Hydrogeological processes and geological settings over Europe controlling dissolved geogenic and anthropogenic elements in groundwater of relevance to human health and the status of dependent ecosystem

Deliverable D.3-2

A litho-geological classification system based on the capacities of rocks to release elements to GW including development of the methods in some EU countries

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LIST WITH ABREVIATIONS

BRGM – Bureau de Recherches Geologiques et Minieres (France)
BRIDGE – acronym for European FP6 Project “Background criteria for identification of groundwater thresholds”
ECDF – empirical cumulative density function
GBA – Geologische Bundesansstalt (Austria)
GEUS – Geological Survey of Denmark and Greenland (Denmark)
GSI – Geological Survey of Ireland (Ireland)
GSO – European Geological Survey Organizations
GSS – Geological Survey of Serbia (Serbia)
HCOV – hydrogeological classification code and system for Flanders
IGME – Geological and Mining Institute of Spain (Spain)
IQR – interquartile range (IQR=Q75-Q25)
KW – Kruskal-Wallis Rank Sum test
MAD – median absolute deviation
MBFSZ – Mining and Geological Survey of Hungary (Hungary)
NA – not available/applicable, missing value
PW – Pairwise Wilcoxon Rank Sum Test
VMM – Flanders Environment Agency (Flanders, Belgium)

1 INTRODUCTION

This deliverable is part of the work package 3 (WP3) in the Horizon2020 GeoERA project HOVER running from 2018 – 2022 with the title: **H**ydrogeological processes and Geological settings **over** Europe controlling dissolved geogenic and anthropogenic elements in groundwater of relevance to human health and the status of dependent ecosystems. The HOVER project addresses groundwater management issues related to drinking water, human and ecosystem health across Europe in relation to both geogenic elements and anthropogenic pollutants by data sharing, technical and scientific exchange between European Geological Survey Organizations (GSO).

WP3 deals with Hydrogeochemistry and health: Mapping groundwater characteristics for the management of aquifers naturally enriched in dissolved elements. WP3 consists of five tasks:

3.1 Harmonization of terminology, inventory of available information on mineral, thermal and highly mineralized groundwater
3.2 Defining lithological/geological water families based on information available at EU scale
3.3 Proposing a common methodology to calculate the national concentration of dissolved elements based on lithological/geological families taking into account possible anthropogenic influences
3.4 Natural background levels and health – determination and selection of indicators for GW management
3.5 Preparing and producing maps, web map service and associated explanatory information

This report concerns task 3.2 about defining lithological/geological water families based on information available at EU scale.

Concentrations of dissolved elements in groundwater are directly linked to the mineral composition of rocks/sediments and geochemical processes such as redox, ion exchange, precipitation, dissolution, weathering etc.

The geological factors controlling occurrence and distribution of dissolved elements in groundwater are numerous and of different importance. Different approaches on grouping rock formations depending on their potential of mineral release have been developed. These approaches can be used to delineate areas of potentially high concentrations in some trace elements.

The present report (deliverable D.3-2) investigates possibilities for proposing a new methodology for defining new lithological/geological water families by:

- Reviewing existing approaches used by the GSOs
- Collecting data from selected study sites
- Analyzing collected data with exiting approaches
- Analyzing possibilities with collected data for a new methodology
- Recommendation for a new methodology

The work in task 3.2 was restricted by the low amount of data collected from the participating GSOs in relation to a questionnaire in the winter/spring 2019. Therefore, task 3.2 can be seen as a pilot study, which can be extended in task 3.3 on a boarder European level when data is available from more European study sites, representing a more diverse picture of geological factors controlling occurrence and distribution of trace elements in groundwater.

2 REVIEW OF EXISTING APPROACHES FOR DEFINING WATER FAMILIES IN EUROPE

2.1 BRIDGE typology

BRIDGE is the acronym for the European FP 6 Project "Background criteria for identification of groundwater thresholds" in which scientists from eleven European countries (including representatives from several national GSOs) jointly defined a harmonized European aquifer typology (Wendland et al., 2008). The main application of the BRIDGE aquifer typology was for differentiation of natural background levels and threshold values of pollutants in groundwaters in Europe. Wendland et al. (2008) posited that petrography should be the prime criterion for developing such groundwater typologies on regional/continental scale, based on the generalization that aquifers with similar petrographic properties have similar composition when the hydrodynamic and hydrologic conditions are similar (Appelo & Postma, 2005).

The BRIDGE aquifer typology organized and simplified the complexity of individual aquifers into nine major aquifer rock types with specific ranges in porosity, permeability and petrochemistry: 1) Sands and gravels, 2) Marls and clays, 3) Sandstones, 4) Chalk, 5) Limestones, 6) Volcanic rocks, 7) Schist and shale, 8) Crystalline rocks, and 9) Saline influence (Wendland et al., 2008). Further, based on data from 12 European countries, a European aquifer typology map was compiled (Figure 1). In this map, to account for particular hydrochemical and hydrological factors, three of the nine typologies were further sub-divided, as follows:

- Limestones – 1) Karstic limestones, 2) Limestones and interbedded silicatic/carbonate rocks, 3) Limestones of mountainous areas, and 4) Paleozoic limestones;
- Sandstones – 1) Triassic sandstones, and 2) Sandstones and silicatic alternating sequences;
- Sands and Gravels – 1) Sands with saline/brakish water, 2) Glacial sand and gravel deposits, 3) Fluviatile deposits of major streams, and 4) Marine depostis.

