0.059	0.075
		Oxic	dkmj_kalk & NO_3 > 2 mg/l	377	0.036	0.040
		-	dkmj_kalk	768	0.043	0.050
	Quaternary sand	Reduced	dkmj_ks & NO_3 ≤ 2 mg/l	2039	0.276	0.300
		Oxic	dkmj_ks & NO_3 > 2 mg/l	908	0.130	0.150
		-	dkmj_ks	2947	0.243	0.250
	Pre-Quaternary sand	Reduced	dkmj_ps & NO_3 ≤ 2 mg/l	744	0.196	0.200
		Oxic	dkmj_ps & NO_3 > 2 mg/l	75	0.094	0.100
		-	dkmj_ps	819	0.190	0.200
Zealand	Carbonate	Reduced	dkms_kalk & NO_3 ≤ 2 mg/l	1522	0.097	0.100
		Oxic	dkms_kalk & NO_3 > 2 mg/l	123	0.032	0.040
		-	dkms_kalk	1645	0.093	0.100
	Quaternary sand	Reduced	dkms_ks & NO_3 ≤ 2 mg/l	815	0.289	0.300
		Oxic	dkms_ks & NO_3 > 2 mg/l	180	0.093	0.100
		-	dkms_ks	995	0.268	0.300
Islands	Quaternary sand	-	dkm_ks	78	0.172	0.200

Conclusion

The purpose of this work was to develop a methodology and to determine for first time natural background levels (NBLs) for barium (Ba) and total phosphorus (P_{tot}). Throughout the previous three chapters, we described in detail the current state of knowledge about the distribution of Ba and P_{tot} in Danish groundwater, provided overview of the available data and related it to relevant parameters (including geology and location of the aquifer, and geochemical characteristics), and finally, calculated the NBLs based on the 90th percentile and specific rounding rules. To conclude this report, we provide a summary of the NBLs, hoping that it would facilitate their future use. We also compare these NBLs to the current environmental quality criteria (for Ba only) or to the old drinking water standard (for P_{tot}). It was beyond the scope of this project to calculate threshold values (TVs) for groundwater, to assess the status of Danish groundwater bodies, or to elaborate on the implications of the NBLs for the environment or human health.

Barium

The NBLs for Ba were calculated for:

1) aquifer type (geology) and location – for 9 different groups of aquifers,
2) aquifer type, location, redox and pH state – for 17 different groups that had at least 50 intakes with data.

This resulted in six different NBLs for Ba: 40 µg/l, 75 µg/l, 100 µg/l, 150 µg/l, 200 µg/l, 250 µg/l (**Table 6**).

Table 6. *Natural background levels (NBLs) for Ba and the groundwater types (aquifers) where these NBLs are applicable.*

NBLs for Ba (µg/l)	Aquifers
40	- Carbonate aquifers in **Jutland** [1]
75	- Pre-Quaternary aquifers with reduced conditions and low pH in **Jutland** [2]
100	- Carbonate aquifers on **Funen** [3] - Carbonate aquifers with oxic conditions and high pH on **Zealand** [4]
150	- Aquifers on **Bornholm** [5] - Quaternary sand with oxic conditions and high pH on **Funen** [6] - Quaternary sand with oxic conditions (irrespective of pH) OR with reduced conditions and low pH in **Jutland** [7] - Carbonate aquifers with reduced conditions and low pH on **Zealand** [8]
200	- Quaternary sand with reduced conditions and high pH on **Funen** [9] - Quaternary sand in **Jutland** without geochemical information [10] - Carbonate aquifers with reduced conditions and high pH on **Zealand** [11] - Quaternary sand aquifers on the small islands (**Læsø, Samsø, Anholt**) [12]
250	- Quaternary sand with reduced conditions and high pH in **Jutland** [13]

[1] For reduced/oxic aquifers (high pH) or without geochemical information
[2] For the rest of the pre-Quaternary aquifers, see NBL = 150 µg/l
[3] Both for reduced (high pH) or without geochemical information
[4] For the rest of the carbonate aquifers on Zealand, see NBLs = 150 & 200 µg/l

