

Roadmap for Determining Natural Background Levels of Trace Metals in Groundwater

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Supplementary text

NBL derivation part of MP2 (River Basin Management Plan 2015-2021) [1]

The chemical data was from the nationwide database Jupiter [2], where almost all laboratory analyses of groundwater are registered and accessible. Both the geology and location of the aquifers were considered. NBLs were calculated for each layer of the National Water Resources Model for Denmark (DK-model, <https://vandmodel.dk/>) and for ten geographical areas comprising the main river basins. The DK-model layers provided information on the type and depth sequence of the aquifers. The redox conditions of the aquifers were also considered, based on groundwater NO₃ concentration: oxic if NO₃ ≥ 1 mg/l and anoxic if NO₃ < 1 mg/l. Sampling points affected by known point-sources of anthropogenic pollution were excluded from the dataset prior to any analysis. The NBLs were established only for geological units with at least 10 sampling points with data, while the redox-dependent NBLs were calculated if there were more than 20 sampling points with data.

Summary of pre-selection criteria, the BRIDGE method [3]

The NBLs in this method are calculated as the 90th (or 97.7th) percentiles of a pre-selected dataset, to approximating the aquifer's natural groundwater composition. These criteria [3] are:

- Excluding samples with incorrect ion balance (> 10%), and/or unknown sampling depth, and/or unknown type of aquifer (lithology)
- Excluding brackish and saline waters, i.e. if [Na⁺] + [Cl⁻] > 1000 mg/l
- Aggregation of time-series at sampling point level is based on median
- Sampling points with median NO₃ > 10 mg/l are excluded (considered polluted)
- If there are both aerobic and anaerobic conditions, the NBLs should be computed for the two separately.
- For anaerobic conditions NO₃ cannot be used as pollution indicator, thus other indicators should be defined based on sound understanding of the local conditions.

Study setting (additional details)

Denmark is situated in Northern Europe – bordering Germany to the South, the Baltic Sea to the East, and the North Sea to the West. Denmark's climate is relatively warm compared with other areas at the same latitude (54.5–57.8°N) due to the North Atlantic Current. It is dominated by a warm humid continental or oceanic climate. The weather is strongly influenced by the proximity to both the sea and the European continent and varies depending on dominant wind direction and season. The country-wide annual average temperature and rainfall were respectively 8.3 °C and 746 mm (climatological normal 1981-2010) and 8.9 °C and 792 mm (2006-2015)¹.

The landscape (Figure S1) is dominated by Weischelian moraines (till) in the eastern part of the county. The main stationary line of the Scandinavian Ice Cap forms a boundary west of which lies a meltwater plain and moraine remnants from the Saalian glaciation. The Pleistocene glaciogenic sediments are composed of glacial till and fluvio-glacial outwash material that interfinger with each other and are occasionally interbedded with interglacial or interstadial deposits [4].

Another widespread feature are the buried tunnel valleys (Figure S1). These are elongated erosional structures filled with and covered by younger sediments, which have typically very complex internal structure because of repeated erosional and depositional events [5]. Most of the buried valleys in the Danish subsurface were formed during the Pleistocene as tunnel valleys eroded by high-pressure meltwater underneath the ice sheets, typically following older geological depressions or faults [5].

The pre-Quaternary geology of Denmark (Figure S1) is tilted to the southwest with deposits getting older in northeastern direction [4]. The oldest sediments in northeastern Denmark are dominated by Maastrichtian chalk and Danian limestone, except for Bornholm, where older deposits can be found. The pre-Quaternary surface progresses southwest through different types of clayey deposits from the Paleocene, Eocene, Oligocene, and Miocene. The major faults locations are also shown in Figure S1.

Supplementary figures

¹ The climate and weather information is from the site of the Danish Meteorological Institute (DMI), accessed on 15 Oct 2020: <https://www.dmi.dk/klima/temaforside-klimaet-frem-til-i-dag/>