The nine major BRIDGE typologies were subdivided based on the following additional secondary criteria:

- Hydrodynamics, e.g. groundwater recharge, residence time, topography, leakage
- Redox conditions
- Particular occurrences, e.g. dykes, sulphide minerals, clays
- Geological age

Wendland et al. (2008) developed BRIDGE as a consistent and simple framework for characterizing major groundwater composition patterns; however, they recognized that further refinements can be done to further enhance the accuracy and reliability of the proposed methodology.

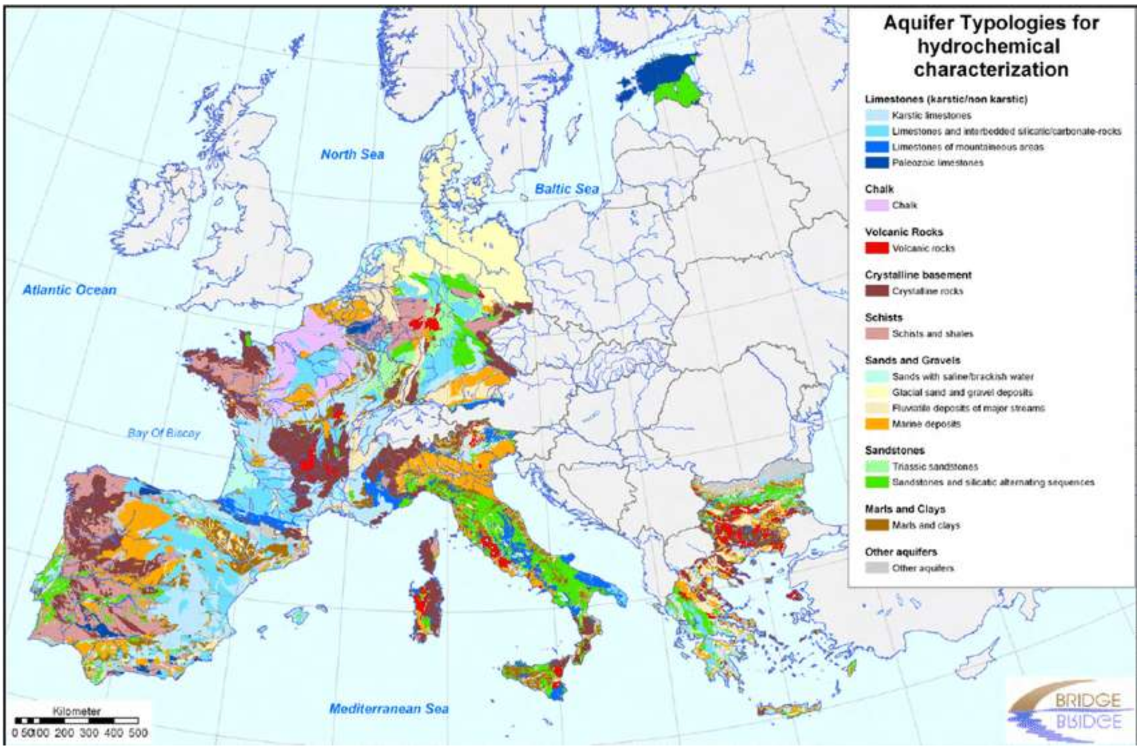

Figure 1: European map of aquifer typologies for hydrochemical characterization, compiled as part of the European FP6 project BRIDGE (Wendland et al 2007)

2.2 National and regional aquifer typologies

2.2.1 Denmark

Gravesen & Fredericia (1984) first documented the official system used in the national geodatabase JUPITER and in the geologic maps of the Geological Survey of Denmark and Greenland (GEUS). The system, amongst other things, includes a list with “stratigraphic DGU-codes” composed of 201 mnemonic codes (1-3 letters) and the official term (the code meaning) in Danish and English. The letters codify information on the geological age, lithology, and depositional type, for example “FG” stands for “Postglacial Freshwater Gravel” (in Danish: “Postglacial ferskvandsgrus”), while “MG” is for Glacial gravelly till (in Danish: “Glacial morænegrus”) (see also Figure 2).

Figure 2: Selection of Gravesen & Fredericia's (1984) codes used in the Surface Geology Map of Denmark (1:25.000, version 4).

In detailed groundwater mapping assessments for specific aquifer bodies in Denmark, 3D geological and hydrogeological models are developed based on interpretation of geophysical surveys and the borehole data from JUPITER (the mnemonic codes). Hansen & Thorling (2018) provide a guideline for systematic interpretation of Danish groundwater chemistry as part of an iterative process combining geological and hydrogeological mapping with groundwater quality assessment. Depending on the purpose of the assessment and the specifics of each area, different mnemonic codes may be grouped together, for example "DS" and "DG" (standing for glacial meltwater sand and gravel, respectively) may form a new aquifer typology "Glacial meltwater sand and gravel".

2.2.2 Flanders

The hydrogeological classification code for Flanders (HCOV) is the generally accepted classification system in Flanders. Each HCOV unit represents a hydrogeological layer, characterized by a four-digit code and its description. HCOV consists of three hierarchical levels allowing for different level of detail (Cools et al., 2006). Table 1 provides an overview of the main HCOV units and Table 2 shows an example of sub- and basic units for one particular HCOV main unit.