[5] Both for those with reduced conditions with high pH or without geochemical information
[6] For the rest of the Quaternary sand aquifers on Funen, see NBL = 200 µg/l
[7] For the rest of the Quaternary sand aquifers in Jutland, see NBLs = 200 & 250 µg/l
[8] For the rest of the carbonate aquifers on Zealand, see NBLs = 100 & 200 µg/l
[9] Valid also for the Quaternary sand aquifers on Funen without geochemical information; for the aquifers with oxic and high pH on Funen, see NBL = 150 µg/l
[10] For the Quaternary sand aquifers in Jutland with geochemical information, see NBLs = 150 & 250 µg/l
[11] Valid also for the carbonate aquifers on Zealand without geochemical information, for the rest see NBLs = 100 & 150 µg/l
[12] the geochemical conditions could not be considered due to low number of intakes
[13] for the rest of the Quaternary sand aquifers in Jutland, see NBLs = 150 & 200 µg/l

All these NBLs for Ba are above the general quality requirement for fresh surface waters (EQS = 19 µg/l) and more importantly, some are even above the maximum acceptable concentration (MAC = 145 µg/l).

Notably, both the lowest and highest NBLs for Ba in groundwater are found in Jutland: the lowest is for the carbonate aquifers (40 µg/l), while the highest is for the Quaternary sand with reduced conditions and high pH (250 µg/l). The Quaternary sand aquifers on Funen and Zealand are also with high NBLs (150 or 200 µg/l). These high NBLs could be explained by the spatial extend of Tertiary clay layers in Denmark. **Figure 13** clearly shows the location of the highest levels of Ba in the easternmost part of Jutland, Funen, and the western part of Zealand, where these types of clays are overlaying the Quaternary-sand aquifers.

The high Ba in groundwater (NBLs > EQS) could have some environmental implications for streams (or other surface waters) fed by groundwater, especially during the low-flow periods (at baseflow conditions), however this requires further investigation.

Phosphorus

The NBLs for P_{tot} were calculated for:

1) aquifer type (geology) and location – for 9 different groups of aquifers,
2) aquifer type, location, and redox state – for 14 different groups that had at least 50 intakes with data.

This resulted in eight different NBLs for P_{tot} in the range 0.04 mg/l to 0.3 mg/l (**Table 7**).

Table 7. *Natural background levels (NBLs) for P_{tot} and the groundwater types (aquifers) where these NBLs are applicable.*

NBLs for P_{tot} (mg/l)	Aquifers
0.04	- Carbonate aquifers with oxic conditions in **Jutland** [1] and on **Zealand** [2]
0.05	- Carbonate aquifers in **Jutland**, without redox information [3]
0.075	- Carbonate aquifers with reduced conditions in **Jutland** [4] - Carbonate aquifers on **Funen** [5]
0.1	- Pre-Quaternary sand with oxic conditions in **Jutland** [6] - Carbonate aquifers with reduced conditions on **Zealand** [7] - Quaternary sand with oxic conditions on **Zealand** [8]
0.15	- **Bornholm** aquifers, without redox information [9]

NBLs for P_{tot} (mg/l)	Aquifers
	- Quaternary sand with oxic conditions on **Funen** [10] or in **Jutland** [11]
0.2	- **Bornholm** aquifers with reduced conditions [12] - Pre-Quaternary sand with reduced conditions in **Jutland** [13] - Quaternary sand aquifers on the small islands (**Læsø, Samsø, Anholt**) [14]
0.25	- Quaternary sand aquifers with reduced conditions on **Funen** [15] - Quaternary sand aquifers in **Jutland** without redox information [16]
0.3	- Quaternary sand aquifers with reduced conditions in **Jutland** [17] or **Zealand** [18]