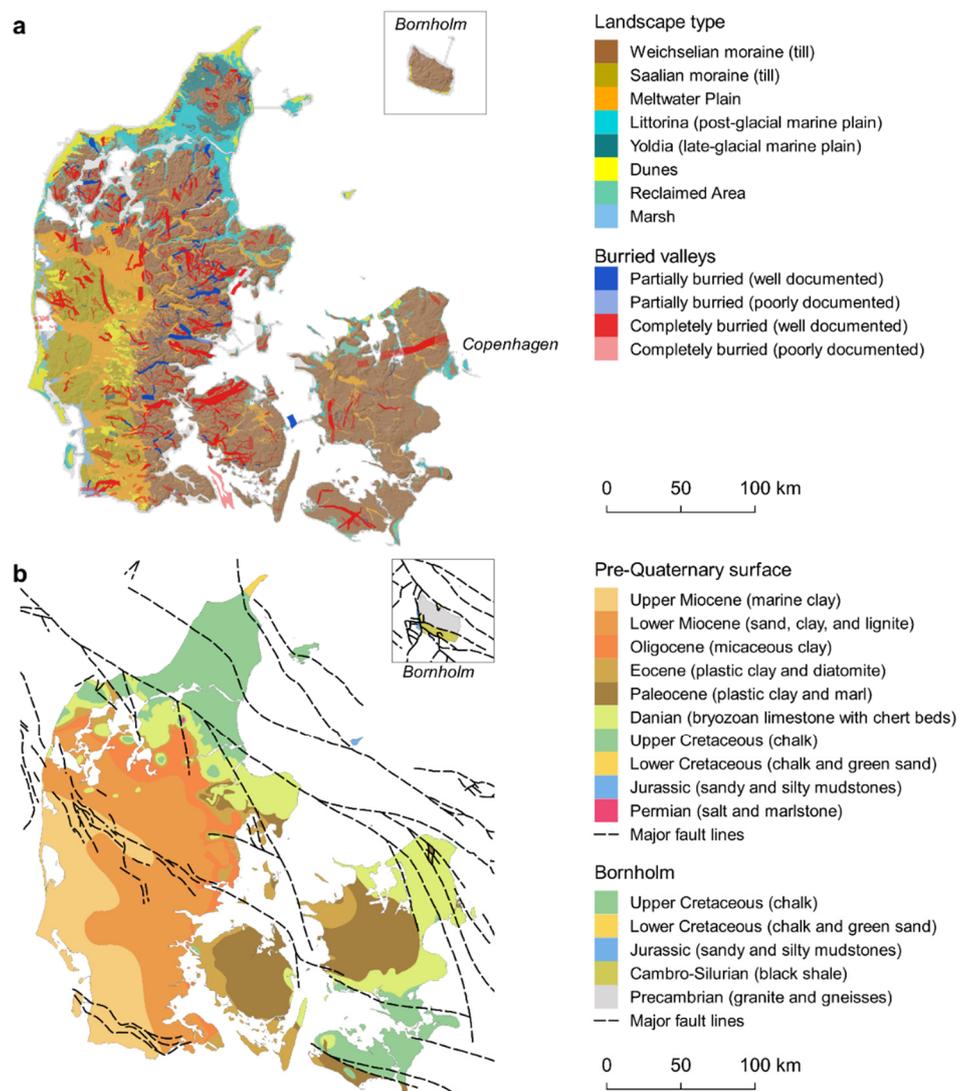


Figure 1. (a) Danish landscape types² with a hill shade effect³ and location of the mapped buried valleys [5], (b) Pre-quaternary stratigraphic succession underlying the Quaternary sedimentary deposits and the major faults⁴.

² Vector layer from the Danish Centre for Food and Agriculture (DCA) <https://dca.au.dk/forskning/den-danske-jordklassificering/>

³ Transparent hillshade layer “DHM Terrain skyggekort overdrevet” from The Danish Map Supply (dk: “Kortforsyningen”)

⁴ The map is “Geologisk kort over den Danske underground” published by Varv in 1992 and described in VARV nr. 2, 1992, downloaded from <https://frisbee.geus.dk/geuswebshop/index.xhtml> (accessed on 5 Nov 2019)

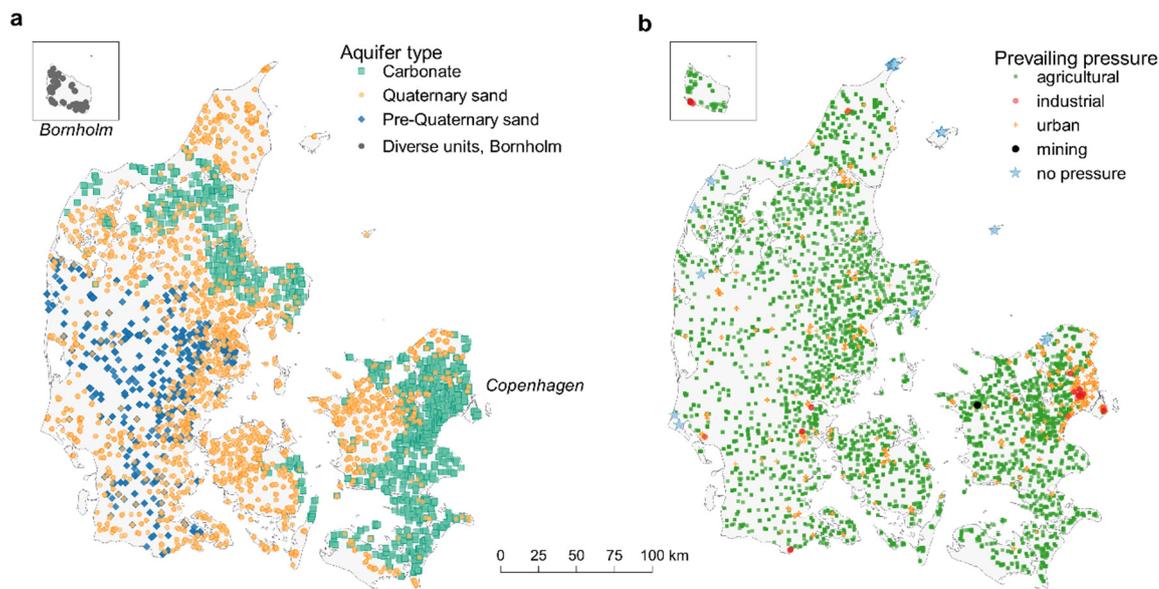


Figure 2. Classification of the sampling points based on aquifer type (a) and prevailing pressure (b).