The final product of the Flanders hydrogeological mapping consists of raster files with the vertical delimitation of the base and depth of the HCOV units and shapefiles with the horizontal delimitation of the HCOV units (VMM, 2007).

Table 1: HCOV main units (Cools et al., 2006)

Geological era	*HCOV main unit*	*Description*

	0000	Undetermined
Quaternary	0100	Quaternary aquifer systems
Tertiary	0200	Campine aquifer system
	0300	Boom aquitard
	0400	Oligocene aquifer system
	0500	Bartoon aquitard system
	0600	Ledo–Paniselian–Brusselian aquifer system
	0700	Paniselian aquifer system
	0800	Yperian aquifer
	0900	Yperian aquitard system
	1000	Paleocene aquifer system
Mesozoic	1100	Cretaceous
	1200	Jurassic–Trias–Perm
Paleozoic	1300	Paleozoic

Table 2: Example with HCOV sub- and basic units for 0600 Ledo-Paniselian-Bruselian aquifer system (Cools et al., 2006)

HCOV main unit	*HCOV sub-unit*	*HCOV basic unit*
0600 Ledo–Paniselian–Bruselian aquifer system	0610 Wemmel-Lede aquifer	0611 Sand of Wemmel
		0612 Sand of Lede
	0620 Sand of Brussels	– Sand of Brussels
	0630 Sediments of upper-Paniselian	0631 Sands of Aalter and Oedelem
		0632 Sandy clay of Beernem
	0640 Sandy sediments of lower-Paniselian	– Sand of Vlierzele and Aalterbrugge

2.3 Relevant geochemical processes

The chemical composition of groundwater is controlled by a number of processes, some of which have a geological origin. Next to that, dissolved elements in groundwater are to a varying extent affected by anthropogenic activities and inputs from the land surface. Therefore, the occurrence and distribution of dissolved elements in groundwater are linked to the mineral composition of rocks/sediments and various geochemical processes.

The geochemical reactions which are normally considered and may be in interplay with each other are:

- **Dissolution and precipitation of minerals**
  Examples: Gypsum, Halite, Fluorite, Silicates, Carbonates etc.
- **Ion exchange**
  Examples: Clay minerals**,** Cation exchange (Na)
- **Sorption of elements to mineral surfaces**
  Examples: Complexation with hydro-oxides, humid acids etc.
- **Oxidation-reduction (redox) processes**
  Examples: Nitrate reduction, pyrite oxidation, iron reduction, organic matter reduction, sulphate reduction etc.

Here we focus on the geogenic trace elements in European groundwaters specifically. Sorption of trace elements to the aquifer material and consequently the trace elements' concentrations in groundwater are often controlled by geological/lithological characteristics of the aquifer, the acidity, and the redox condition of the groundwater (e.g. van Riemsdijk & Hiemstra 1993).

Redox reactions, the coupled loss and gain of electrons, alter the sorptive properties of aquifer materials, and generate products, which can be very different from the reactants in their solubility, toxicity, reactivity, and mobility (Fish W., 1993). In uncontaminated aquifers, natural organic matter (OM) is oxidized by a sequence of electron-accepting compounds. In the first step, the process uses dissolved oxygen (O_2) and produces carbonic acid from the OM oxidation (Equation 1, Appelo & Postma 2005):

$$CH_2O + O_2 \longrightarrow H_2O + CO_2 \qquad (1)$$

In Equation 1, a carbohydrate (CH_2O) is used as a simple representation of natural OM. Once the O_2 has been used completely, the OM oxidation is progressing through other electron acceptors, e.g. NO_3^-, Mn-oxides, Fe-oxides, and SO_4^{2-}, etc. (Appelo & Postma 2005, 3]. Redox reactions produce dramatic chemical change through this sequence and are essential feature of the geochemical evolution of natural groundwaters (Fish W., 1993). For some electron acceptors (O_2, NO_3^-, SO_4^{2-}) it is the disappearance of the reactant, while for others (Mn^{2+}, Fe^{2+}, H_2S, CH_4) it is the appearance that is notable in the groundwater composition (Appelo & Postma 2005). The redox reaction sequence is visualized and explained in further detail in Chapter 9.3 "Sequence of Redox Reactions and Redox zoning" (Appelo & Postma, 2005).

The standard redox potential (Eh) measurement has been used widely as a "redox state" indicator, but its interpretation is limited because it only indicates the redox state of those couples that are reactive enough to produce a sufficient current at the electrode surface (e.g. Fe(II)/Fe(III)) (Fish W., 1993). However, because many redox reactions are strongly influenced by pH, redox diagrams (Eh-pH, pE-pH, etc.) have been very useful in overviewing these complex hydrogeochemical systems (Appelo & Postma, 2005).

Next to redox and the influence of pH on redox processes, pH is also a very important chemical parameter because the sorption/desorption of metals is also a pH-dependent process. An excellent illustration is provided in Chapter 7.1 “The origin and occurrence of heavy metals in groundwater” (Appelo & Postma, 2005), where the adsorption of heavy metals on the surface of ferrihydrite is shown as a function of pH. All heavy metals (Cr^{3+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}) showed zero sorption at low pH, the sorption increased with pH increase, and the pH level at which 50% sorption (also zero sorption) occurred were element-dependent (Appelo & Postma, 2005).