[1] for the rest of the carbonate aquifers in Jutland, see NBLs = 0.05 & 0.075 mg/l
[2] for the rest of the carbonate aquifers on Zealand, see NBL = 0.1 mg/l
[3] if there is redox information, see NBLs = 0.04 & 0.075 mg/l
[4] for the rest of the carbonate aquifers in Jutland, see NBLs = 0.04 & 0.05 mg/l
[5] valid for both aquifers with reduced conditions, and for those without geochemical information
[6] for the rest of the pre-Quaternary sand aquifers in Jutland, see NBL = 0.2 mg/l
[7] valid also for the carbonate aquifers without geochemical information; for the oxic ones, see NBL = 0.04 mg/l
[8] for the rest of the Quaternary sand aquifers on Zealand, see NBL = 0.3 mg/l
[9] for aquifers with reduced conditions, see NBL = 0.2 mg/l
[10] for the rest Quaternary sand aquifers on Funen, see NBL = 0.25 mg/l
[11] for the rest of the Quaternary sand aquifers in Jutland, see NBLs = 0.25 & 0.3 mg/l
[12] for the rest, see NBL = 0.15 mg/l
[13] valid also when there is no geochemical information; for oxic pre-quaternary sand aquifers see NBL = 0.1 mg/l
[14] the geochemical conditions could not be considered due to low number of intakes
[15] valid also when there is no geochemical information; for oxic conditions, see NBLs = 0.15 mg/l
[16] if there is redox information, see NBLs = 0.15 & 0.3 mg/l
[17] for the rest, see NBLs = 0.15 & 0.25 mg/l
[18] valid also when there is no geochemical information; for oxic conditions, see NBLs = 0.1 mg/l

As mentioned in the **Introduction**, currently there are no environmental or drinking water (or groundwater) standards for P_{tot}. Thus, the NBLs calculated here can only be compared to the previous drinking water standard for P_{tot} (0.15 mg/l), which is no longer enforced. This is only done to provide some relative measure of high/low NBLs.

Overall, the sand aquifers (both Quaternary and pre-Quaternary) have higher NBLs for P_{tot} than the carbonate aquifers. In addition, the reduced aquifers ($NO_3^- \leq 2$ mg/l) have consistently higher NBLs. Indeed, the aquifers with NBL for P_{tot} > 0.15 mg/l (the previous drinking water standard) are:

- all Quaternary sand aquifers with reduced conditions (NBLs = 0.3 or 0.25 mg/l)
- all pre-Quaternary sand aquifers with reduced conditions (NBL = 0.2 mg/l)
- all aquifers with reduced conditions on Bornholm (NBL = 0.2 mg/l)
- all Quaternary sand aquifers on Læsø, Samsø, and Anholt (NBL = 0.2 mg/l)

It should also be noted, that even though the carbonate aquifers have lower NBLs in general, a relatively large area in North Zealand with carbonate aquifers has consistently high P_{tot} concentrations (**Figure 14**). It may be important to take this into consideration when using further the NBLs.

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Appendix 1: Project task (Danish EPA)

Miljøministeriet
Miljøstyrelsen

Opgavebeksrivelse - Fastsættelse af naturlige baggrundsværdier for fosfor og barium i de danske grundvandsforekomster

Baggrund

I forbindelse med vandplanlægningen skal der, jf. vandrammedirektivet, som en del af den kemiske tilstandsvurdering, foretages en vurdering af om kemisk påvirkning fra grundvandsforekomsterne forhindrer målopfyldelse for målsatte overfladevande.
Denne vurdering er ikke tidligere foretaget, og der er ikke udviklet en færdig metode, som kan bruges til tilstandsvurderingen. Formålet med dette projekt at fastsætte naturlige baggrundsværdier for fosfor og barium i grundvandet. Fosfor er den primære begrænsning i forhold til målopfyldelse i de danske søer og en del af denne fosfor kan komme fra grundvandet og kan enten være naturlig eller komme fra menneskelige aktiviteter. Barium fører til overskrideler i både søer og vandløb. For at kunne skelne det naturlige biddrag af fosfor og barium fra det biddrag, som skuldes menneskelig aktivitet er det nødvendigt at kunne fastsætte naturlige baggrundsværdier for fosfor og barium i de danske grundvandsforekomster.
Da der i den enkelte grundvandsforekomst kan være geokemisk betinget meget forskellige naturlige baggrundsværdier, fx i oxideret og reduceret vand, leveres der naturlige baggrundværdier opdelt efter relevante geokemiske parametre, som er observeret i almindelige grundvandsanalyser.