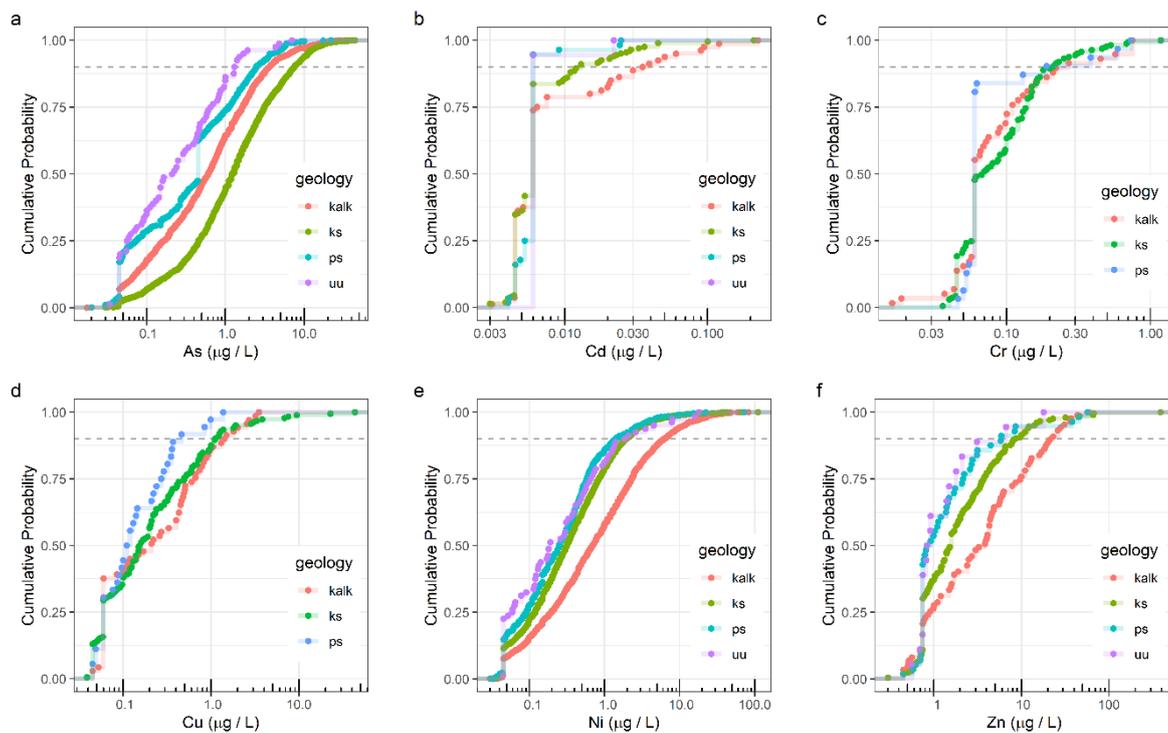


Figure 3. Empirical cumulative distribution function for As, Cd, Cr, Cu, Ni, and Zn in Danish groundwater used for drinking water production, stratified by aquifer type: limestone/chalk (“kalk”), Quaternary sand (“ks”), pre-Quaternary sand (“ps”), various units on Bornholm (“uu”).

HOVER_pH ● Acidic (pH < 7) ● Basic (pH > 7.5) ● Neutral (7 ≤ pH ≤ 7.5)