Metal concentrations in calcareous aquifers are also controlled by solubility and sorption processes (Zachara, Cowan, and Resch, 1993). Calcite ($CaCO_3$(s)) is a common mineral phase that influences groundwater composition via its precipitation/dissolution behavior (Zachara, Cowan, and Resch, 1993). Metal cation (Me^{2+}) adsorption in equilibrium $CaCo_3$(aq) suspension is influenced by: 1) pH and partial CO_2 pressure, which control the aqueous Ca concentrations, and 2) the calcite surface area, which determines the concentration of cation-specific surface sites (X) (Equation 2, Zachara, Cowan, and Resch, 1993):

$$X - Ca + Me^{2+} \rightleftarrows X - Me + Ca^{2+} \qquad (2)$$

In other words, sorption of Me^{2+} increases with increasing pH, and low aqueous concentrations of Ca^{2+} promote Me^{2+} surface exchange (Equation 2). Specific metallic cations and anions that have been shown to be sorbed to calcite are Ba^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pu^{2+}, Sr^{2+}, Zn^{2+}, PO_4^{3-}, SeO_3^{2-} (Zachara, Cowan, and Resch, 1993).

3 DATA COLLECTION

3.1 Questionnaire

Taks 3-2 lead (GEUS) and Task 3-3 lead (BRGM) held a two-day workshop to discuss and design a common questionnaire for data collection for the purposes of these WP3 tasks. The resulting data collection template is provided in Appendix 3. Four GSOs were selected as Task 3-2 pilot areas based on their positive answers from the first WP3 specific questionnaire (Q: *“Do you have special investigation areas (pilot areas) in your country with high observation density of ground water quality?”*) and their specific allocation of man-hours to WP3. The questionnaire was sent to the identified four GSOs in order to collect data on trace elements in groundwater monitoring stations along with a number of geological and hydrological variables (see Appendix 3).

Mining and Geological Survey of Hungary (MBFSZ) withdrew their pilot area from Task 3-2. Geological Survey of Serbia (GSS) could only supply samples from thermal/mineral waters, but these special groundwaters are excluded from Task 3-2. Thus, from the four contacted GSOs, only the Geological Survey of Ireland (GSI, Department of Communications, Climate Action and Environment) and the Flanders Environment Agency (VMM) provided applicable data before the set deadline. Additionally, the Geological and Mining Institute of Spain (IGME) volunteered an additional pilot area and supplied data, but after the analyses for this report were completed.

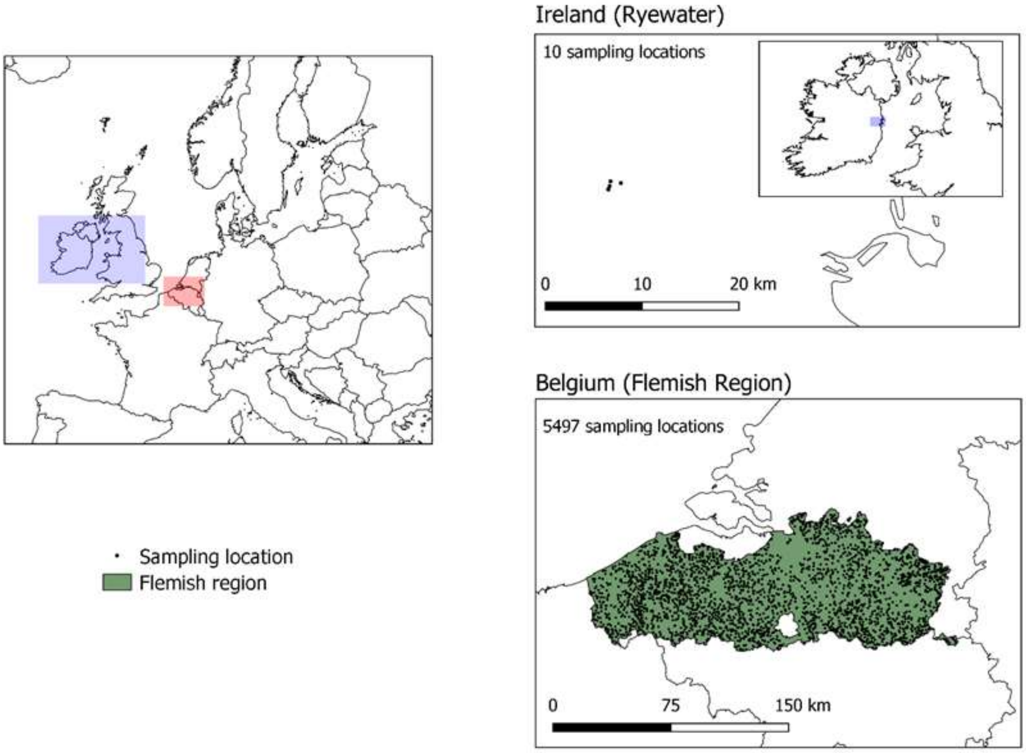

Figure 3: Locations of the sampling points retrieved for this report in Ireland and Belgium. Data source: Irish EPA, GSI and VMM. Background: @EuroGeographics. The pilot area in Ireland covers approx. 1 km^2, while the Flemish data is distributed throughout the entire region (approx. 13,500 km^2)

3.2 Overview of collected data

Two datasets with very different characteristics were obtained in time for data analysis. The VMM dataset covers the entire Flemish region (approx. 13,500 km^2) and includes water samples taken in the period between 2013 and 2017, while the GSI dataset covers the Ryewater area near Dublin (approx. 1 km^2) and the water samples are taken between 2009 and 2017. The sampling locations are shown in Figure 3. Prior to any data overviews and analysis, the provided chemical data was aggregated, such that when there was more than one measurement per sampling point (ID), the median was used. These aggregated datasets are further referred to as master datasets. Table 3 and Table 4 present overview of the chemical concentrations found in these two master datasets and summary of the categorical variables is provided next.