Opgavebeskrivelse

På baggrund af data fra GROUMO og vandværksboringer, skal GEUS:

1. Fastlægge hvilke parametre, der er betydende for den naturlige koncentration af fosfor og barium i grundvandet.

2. Opsættes kriterier for fastsættelsen af naturlige baggrundsværdier for fosfor og barium i grundvandet.

3. Udregne forslag til forekomstspecifikke naturlige baggrundskoncentrationer af fosfor og barium i grundvandet. Dette skal ske for grupper af grundvandsforekomster, opdelt efter relevant grundvandskemi og geologi.

Arbejdet skal tage udgangspunkt i den metode, som blev benyttet til at fastsætte naturlige baggrundsværdier i forbindelse med udviklingen af en metode til at tilstandsvurderer grundvandet i forhold til salte og sporstoffer.

Leverancer

GEUS leverer et samlet notat, som indeholder:

1. En forklaring af hvilke parametre, som er afgørende for den naturlige baggrundskoncentration af fosfor og barium i grundvandet.
2. En begrundet oversigt over hvilke kriterier, som skal ligges til grund for den naturlige baggrundskoncentration.
3. En oversigt over naturlige baggrundskoncentrationer af fosfor og barium, typer af danske grundvandsforekomster, underopdelt efter grundvands- og geokemiske kriterier.

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Omfang
Opgaven skal holdes inden for en ramme af 75 timer.

Appendix 2: Dominating lithology within the intake

G1: Quaternary clay and silt *(dk: Kvartært ler og silt): di, dl, mg, ml, ms, mz*

G1	DK	ENG	Period
di	Glacial smeltevandssilt	Glacial melt water silt	Quaternary
dl	Glacial smeltevandsler	Glacial melt water clay	Quaternary
mg	Glacial morænegrus	Glacial gravelly till	Quaternary
ml	Glacial moræneler (leret til)	Glacial clayey till	Quaternary
ms	Glacial morænesand (sandet till)	Glacial sandy till	Quaternary
mz	Glacial morænesten	Glacial stony till	Quaternary

G2: Quaternary sand/gravel and thin alternating beds *(dk: Kvartært sand/grus, og vekslende små lag): dg, ds, dv, dz, is, ts*

G2	DK	ENG	Period
dg	Glacial smeltevandsgrus	Glacial melt water gravel	Quaternary
ds	Glacial smeltevandssand	Glacial melt water sand	Quaternary
dv	Glacial vekslende små smeltevandslag	Glacial; alternating thin melt water beds	Quaternary
dz	Glacial smeltevandssten	Glacial melt water stone	Quaternary
is	Interglacial ferskvandssand	Interglacial fresh water sand	Quaternary
ts	Senglacialt ferskvandssand	Late-glacial fresh-water sand	Quaternary

G3: Quaternary layers rich in organic materials *(Kvartære aflejringer rige på organisk materiale): d (not present in this dataset: t, p, ip/it, fp/ft, hp/ht)*

G3	DK	ENG
d	Diatomeaflejringer (ikke postglaciale)	Diatomite (not postglacial)

G4: Quaternary marine sand, gravel, and silt *(dk: Kvartært marint saltvandssand, -grus og -silt): hg, hs, qs, yg, yi, ys*

G4	DK	ENG	Period
hg	Postglacial saltvandsgrus	Post-glacial salt-water gravel	Quaternary
hs	Postglacial saltvandssand	Post-glacial salt-water sand	Quaternary
qs	Interglacialt saltvandssand	Interglacial salt-water sand	Quaternary
yg	Senglacial saltvandsgrus	Late-glacial salt-water gravel	Quaternary
yi	Senglacialt saltvandsilt	Late-glacial salt-water silt	Quaternary
ys	Senglacialt saltvandsand	Late-glacial salt-water sand	Quaternary

***G5: Quaternary marine clay** (Kvartært marint saltvandsler): ql (not present in this dataset: yl, hl).*

G5	DK	ENG	Period
ql	Interglacialt saltvandsler	Interglacial salt-water clay	Quaternary

***G6: Pre-quaternary limestone and chalk** (dk: Prækvartær kalk, Skrivekridt, Danienkalk, grønsandskalk, flint): bk, bs, dk, k, kk, lk, pk, ps, pv, sk, z, zk*