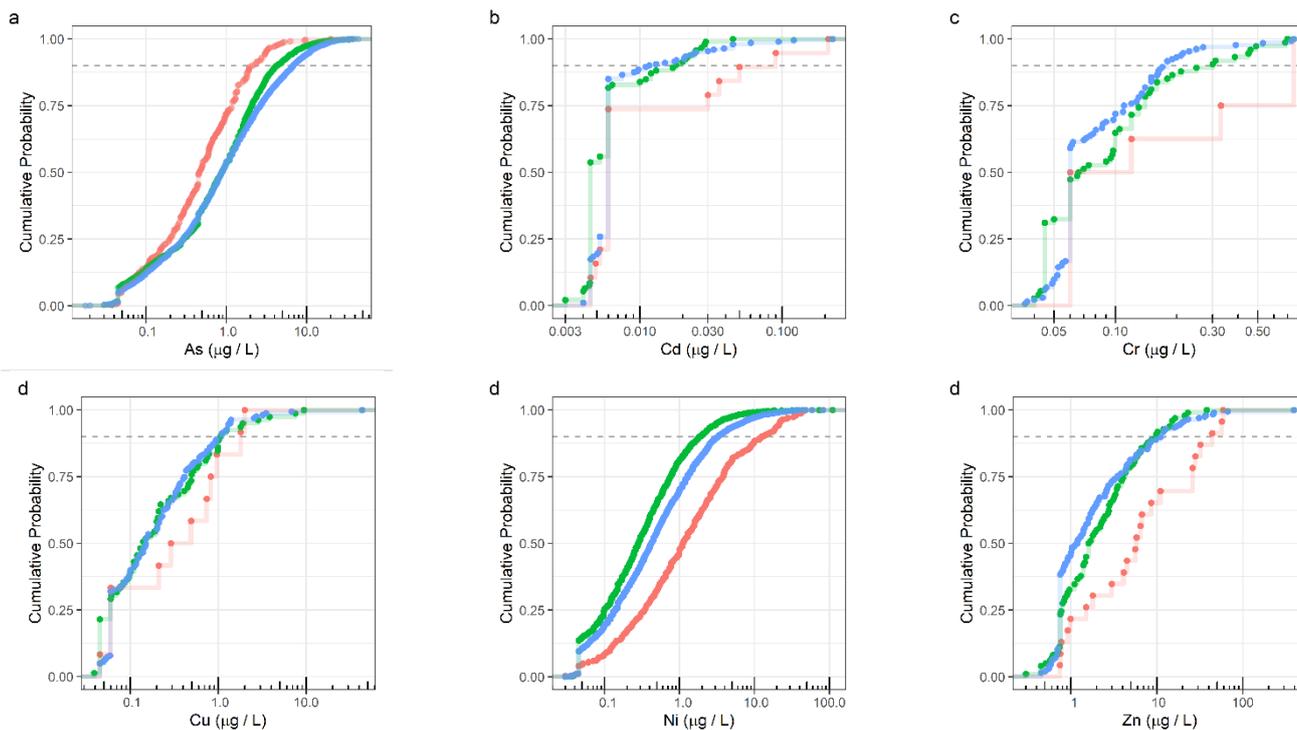


Figure S4. Empirical cumulative distribution function for As, Cd, Cr, Cu, Ni, and Zn in Danish groundwater at waterworks wells used for drinking water production, stratified by pH class.

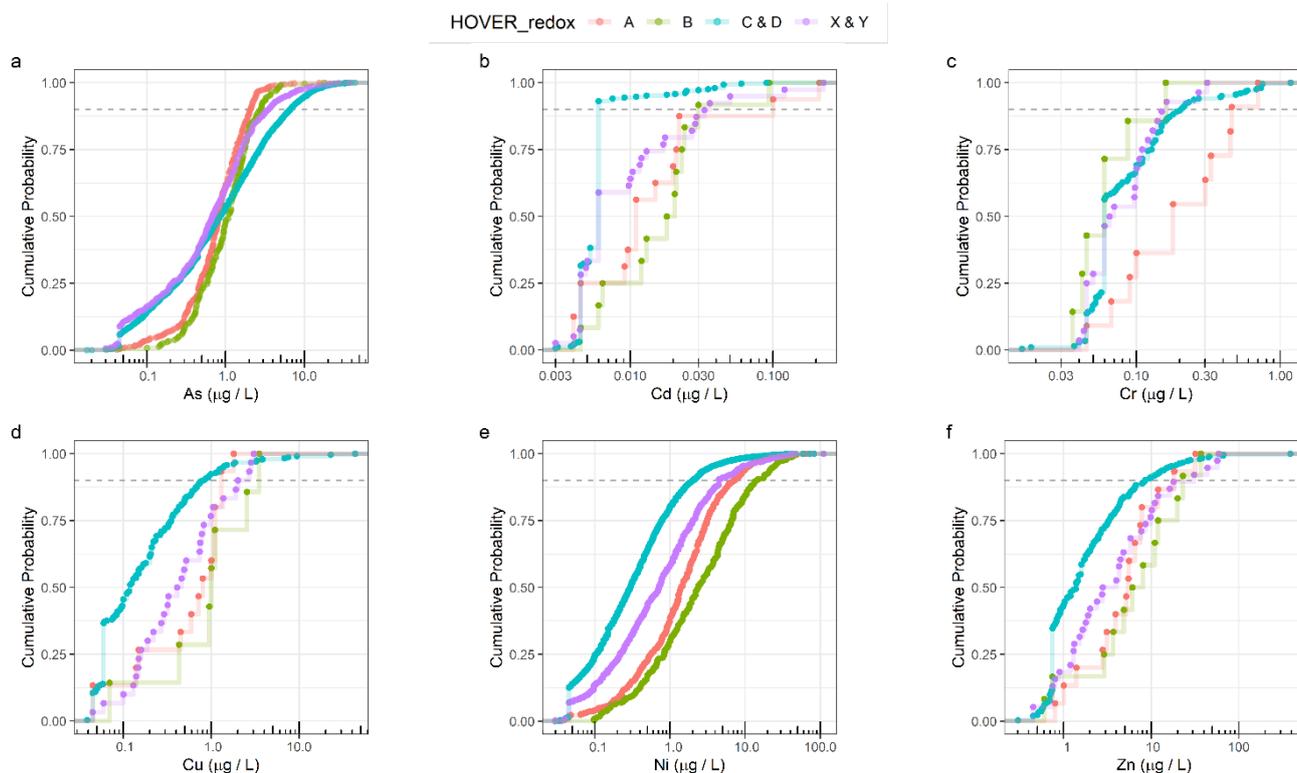


Figure 5. Empirical cumulative distribution function for As, Cd, Cr, Cu, Ni, and Zn in Danish groundwater at waterworks wells for drinking water production, stratified by redox class.