3.2.1 Flemish region (Belgium, source: VMM)

This master dataset consists of 5497 unique IDs, all representing “well” types with sampling depths varying from 0.75 m below terrain (mbt) to 566.12 mbt (median 7.25 mbt, mean 21.51 mbt, not available, NA, depth information for 33 IDs).

The distribution of observations (IDs) in the geological/hydrological variables was as follows:

- *BRIDGE typology*: Fluviatile deposits of major streams (n=569), Glacial sand and gravel deposits (n=4), Marine deposits (n=2523), Marls and clays (n=8), Others (n=2390), Paleozoic limestones (n=3);
- *Lithology*: Metamorphic rocks (n=83), Others (n=1990), Sedimentary: carbonates (limestone, chalk) (n=81), Sedimentary: clays and/or marls (n=253), Sedimentary: gravel (n=222), Sedimentary: other (n=994), Sedimentary: sand (n=1874)
- *Deposition type*: Aerial (e,g, loess) (n=251), Fresh water (n=569), Marine (n=2616), Others (n=2061)
- *Age stratigraphy*: Cenozoic/Tertiary (n=2462), Mesozoic (Cretaceous, Jurassic, Triassic) (n=174), Others (n=164), Paleozoic (n=83), Quaternary (n=2614)
- *Aquifer type*: confined (n=530), unconfined (n=4408), unknown (n=559)
- *Recharge, approximately*: <100 mm (n=277), 100-300 mm (n=3963), 300-800 mm (n=1257)
- *Flow media*: karst (n=3), matrix (n=5414), mixed (n=80)
- all NAs (no information) for “Signs of anthropogenic influence”, “Redox conditions”, and “Hydraulic conductivity”.

3.2.2 Ryewater area (Ireland, source: GSI)

This master dataset consists of 10 unique IDs, all representing “borehole” type with sampling depths varying from 2.9 mbt to 82.3 mbt (median 27.4 mbt, mean 33.19 mbt, n=10).

The distribution of observations (IDs) in the geological/hydrological variables was as follows:

- *BRIDGE typology*: Paleozoic limestones (n=10)
- *Lithology*: Sedimentary: carbonates (limestone, chalk) (n=10)
- *Deposition type*: Marine (n=10)
- *Age stratigraphy*: Paleozoic (n=10)
- *Aquifer type*: confined (n=1), unknown (n=9)
- *Flow media:* fractured (n=10)

- *Signs of anthropogenic influence*: no (n=10)
- *Recharge*: approximately <100 mm (n=10),
- *Hydraulic conductivity:* unknown (n=4), $1x10^{-7}$ m/s (n=3), $1x10^{-8}$ m/s (n=1), $1x10^{-9}$ m/s (n=2).

Table 3: Descriptive statistics for chemical variables in the VMM master dataset, covering the entire Flemish region (Figure 3, n=5497, 13,500 km^2)

	unit	***Min***	***Q10***	***Q25***	***Q50***	***Q75***	***Q90***	***Q95***	***max***	***IQR***	***MAD***	***NA***	***n***	***NA (%)***
pH	-	3.1	5.2	6.1	6.9	7.2	7.4	7.8	11.4	1.1	0.45	0	5497	0
T	°C	4.7	10.8	11.5	12	12.7	13.7	14.4	23.7	1.2	0.6	2	5495	0.04
Oxygen	mg/l	0.03	0.21	0.47	1.1	2.4	5.0	7.3	12.6	1.9	0.8	59	5438	1.07
EC	uScm	0.00	0.31	0.46	0.69	0.97	1.27	1.94	49	0.51	0.25	0	5497	0
Nitrite	mg/l	0.01	0.03	0.03	0.03	0.03	0.03	0.08	10.3	0	0	1	5496	0.02
Nitrate	mg/l	0.05	0.15	0.20	0.61	29	88	121	430	28.8	0.47	4	5493	0.07
P_tot	mg/l	-	-	-	-	-	-	-	-	-	-	5497	0	**100**
ortho_PO$_4$	mg/l	0.05	0.09	0.10	0.10	0.26	0.71	1.35	53	0.16	0.02	3	5494	0.06
TDS	mg/l	24	202	309	520	759	957	1113	24197	450	221	914	4583	16.63
F	µg/L	65	100	120	210	790	3456	5018	10000	670	110	4704	793	**85.57**
SO$_4$	mg/l	1.0	14.8	38	74	121	184	248	2600	83	40	1	5496	0.02
Na	mg/l	1.9	8.2	12.3	19.7	32	89	341	11000	19.6	8.6	0	5497	0
K	mg/l	0.24	1.1	1.95	3.85	9.1	20.5	33	455	7.2	2.4	1	5496	0.02
HCO$_3$	mg/l	0.60	8.5	49	233	398	522	636	3646	349	176	2	5495	0.04
Mg	mg/l	0.10	3.1	5.8	10.6	18	25.1	31	1600	11.9	5.6	0	5497	0
Ca	mg/l	0.28	14.9	34	82	145	185	212	2900	111	53	0	5497	0
Fe	µg/L	20	20	52	349	3578	15919	29118	195638	3526	329	0	5497	0
Mn	µg/L	10	10	24	110	298	585	858	7400	274	99	1	5496	0.02
B	µg/L	10	20	21	33	69	183	710	13000	48	13.2	56	5441	1.02
Al	µg/L	20	20	20	30	67	247	698	16000	47	10	527	4970	9.59
Cr	µg/L	1.0	1.0	1.0	1.3	2.1	3.9	5	83	1.1	0.26	57	5440	1.04
Ni	µg/L	1.0	3.1	4.0	5.0	6.2	18.5	37	1225	2.2	1	56	5441	1.02
Cu	µg/L	0.40	2.0	5.0	5.0	5.0	5	5.7	135	0	0	57	5440	1.04
Zn	µg/L	0.00	10	10	12.5	30	72	125	21759	20	3.45	55	5442	1.00
As	µg/L	0.50	2.0	2.0	2.81	5	7.2	11.8	1313	3	0.81	56	5441	1.02
Cd	µg/L	0.03	0.23	0.40	0.40	0.40	0.50	0.80	34	0	0	57	5440	1.04
Sb	µg/L	-	-	-	-	-	-	-	-	-	-	5497	0	**100**
Ba	µg/L	50	50	50	52	74	538	544	565	24	2	5454	43	**99.22**
Pb	µg/L	0.50	2.0	2.0	2.0	3.5	5	5	140	1.5	0	56	5441	1.02
U	µg/L	-	-	-	-	-	-	-	-	-	-	5497	0	**100**
Hg	µg/L	0.01	0.15	0.20	0.20	0.20	0.20	0.26	0.50	0	0	287	5210	5.22
Sr	µg/L	-	-	-	-	-	-	-	-	-	-	5497	0	**100**
Li	µg/L	-	-	-	-	-	-	-	-	-	-	5497	0	**100**