G6	DK	ENG	Period
bk	Danien bryozokalk, koralkalk	Danian bryozoan limestone, corallian limestone	Paleocene
bs	Coniacien-santonien, Bavnodde Grønsand (Kridt)	Coniacian-Santonian Sand; Bavnodde Greensand	Late Cretaceous
dk	Campanien-maastrichtien kalksten	Campanian-Maastrichtian limestone	Late Cretaceous
k	Kalk, kridt, kalksten	Limestone, chalk	Unspecified
kk	Danien kalksandskalk	Danian calcarenite	Paleocene
lk	Danien slamkalk, skrivekridt	Danian calcilutite, chalk	Paleocene
pk	Selandien sandsten, palæocæn grønsandsten	Selandian sandstone, Paleocene green sandstone	Paleocene
ps	Selandien sand, palæocæn grønsand	Selandian sand, Paleocene greensand	Paleocene
pv	Selandien vekslende små lag	Selandian; alternating thin beds	Paleocene
sk	Campanien-maastrichtien skrivekrid	Campanian-Maastrichtian chalk	Late Cretaceous
z	Flint, sten	Chert, stone	Unspecified
zk	Danienkalk, kalk og flint	Danian limestone, limestone, and chert	Paleocene

***G7: Pre-quaternary clay, silt, and brown coal** (dk: Prækvartær ler, silt og brunkul): bl, ed, gc, gi, gl, kj, ll, nl, oi, pi, pl, pr, sl, sr, wl*

G7	DK	ENG	Period
bl	Coniacien-santonien, ler i Bavnodde Grønsand (Kridt)	Coniacian-Santonian clay; clay in the Bavnodde	Late Cretaceous
ed	Eocæn moler	Eocene diatomite	Paleogene
gc	Oligocæn -miocæn -pliocæn brunkul	Oligocene -Miocene - Pliocene brown coal	
gi	Oligocæn -miocæn -pliocæn glimmersilt, silt i Vejlefjord formation	Oligocene -Miocene - Pliocene mica silt; silt in the Vejlefjord Formation	Neogene-Paleogene
gl	Oligocæn -miocæn -pliocæn glimmerler, ler i Vejlefjord formation	Oligocene -Miocene - Pliocene mica clay; clay in the Vejlefjord Formation	Neogene-Paleogene
kj	Siltsten, Kambrium Grønne Skifre	Cambri an Green shales	Cambrian
ll	Eocæn ler, Lillebælt, Ler, plastisk ler	Eocene clay, Lillebælt clay, plastic clay	

G7	DK	ENG	Period
nl	Cenomanien ler, ler i Arnager grønsand	Ceenomanian clay; clay in the Arnager Greensand	Late Cretaceous
oi	Oligocæn silt	Oligocene silt	Paleogene
pi	Selandien silt, palæocæn silt	Selandian silt, Paleocene silt	Paleocene
pl	Selandien ler, paleocæn ler, Kerteminde Mergel	Selandian clay, Paleocene clay, Kerteminde Marl	Paleocene
pr	Selandien skifer, palæocæn skifer	Selandian shale, Paleocene shale	Paleocene
sl	Eocæn søvind mergel	Eocene Søvind Marl	Paleogene
sr	Silur skifer	Silurian shale	Silurian
wl	Nedre kridt ler, ler i Jydegård Formation	Lower Cretaceous clay, clay in the Jydegård Formation	Cretaceous

G8: Pre-quaternary sand and gravel *(Prækvartært sand og grus): as, eq, gs, gv, kg, kq, ks, oq, q, rg, rs, vs*