prevailing — agricultural — industrial — urban

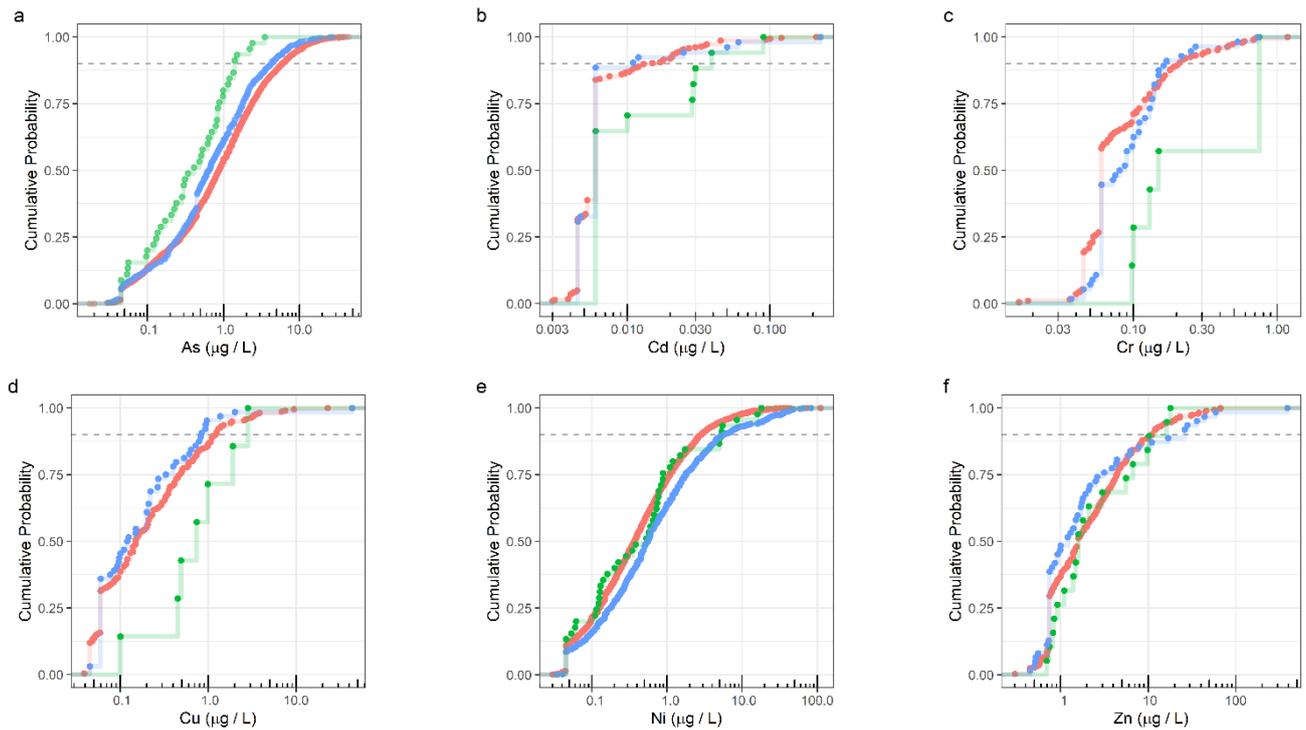


Figure 6. Empirical cumulative distribution function for As, Cd, Cr, Cu, Ni, and Zn stratified by prevailing anthropogenic pressure (“mining” and “natural” were excluded due to too few water sampling points).

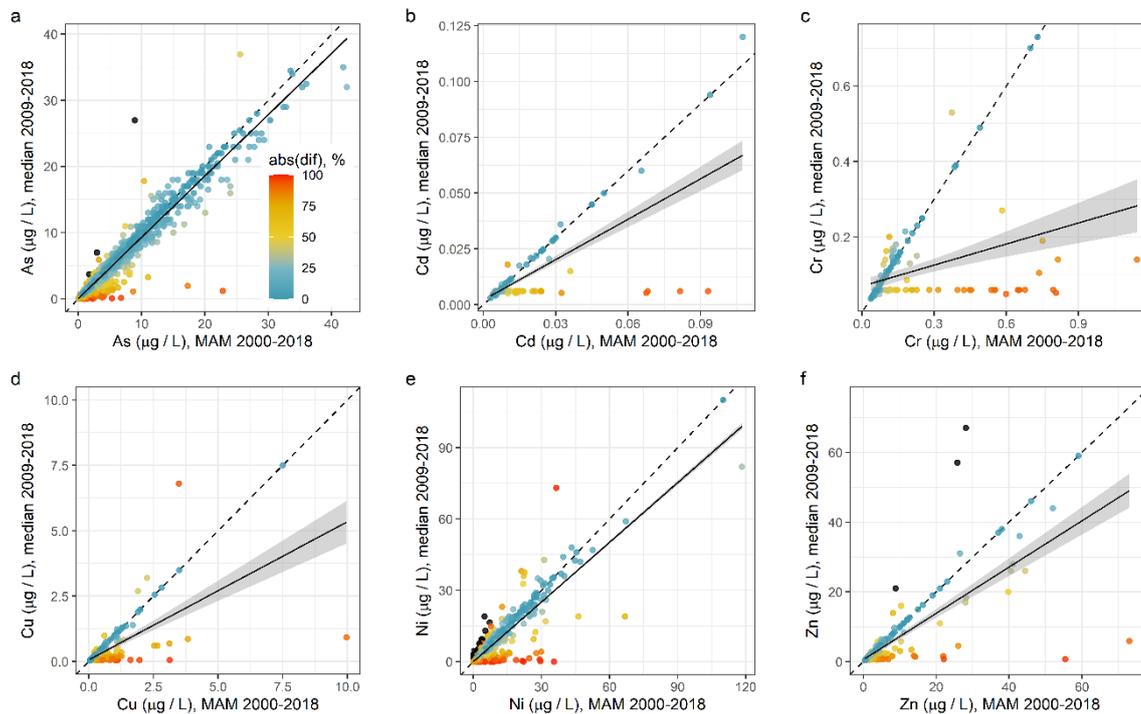


Figure 7. Comparison between the aggregated datasets for *HOVER basis* and *MP3 basis* including the sampling points present in both datasets; MAM stands for mean computed from the annual means; abs(dif) stands for the absolute difference between the median and MAM in % calculated with the formula: $\text{abs}((\text{Median} - \text{MAM})/\text{MAM} * 100)$.