Table 4: Descriptive statistics for chemical variables in the GSI master dataset, covering the Ryewater area in Ireland (Figure 3, n=10, approx. 1 km^2)

	unit	min	Q10	Q25	median	Q75	Q90	Q95	max	IQR	MAD	NAs	n	NA (%)
pH	-	6.9	6.9	6.9	7.2	7.2	7.5	7.6	7.7	0.3	0.2	0	10	0
T	°C	10.3	10.3	10.4	10.6	10.7	10.9	10.9	10.9	0.3	0.16	0	10	0
Oxygen	mg/l	0.3	0.3	0.3	0.38	0.73	0.99	1.40	1.8	0.43	0.08	0	10	0
EC	uScm	5.6	5.7	5.9	6.6	7.5	9.7	9.9	10.1	1.6	0.80	0	10	0
Alkalinity (as $CaCO_3$*)*	mg/l	235	251	282	309	354	361	366	372	72	40	0	10	0
Hardness_tot	mg/l	176	208	291	342	381	413	433	454	90	53	0	10	0
Ammonium	mg/l	0.03	0.03	0.03	0.06	0.08	0.18	0.27	0.35	0.05	0.03	0	10	0
Nitrite	mg/l	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0	0	0	10	0
Nitrate	mg/l	0.53	0.53	0.53	0.55	0.84	2.61	8.28	14.0	0.31	0.02	0	10	0
P_tot	mg/l	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0	0	0	10	0
TOC	mg/l	1.5	1.5	1.5	1.5	1.5	1.70	2.25	2.8	0	0	0	10	0
SiO_2	mg/l	8.1	9.8	10.2	10.9	13.5	18.1	18.9	19.6	3.30	0.93	0	10	0
Cl	mg/l	16	17.8	19.5	25	42	82	93	105	22.7	6.4	0	10	0
F	mg/l	0.17	0.20	0.21	0.36	0.47	0.95	1.18	1.4	0.26	0.15	0	10	0
SO_4	mg/l	23	26	28	34	38	53	66	80	10	6.1	0	10	0
Na	mg/l	13.3	13.9	17.8	20.6	45	53	59	65	26.7	6.9	0	10	0
K	mg/l	0.49	0.58	1.40	2.05	3.2	3.6	4.6	5.6	1.8	1.01	0	10	0
Mg	mg/l	6.8	9.5	12.2	17	19.7	20.3	22	23	7.4	3.0	0	10	0
Ca	mg/l	28	52	78	98	132	151	157	164	54	33	0	10	0
Fe	µg/L	10	12.2	18	85	274	983	1736	2490	256	74	0	10	0
Mn	µg/L	5	7.61	29	110	171	363	512	660	142	86	0	10	0
B	µg/L	22	25.3	32	50	112	142	197	253	80	22	0	10	0
Al	µg/L	5	5	5	5	6.9	8.3	9.2	10	1.9	0	0	10	0
Cr	µg/L	0.85	0.99	1	1	1	1	1	1	0	0	0	10	0
Ni	µg/L	0.7	0.97	1	1	1	1.26	1.50	1.75	0	0	0	10	0
Cu	µg/L	0.9	0.99	1	1	1	1	1	1	0	0	0	10	0
Zn	µg/L	1	1.05	1.28	1.63	2.9	4.1	8.0	12	1.58	0.6	0	10	0
As	µg/L	0.5	0.55	0.57	1.58	4.9	5.9	6.5	7.2	4.32	1.05	0	10	0
Cd	µg/L	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0	0	0	10	0
Sb	µg/L	0.5	0.5	0.5	0.75	1	1	1	1	0.5	0.25	0	10	0
Ba	µg/L	34	40	46	70	82	121	126	130	36	20	0	10	0
Pb	µg/L	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0	0	0	10	0
U	µg/L	0.6	0.96	1	1	1.45	1.66	1.68	1.7	0.45	0.15	0	10	0