G8	DK	ENG	Period
as	Ceenomanien sand Arnager Grønsand	Ceenomanian sand, Arnager Greensand	Late Cretaceous
eq	Kambrium Nexø sandsten	Cambrian Nexø Sandstone	Cambrian
gs	Oligocæn -miocæn -pliocæn glimmersand sand i Vejlefjord formation	Oligocene -Miocene - Pliocene mica sand; sand in the Vejlefjord Formation	Neogene-Paleogene
gv	Oligocæn -miocæn -pliocæn vekslende små lag	Oligocene -Miocene - Pliocene alternating thin beds	Neogene-Paleogene
kg	Miocæn kvartsgrus	Miocene quartz gravel	Neogene
kq	Kambrium Balka Sandsten	Cambrian Balka Sandstone	Cambrian
ks	Miocæn kvartssand	Miocene quartz sand	Neogene
oq	Oligocæn sandsten, Øksenrade Sandsten	Oligocene sandstone, Oksenrade sandstone	Paleogene
q	Sandsten	Sandstone	Uncpecified
rg	Nedre kridt/Øvre jura grus, grus I Robbedale Formation	Lower Cretaceous/Upper Jurassic gravel , gravel in the Robbedale Formation	Cretaceous-Jurasic
rs	Nedre kridt/Øvre jura, sand i Robbedale Formation	Lower Cretaceous/Upper Jurassic, sand in the Robbedale Formation	
vs	Nedre kridt sand	Lower Cretaceous sand	Cretaceous

G9: Basement *(dk: Grundfjeld): a, pa*

G9	DK	ENG	Period
a	Grundfjeld	Basement	-
pa	Prækambrium, gnejs, granit, pegmatit	Precambrian gneiss, granite, pegmatite	Precambrian

G10: Unspecified clay or silt *(dk: Uspecificeret ler og silt) i, l, r*

G10	DK	ENG	Period
i	Silt	Silt	Uncpecified
l	Ler	Clay	Uncpecified
r	Skifer	Shale	Uncpecified

G11: Unspecified sand or gravel *(dk: Uspecificeret sand og grus): g, s, v*

G11	DK	ENG	Period
g	Grus, sand og grus	Gravel; sand and gravel	Uncpecified
s	Sand	Sand	Uncpecified
v	Vekslende små lag	Alternating thin beds	Uncpecified

Appendix 3: Descriptive statistics

Barium

Table 8. Summary statistics for Ba (µg/l) in reduced and oxic groundwaters.

Redox class	n	min	q25	Median ± MAD	Mean ± SD	q75	max
Reduced (NO_3^- ≤ 2 mg/l)	6020	1.1	31.4	68.5 ± 43.7	87.7 ± 80.2	125.0	1283.3
Oxic (NO_3^- > 2 mg/l)	1397	1.2	15.6	35.2 ± 22.7	46.6 ± 45.9	63.3	750.0

Table 9. Summary statistics for Ba (µg/l) in groundwaters with high and low pH.

pH class	n	min	q25	Median ± MAD	Mean ± SD	q75	max
Low (pH ≤ 7)	703	2.3	28.4	47.5 ± 22.3	62.0 ± 61.8	76.9	780.0
High (pH > 7)	6101	1.1	29.5	66.0 ± 43.3	85.2 ± 79.2	122.0	1283.3

Table 10. Summary statistics for Ba (µg/l) in the four different aquifer types (DK-model).

Aquifer type	n	min	q25	Median ± MAD	Mean ±SD	q75	max
Carbonate (kalk)	2382	1.1	14.0	38.2 ± 27.2	61.9 ± 90.0	74.0	1283.3
Quaternary sand (ks)	3915	1.5	40.8	81.0 ± 45.2	95.4 ± 69.5	137.5	1000.0
Pre-Quaternary sand (ps)	730	1.3	19.5	42.9 ± 29.5	62.1 ± 53.7	96.8	328.8
Diverse, Bornholm (uu)	100	18.3	35.8	53.6 ± 21.4	61.4 ± 34.2	80.6	176.0

Table 11. Summary statistics for Ba (µg/l), considering aquifer type and location (DK-model).

Location	Aquifer Type	Code	n	min	q25	Median ± MAD	Mean ± SD	q75	max
Islands	Quaternary sand	dkm_ks	46	4.3	6.7	52.6 ± 46.7	71.1 ± 70.0	135.3	253.2
Bornholm	Diverse units	dkmb_uu	100	18.3	35.8	53.6 ± 21.4	61.4 ± 34.2	80.6	176.0
Funen	Carbonate	dkmf_kalk	73	1.7	9.1	21.7 ± 17.6	36.5 ± 36.3	60.6	152.5
	Quaternary sand	dkmf_ks	580	1.5	105.3	133.0 ± 27.1	135.6 ± 46.4	159.9	296.0
Jutland	Carbonate	dkmj_kalk	715	1.1	5.0	10.4 ± 6.6	15.7 ± 17.7	20.3	172.5
	Quaternary sand	dkmj_ks	2438	1.5	31.0	57.6 ± 35.6	83.9 ± 72.4	120.0	1000.0
	Pre-Quat. sand	dkmj_ps	730	1.3	19.5	42.9 ± 29.5	62.1 ± 53.7	96.8	328.8
Zealand	Carbonate	dkms_kalk	1594	1.3	33.9	57.6 ± 28.0	83.8 ± 102.1	92.8	1283.3