Supplementary tables

Table 1. Groundwater sampling points (n) with heavy metal analyses in the raw dataset and the final, clean dataset after all quality controls and pre-treatments.

	As	Cd	Cu	Cr	Ni	Zn
Raw data [6] (n)	6472	363	295	255	6478	368
Excluded (n, %)	120, 1.9%	8, 2.2%	6, 2.0%	5, 2.0%	120, 1.9%	5, 1.4%
HOVER basis dataset (n = 6388)	6352	355	289	250	6358	363

Table 2. Natural background levels of As, Cd, Cr, Cu, Ni, and Zn for the three main aquifer types in Denmark, based on HOVER basis, HOVER land-use, and BRIDGE modified; Abbreviations: NBL – natural background level, calculated as the 90th percentile; 95% CI – 95% confidence interval for the NBL; bold – the value is above the national TV, grey highlight – the 95% CI are not overlapping, so the difference in NBLs is significant.

Element	Aquifer type	BRIDGE modified		HOVER basis		HOVER land-use	
		NBL (95% CI) [$\mu\text{g/l}$]	n	NBL (95% CI) [$\mu\text{g/l}$]	n	NBL (95% CI) [$\mu\text{g/l}$]	n
As	Carbonates	3.9 (3.6, 4.4)	1872	3.6 (3.3, 4.0)	2239	3.9 (3.4, 4.4)	1830
	Pre-Quaternary sand	2.5 (2.2, 3.1)	650	2.5 (2.2, 3.1)	665	2.5 (2.3, 3.1)	560
	Quaternary sand	8.4 (7.6, 9.0)	2816	7.5 (7.0, 8.1)	3368	7.7 (7.2, 8.4)	3049
Cd	Carbonates	0.024 (0.006, 0.051)	68	0.035 (0.020, 0.106)	80	0.026 (0.016, 0.090)	77
	Pre-Quaternary sand	0.006 (0.006, 0.025)	53	0.006 (0.006, 0.020)	56	0.006 (0.006, 0.020)	56
	Quaternary sand	0.006 (0.006, 0.013)	159	0.013 (0.010, 0.022)	201	0.012 (0.009, 0.021)	197
Cr	Carbonates	0.194 (0.121, 0.716)	49	0.235 (0.149, 0.750)	58	0.178 (0.120, 0.447)	55
	Pre-Quaternary sand	0.210 (0.060, 0.806)	30	0.190 (0.060, 0.791)	31	0.190 (0.060, 0.791)	31
	Quaternary sand	0.172 (0.145, 0.245)	129	0.210 (0.162, 0.304)	161	0.192 (0.160, 0.299)	155
Cu	Carbonates	0.89 (0.66, 1.67)	57	1.42 (0.90, 2.71)	69	1.34 (0.86, 2.74)	67
	Pre-Quaternary sand	0.42 (0.33, 1.38)	35	0.42 (0.32, 1.34)	36	0.42 (0.32, 1.34)	36
	Quaternary sand	1.10 (0.70, 1.93)	147	1.12 (0.94, 1.83)	184	1.10 (0.80, 1.35)	182
Ni	Carbonates	4.7 (4.2, 5.4)	1876	6.3 (5.5, 7.2)	2245	5.3 (4.8, 6.2)	1856
	Pre-Quaternary sand	1.4 (1.1, 2.0)	650	1.4 (1.2, 2.0)	665	1.4 (1.2, 2.0)	565
	Quaternary sand	1.5 (1.4, 1.7)	2816	2.0 (1.8, 2.2)	3368	1.9 (1.7, 2.1)	3057
Zn	Carbonates	12.0 (7.4, 20.8)	70	21.8 (16.0, 34.9)	87	19.6 (9.8, 31.0)	85
	Pre-Quaternary sand	4.2 (2.7, 39.2)	53	5.9 (2.8, 43.4)	56	5.9 (2.8, 43.4)	56
	Quaternary sand	9.7 (5.5, 14.4)	160	8.6 (6.5, 12.0)	202	8.2 (6.4, 12.0)	200

Table 3. Natural background levels of As for the three main aquifer types and different pH and redox conditions, based on HOVER basis, HOVER land-use, and BRIDGE modified; Abbreviations: NBL – natural background level, calculated as the 90th percentile; 95% CI – 95% confidence interval for the NBL; bold – the value is above the national TV, all 95% CI are overlapping, so the difference in NBLs is not significant.