	unit	***min***	***Q10***	***Q25***	***median***	***Q75***	***Q90***	***Q95***	***max***	***IQR***	***MAD***	***NAs***	***n***	***NA (%)***
Hg	µg/L	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0	0	0	10	0
Co	µg/L	0.5	0.73	1	1	1	1	1	1	0	0	0	10	0
Mo	µg/L	0.5	0.95	1	1	1.23	2.29	3.34	4.4	0.26	0	0	10	0
Sr	µg/L	385	435	475	761	1120	3135	3293	3450	645	307	0	10	0
Ag	µg/L	0	0	0.31	0.5	0.5	0.51	0.56	0.6	0.19	0	0	10	0
Be	µg/L	0.5	0.5	0.81	1	1	1	1	1	0.19	0	0	10	0

4 EVALUATION OF BRIDGE AQUIFER TYPOLOGY AND THE HOVER WP3-2 LITHOLOGY CLASSIFICATION

4.1 Objectives

In this part of the report, we are testing if the BRIDGE aquifer typology and the Lithology classification from the Task 3-2 Questionnaire can be used for defining geological/lithological water families with different trace element concentrations. The BRIDGE typology was presented in detail in Chapter 1, while the Lithology classification was formulated during the workshop (Feb. 2019 in Denmark) with Task 3-3 lead (BRGM) and is presented in Appendix 3. We further refer to this classification as HOVER-Lithology.

Our method evaluation and development is limited by the available master datasets. We have excluded the GSI dataset from our analysis because it does not represent sufficient variation in the geological and hydrogeological variables (see Chapter 3). Thus, we focus only on the VMM master dataset covering the Flemish region (n=5497, approx. 13,500 km^2, Figure 3).

4.2 Statistical methods

The distributions of chemical concentrations in different groups based on the BRIDGE typology and the HOVER-Lithology classification was examined based on boxplots and empirical cumulative density function (ECDF) plots (see Appendix 1).

To formally test for significant differences (significance level α=0.05) in the chemical concentrations found in the different types of aquifers, we used the non-parametric statistical tests Kruskal-Wallis Rank Sum Test (KW) and Pairwise Wilcoxon Rank Sum Tests (PW). KW assesses the null hypothesis H_0 that the groups (BRIDGE or Lithology) are sampled from populations with identical distributions. The alternative hypothesis (H_1) is that at least one of the groups is from a population with a different distribution. This test does not provide information on which specific group(s) is/are different. Thus, for pairwise comparison between groups, we used PW. Because we are testing for multiple groups, we used p-value-adjustment that controls the false discovery rate (used method: "fdr", see R function documentation for details). The test provides information on which specific group is significantly different from another group in the dataset (H_1).

All statistical summaries and tests were performed in R version 3.6.0 (2019-04-26) aka “Planting of a Tree”. The KW test was done with “kruskal.test” function and the PW tests was done with “pairwise.wilcox.test” function, both from the R package “stats” v.3.6.0.

Before the KW and PW tests were performed on the VMM master dataset, the dataset was cleaned from variables without any observations (100% NAs) or with more than 80% NAs, which resulted in excluding P_tot, F, Sb, Ba, U, Sr, Li from the VMM master dataset.

Further, when performing the tests for BRIDGE categories, we excluded the observations for "Paleozoic limestones" (n=3), "Glacial sand and gravel deposits" (n=4), and "Marls and clays" (n=8) from the dataset due to the low number of observations. Consequently, the master dataset was left with 5482 observations and 40 variables. However, when the tests were performed for the HOVER-Lithology groups, there was no need to exclude additional observations from the master dataset; all groups had at least 80 observations. Thus, the dataset used for statistical test by HOVER-Lithology has 5497 observations and 40 variables. Twenty-two of the 40 available variables were used for the statistical tests, namely: Nitrite, Nitrate, ortho_PO_4, TDS, SO_4, Na, K, HCO_3, Mg, Ca, Fe, Mn, B, Al, Cr, Ni, Cu, Zn, As, Cd, Pb, and Hg.

The BRIDGE groups we used for both KW and WR tests are: “Fluviatile deposits of major streams”, “Marine deposits”, “Others”. The HOVER-Lithology groups we used for both KW and PW tests are: “Others”, “Sedimentary: other”, “Sedimentary: clays and/or marls”, “Sedimentary: sand”, “Sedimentary: carbonates (limestone, chalk)”, “Sedimentary: gravel”, and “Metamorphic rocks”.

4.3 Results and Discussion

4.3.1 BRIDGE typology

The KW tests showed that there was a significant (α=0.05) difference among the three BRIDGE groups for all of the tested chemical elements (n=22), except for nitrate. In order to assess which specific groups are different from each other, we used the WR tests and the results are summarized and presented in Table 5. Next to that, we also examined visually the elemental distribution in the three BRIDGE typologies on the boxplots and ECDF plots (Appendix 1).