Location	Aquifer Type	Code	n	min	q25	Median ± MAD	Mean ± SD	q75	max
	Quaternary sand	dkms_ks	851	4.0	60.1	84.4 ± 31.1	102.1 ± 62.4	132.5	594.0

__Table 12.__ Summary statistics for Ba (µg/l) for the groups with dominating lithology type within the intake.

Dominating lithology, intake	Code	n	min	q25	Median ± MAD	Mean ± SD	q75	max
Quaternary clay and silt	G1	2	112.3	-	161.2 ± 48.9	161.2 ± 69.1	-	210.0
Quat. sand, gravel, or thin alternating beds	G2	2875	1.5	43.5	84.3 ± 44.7	97.0 ± 66.8	137.1	594.0
Quaternary marine sand, gravel, and silt	G4	76	3.2	7.0	10.6 ± 5.1	28.6 ± 35.1	36.1	160.0
Quaternary marine clay	G5	1	84.7	-	-	-	-	-
Pre-Quaternary limestone and chalk	G6	2117	1.1	13.8	37.8 ± 26.8	62.9 ± 93.7	73.7	1283.3
Pre-Quaternary clay, silt, and brown coal	G7	95	1.6	9.8	38.1 ± 29.0	54.5 ± 60.3	80.3	328.8
Pre-quaternary sand and gravel	G8	563	1.3	18.3	37.2 ± 22.8	54.1 ± 48.8	74.3	240.0
Basement	G9	14	27.2	54.0	62.3 ± 16.4	79.2 ± 36.4	114.0	138.0
Unspecified clay or silt	G10	49	1.5	41.5	92.4 ± 50.9	93.7 ± 63.1	143.0	315.0
Unspecified sand or gravel	G11	935	1.5	36.7	71.8 ± 43.0	88.9 ± 66.0	130.0	400.0
Mixed (two diff. types equally represented)	M	40	5.2	30.3	60.2 ± 33.5	76.7 ± 54.2	122.1	188.0

__Table 13__. Summary statistics for Ba (µg/l) for different types of carbonates (based on dominating lithology type).

Dominating lithology, carbonates only (G6)	code	n	min	q25	Median ± MAD	Mean ± SD	q75	max
Danian bryozoan limestone, corallian limestone	bk	377	1.2	23.8	44.0 ± 23.0	55.0 ± 52.1	69.8	558.8
Limestone, chalk (unspecified)	k	504	1.1	12.2	37.5 ± 26.8	66.5 ± 106.4	72.0	1030.0
Danian calcarenite	kk	429	1.2	15.2	40.9 ± 27.7	49.4 ± 41.3	74.0	302.0
Danian calcilutite, chalk	lk	77	1.1	5.6	24.0 ± 21.2	38.0 ± 40.9	58.0	245.0
Selandian sandstone, Palaeocene greensand stone	pk	111	1.3	12.6	32.0 ± 25.5	48.6 ± 50.6	71.7	330.0
Campanian-Maastrichtian chalk	sk	507	1.6	11.9	31.7 ± 24.2	87.1 ± 141.0	93.4	1283.3
Danian limestone, limestone, and chert	zk	80	1.2	11.3	41.1 ± 31.1	49.5 ± 47.5	73.8	230.0

Phosphorus

Summary statisctics for total phosphorus, $P_{tot.}$

Table 14. Summary statistics for P_{tot} (mg/l) in reduced and oxic groundwaters.

Redox class	n	min	q25	Median ± MAD	Mean ± SD	q75	max
Reduced (NO_3^- ≤ 2 mg/l)	6554	0.003	0.030	0.082 ± 0.056	0.109 ± 0.121	0.147	3.400
Oxic (NO_3^- > 2 mg/l)	1906	0.004	0.014	0.025 ± 0.014	0.049 ± 0.152	0.054	5.951

Table 15. Summary statistics for P_{tot} (mg/l) in the four different aquifer types (DK-model).