Aquifer type	Redox & pH type	BRIDGE modified		HOVER basis		HOVER land-use	
		NBL (95% CI) [$\mu\text{g As/l}$]	n	NBL (95% CI) [$\mu\text{g As/l}$]	n	NBL (95% CI) [$\mu\text{g As/l}$]	n
Carbonate	Anoxic & Neutral	-	-	2.5 (2.2, 4.4)	84	2.7 (2.2, 4.6)	65
	Mixed & Basic	3.3 (2.7, 5.8)	111	3.3 (2.6, 5.7)	115	3.3 (2.3, 5.8)	97
	Mixed & Neutral	6.0 (2.6, 11.0)	154	5.8 (2.5, 11.3)	175	7.7 (3.1, 12.9)	141
	Oxic & Basic	-	-	2.3 (2.1, 3.8)	108	2.2 (2.1, 3.3)	100
	Oxic & Neutral	-	-	2.1 (1.8, 2.8)	132	2.0 (1.8, 2.8)	114
	Reduced & Basic	4.0 (3.4, 4.8)	225	3.9 (3.3, 4.7)	230	4.0 (3.5, 4.9)	204
	Reduced & Neutral	4.4 (3.8, 5.4)	1031	4.3 (3.8, 5.3)	1103	4.7 (4.1, 5.8)	886
Pre-Quaternary sand	Reduced & Acidic	1.4 (1.0, 2.4)	115	1.4 (1.0, 2.5)	118	1.5 (1.0, 3.1)	98
	Reduced & Basic	1.9 (1.5, 2.9)	136	1.9 (1.4, 2.8)	138	1.9 (1.5, 2.8)	119
	Reduced & Neutral	3.5 (2.5, 4.7)	309	3.5 (2.7, 4.8)	312	3.2 (2.6, 4.4)	262
Quaternary sand	Anoxic & Basic	-	-	2.9 (2.0, 4.8)	50	-	-
	Mixed & Basic	3.9 (2.8, 5.2)	129	3.5 (2.6, 4.5)	164	3.6 (2.6, 4.7)	148
	Mixed & Neutral	4.1 (3.6, 7.2)	114	4.0 (3.5, 5.2)	168	3.9 (3.1, 5.3)	151
	Oxic & Basic	-	-	2.4 (2.0, 2.5)	79	2.3 (2.0, 2.6)	73
	Oxic & Neutral	-	-	1.2 (0.9, 1.4)	83	1.3 (0.9, 1.3)	75
	Reduced & Acidic	3.2 (3.0, 6.0)	65	3.3 (3.0, 4.9)	73	3.3 (3.0, 5.3)	69
	Reduced & Basic	6.1 (5.5, 7.3)	760	6.2 (5.6, 7.3)	799	6.0 (5.3, 7.1)	718
	Reduced & Neutral	10.9 (9.6, 11.0)	1334	10.0 (9.4, 11.0)	1460	11.0 (9.6, 11.2)	1335

Table 4. Natural background levels of Ni for the three main aquifer types and different pH and redox conditions, based on HOVER basis, HOVER land-use, and BRIDGE modified; Abbreviations: NBL – natural background level, calculated as the 90th percentile; 95% CI – 95% confidence interval for the NBL; bold – the value is above the national TV, all 95% CI are overlapping, so the difference in NBLs is not significant.

Aquifer type	Redox & pH type	BRIDGE modified		HOVER basis		HOVER land-use	
		NBL (95% CI) [$\mu\text{g Ni/l}$]	n	NBL (95% CI) [$\mu\text{g Ni/l}$]	n	NBL (95% CI) [$\mu\text{g Ni/l}$]	n
Carbonate	Anoxic & Neutral	-	-	21.7 (18.0, 32.1)	84	20.0 (15.0, 26.0)	65
	Mixed & Basic	2.5 (2.2, 4.4)	111	2.8 (2.2, 5.5)	115	3.2 (2.2, 5.8)	97
	Mixed & Neutral	7.1 (4.5, 9.0)	154	7.8 (6.1, 9.6)	175	7.7 (4.5, 11.0)	141
	Oxic & Basic	-	-	4.4 (3.4, 8.8)	108	4.0 (3.4, 8.0)	100
	Oxic & Neutral	-	-	12.5 (11.0, 15.8)	132	12.0 (10.0, 15.5)	114
	Reduced & Basic	2.0 (1.6, 2.8)	225	2.0 (1.6, 2.7)	230	2.1 (1.6, 2.9)	204
	Reduced & Neutral	3.1 (2.8, 3.9)	1032	3.5 (3.0, 4.4)	1104	3.0 (2.6, 3.5)	903
Pre-Quaternary sand	Reduced & Acidic	3.6 (2.0, 8.8)	115	3.5 (2.0, 5.4)	118	3.5 (2.0, 9.8)	98
	Reduced & Basic	0.8 (0.6, 1.3)	136	0.8 (0.6, 1.2)	138	0.6 (0.6, 1.3)	121
	Reduced & Neutral	1.0 (0.7, 1.3)	309	1.0 (0.7, 1.3)	312	1.1 (0.8, 1.5)	264
Quaternary sand	Anoxic & Basic	-	-	2.3 (1.1, 4.0)	50	-	-
	Mixed & Basic	1.2 (1.0, 1.8)	129	1.4 (1.1, 1.7)	164	1.4 (1.2, 1.8)	151
	Mixed & Neutral	2.8 (2.4, 4.5)	114	3.4 (2.9, 4.5)	168	3.8 (3.0, 4.5)	151
	Oxic & Basic	-	-	1.3 (0.9, 3.4)	79	1.3 (1.0, 3.4)	73
	Oxic & Neutral	-	-	2.3 (1.9, 4.5)	83	2.3 (1.8, 4.1)	75
	Reduced & Acidic	5.8 (3.9, 19.3)	65	5.9 (4.2, 18.8)	73	5.8 (4.1, 18.5)	69
	Reduced & Basic	1.0 (0.9, 1.1)	761	1.0 (0.9, 1.2)	800	1.0 (0.9, 1.2)	721
	Reduced & Neutral	1.4 (1.2, 1.6)	1334	1.4 (1.3, 1.6)	1460	1.4 (1.2, 1.6)	1337