Aquifer type	n	Min	q25	Median ± MAD	Mean ±SD	q75	max
Carbonate (kalk)	2489	0.006	0.014	0.020 ± 0.007	0.037 ± 0.047	0.040	0.647
Quaternary sand (ks)	4668	0.003	0.046	0.094 ± 0.054	0.124 ± 0.157	0.162	5.951
Pre-Quaternary sand (ps)	820	0.005	0.057	0.103 ± 0.044	0.110 ± 0.107	0.146	2.400
Diverse, Bornholm (uu)	113	0.007	0.013	0.020 ± 0.009	0.063 ± 0.139	0.041	1.145

Table 16. Summary statistics for P_{tot} (mg/l), considering aquifer type and location (DK-model).

Location	Aquifer Type	nbl_unit	N	min	q25	Median ± MAD	Mean ±SD	q75	max
Islands	Quaternary sand	dkm_ks	78	0.006	0.015	0.050 ± 0.037	0.079 ± 0.097	0.118	0.557
Bornholm	Diverse units	dkmb_uu	113	0.007	0.013	0.020 ± 0.009	0.063 ± 0.139	0.041	1.145
Funen	Carbonate	dkmf_kalk	76	0.010	0.018	0.024 ± 0.008	0.034 ± 0.030	0.037	0.198
	Quaternary sand	dkmf_ks	648	0.007	0.058	0.094 ± 0.039	0.115 ± 0.105	0.136	1.300
Jutland	Carbonate	dkmj_kalk	768	0.008	0.013	0.016 ± 0.004	0.026 ± 0.034	0.025	0.596
	Quaternary sand	dkmj_ks	2947	0.004	0.045	0.090 ± 0.053	0.121 ± 0.140	0.158	3.400
	Pre-Quat. sand	dkmj_ps	820	0.005	0.057	0.103 ± 0.044	0.110 ± 0.107	0.146	2.400
Zealand	Carbonate	dkms_kalk	1645	0.006	0.015	0.023 ± 0.010	0.043 ± 0.051	0.048	0.647
	Quaternary sand	dkms_ks	995	0.003	0.048	0.115 ± 0.066	0.141 ± 0.221	0.180	5.951

Table 17. *Summary statistics for P_{tot} (mg/l) for the groups with dominating lithology type within the intake.*

Dominating lithology, intake	Code	n	min	q25	Median ± MAD	Mean ±SD	q75	max
Quaternary clay and silt	G1	4	0.034	0.060	0.082 ± 0.031	0.095 ± 0.062	0.117	0.180
Quat. sand, gravel, or thin alternating beds	G2	3429	0.004	0.048	0.093 ± 0.053	0.121 ± 0.156	0.160	5.951
Quaternary layers rich in organic materials	G3	1	0.065					
Quaternary marine sand, gravel, and silt	G4	96	0.015	0.065	0.197 ± 0.138	0.282 ± 0.386	0.366	3.400
Quaternary marine clay	G5	1	0.142					
Pre-Quaternary lime-stone and chalk	G6	2209	0.006	0.014	0.020 ± 0.007	0.036 ± 0.047	0.039	0.647
Pre-Quaternary clay, silt, and brown coal	G7	99	0.009	0.019	0.033 ± 0.019	0.060 ± 0.056	0.090	0.260
Pre-quaternary sand and gravel	G8	622	0.005	0.060	0.108 ± 0.046	0.114 ± 0.117	0.152	2.400
Basement	G9	14	0.009	0.013	0.017 ± 0.004	0.097 ± 0.302	0.020	1.145
Unspecified clay or silt	G10	66	0.003	0.020	0.054 ± 0.039	0.082 ± 0.081	0.102	0.320
Unspecified sand or gravel	G11	1095	0.006	0.039	0.082 ± 0.052	0.108 ± 0.113	0.147	1.594
Mixed (two diff. types equally represented)	M	58	0.011	0.034	0.079 ± 0.051	0.110 ± 0.131	0.154	0.915