Table 5. Natural background levels for the three main aquifer types at different locations in Denmark, based on HOVER basis and MP3 basis; Abbreviations: NBL – natural background level, calculated as the 90th percentile; 95% CI – 95% confidence interval for the NBL.

Element	Aquifer type	Location	HOVER basis		MP3 basis		
			NBL	n	NBL	n	
As	Carbonate	Fyn	6.3 (5.4, 6.8)	72	5.9 (3.9, 6.5)	73	
		Jylland	3.4 (3.1, 3.8)	672	3.1 (2.6, 3.5)	484	
		Sjælland	3.7 (3.2, 4.1)	1495	4.5 (4.0, 5.7)	1281	
		Jylland	2.5 (2.2, 3.1)	665	3.0 (2.6, 3.5)	534	
	Pre-Quaternary sand	Fyn	11.0 (10.4, 12.6)	524	11.0 (10.3, 11.7)	545	
		Quaternary sand	Jylland	5.3 (5.0, 5.9)	2141	5.0 (4.5, 5.5)	1856
			Sjælland	9.5 (8.3, 11.7)	668	9.5 (8.1, 11.4)	764
		Cd	Carbonate	Jylland			0.033 (0.029, 0.044)
Sjælland	0.039 (-0.008, 0.110)			62	0.045 (0.028, 0.065)	165	
Pre-Quaternary sand	Jylland		0.006 (0.006, 0.020)	56	0.106 (0.034, 0.184)	186	
	Fyn				0.043 (0.026, 0.063)	143	
Quaternary sand	Jylland		0.013 (0.009, 0.021)	162	0.175 (0.141, 0.238)	716	
	Sjælland				0.038 (0.030, 0.050)	230	
Cr	Carbonate		Jylland			0.929 (0.532, 1.236)	55
			Sjælland	0.220 (0.119, 0.750)	51	0.536 (0.343, 0.882)	118
	Pre-Quaternary sand	Jylland	0.190 (0.060, 0.791)	31	0.907 (0.706, 1.548)	88	
		Fyn			0.555 (0.371, 5.049)	76	
	Quaternary sand	Jylland	0.180 (0.157, 0.369)	124	0.880 (0.816, 1.100)	392	
		Sjælland			1.100 (0.977, 1.300)	145	
Cu	Carbonate	Jylland			1.24 (0.97, 2.22)	94	
		Sjælland	1.46 (0.88, 3.19)	55	2.25 (1.68, 4.56)	152	
	Pre-Quaternary sand	Jylland	0.42 (0.32, 1.34)	36	1.16 (0.95, 1.93)	145	
		Fyn	0.77 (0.53, 1.34)	37	2.22 (1.61, 4.50)	124	
	Quaternary sand	Jylland	1.10 (0.95, 1.93)	135	3.96 (3.07, 5.48)	617	
		Sjælland			7.00 (4.14, 15.52)	227	
Ni	Carbonate	Fyn	0.8 (0.7, 1.7)	72	1.0 (0.9, 2.8)	73	

Element	Aquifer type	Location	HOVER basis		MP3 basis		
			NBL	n	NBL	n	
Zn	Pre-Quaternary sand	Jylland	5.5 (4.9, 5.9)	672	5.3 (4.7, 6.3)	484	
		Sjælland	7.4 (6.4, 8.4)	1501	8.3 (7.2, 10.8)	1282	
		Jylland	1.4 (1.2, 2.0)	665	3.2 (2.7, 4.9)	534	
		Fyn	1.6 (1.4, 2.0)	524	2.0 (1.8, 2.5)	545	
	Quaternary sand	Jylland	1.8 (1.5, 2.0)	2141	4.0 (3.5, 4.6)	1856	
		Sjælland	2.6 (2.4, 2.9)	668	3.2 (2.9, 3.7)	764	
	Carbonate	Jylland			16.7 (11.6, 35.7)	121	
		Sjælland	26.0 (17.1, 42.6)	62	36.7 (26.4, 46.2)	167	
		Pre-Quaternary sand	Jylland	5.9 (2.8, 43.4)	56	28.0 (17.0, 39.5)	191
			Fyn			13.6 (12.0, 21.6)	163
Quaternary sand		Jylland	8.1 (6.3, 12.7)	161	30.3 (25.4, 38.7)	720	
		Sjælland			35.9 (26.9, 45.1)	234	

bold – the value is above the national TV, grey highlight – the 95% CI are not overlapping, so the difference in NBLs is significant

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