Table 5 Pairwise Wilcoxon Rank Sum Test results (grouping by BRIDGE classification); NOTE: different letters means the groups are significantly different from each other, i.e. if letters are shared between groups, then the groups are not significantly different at α=0.05

	Chemical elements	*Fluviatile deposits of major streams*	*Marine deposits*	*Others*
1	Nitrite	a	b	a
2	Nitrate	a	a	a
3	ortho_PO_4	a	b	c
4	TDS	a	b	c
5	SO_4	a	a	b
6	Na	a	a	b
7	K	a	b	a
8	HCO_3	a	b	c
9	Mg	a	b	c
10	Ca	a	b	c
11	Fe	a	b	c
12	Mn	a	b	a
13	B	a	b	c
14	Al	a	b	b
15	Cr	a	b	b
16	Ni	a	b	c
17	Cu	a	b	c
18	Zn	a	b	a, b
19	As	a	b	b
20	Cd	a	b	b
21	Pb	a	a	b
22	Hg	a	b	b

Table 5 revealed that the three BRIDGE typologies (Fluviatile deposits of major streams, Marine deposits, and Others) are all significantly different from each other with respect to the major elements ortho-PO_4, TDS, HCO_3, Mg, Ca, and Fe and the trace elements B, Ni, Cu. However, similar to the KW test, the WR showed that there is no difference with respect to NO_3^-. Additionally, there was no statistical difference (α=0.05) between the pairs:

- *Fluviatile deposits of major streams* and *Others* with respect to nitrite, K, Mn, and Zn;
- *Fluviatile deposits of major streams* and *Marine deposits* with respect to SO4, Na, and Pb;
- *Marine deposits* and *Others* with respect to Al, Cr, Zn, As, Cd, and Hg.

These results show that BRIDGE typology is not consistent in distinguishing between aquifers with different trace element concentrations, based on the VMM master dataset. It should be noted that here we can only evaluate the three represented BRIDGE typologies: Fluviatile deposits of major streams, Marine deposits, and Others. This test should be performed again when a pan-European dataset is compiled, containing the full range of BRIDGE typologies.

4.3.2 HOVER-Lithology classification

KW test showed that there was a significant (α=0.05) difference among the HOVER-Lithology groups for all of the tested chemical elements (n=22). Results from the PW test are summarized and presented in Table 6. Next to that, we also examined visually the elemental distribution in the seven HOVER-Lithology classes on the boxplots and ECDF plots (Appendix 1).

Table 6: Pairwise Wilcoxon Rank Sum Test results (grouping by HOVER-Lithology); NOTE: different letters means the groups are significantly different from each other, i.e. if letters are shared between groups, then the groups are not significantly different at α=0.05

Element	*Metamorphic rocks*	*Others*	*Sedimentary: carbonates (limestone, chalk)*	*Sedimentary: clays and/or marls*	*Sedimentary: gravel*	*Sedimentary: other*	*Sedimentary: sand*
Nitrite	a	b	cd	c	C	d	d
Nitrate	a	b	b	c	B	b	bc
ortho_PO4	ab	a	cd	ab	C	a	bd
TDS	abc	a	d	a	E	bd	c
SO4	abcd	a	e	b	cd	ac	d
Na	a	b	c	d	E	f	g
K	a	b	c	d	D	e	e
HCO3	a	b	ac	d	E	c	d
Mg	a	b	c	c	D	c	e
Ca	a	b	c	d	e	b	f
Fe	a	b	c	bd	bd	e	d
Mn	a	b	a	bc	c	d	d
B	a	b	c	d	e	b	f
Al	a	b	c	b	c	b	b
Cr	a	b	a	c	bc	a	b
Ni	ab	ac	d	e	e	c	b
Cu	a	b	c	b	d	e	e
Zn	a	b	c	bd	d	c	e
As	a	abc	d	bc	abc	b	ac
Cd	a	b	c	bd	e	cd	bd
Pb	abc	d	d	ad	b	a	c
Hg	abc	d	a	bd	ac	a	bc

Table 6 revealed that all seven HOVER-Lithology classes are significantly different from each other for only Na. However, this classification does a better job at differentiating some of the lithological groups based on major and trace elements than the three BRIDGE typologies. This is evident from the letter combinations in Table 6: the same way as seven letters signify that all seven lithological classes are different, we can also see that there are multiple groups of significantly different lithologies forming based on specific chemical element, e.g. there are:

- Six significantly different groups for Ca and B
- Five for SO4, K, Mg, Fe, Cu, and Zn
- Four for nitrite, ortho-PO4, TDS, HCO3, Mn, As, Cd, Pb, and Hg
- Three for nitrate, Al, Cr, and Ni

4.4 Conclusion

To summarize, for the VMM dataset, the HOVER-Lithology classes (Appendix 3) delineate better between water families with regards to these trace elements than BRIDGE, but do not perform consistently across all trace elements (i.e. from most to least suited: B > Cu, Zn > Mn, As, Cd, Pb, Hg > Al, Cr, Ni).

We conclude that:

1. Neither methodology (BRIDGE typology and HOVER-Lithology classification) perform consistently well with respect to trace elements in groundwater; however, we also see potential in modifying these two geological/lithological classification systems.
2. There is need to further examine possibilities to build upon the BRIDGE typology, so it is applicable not only to major ions, but also to trace elements. A potential improvement is to combine it with the HOVER-Lithology classification.
3. Geochemical processes are important to trace element variation in groundwater (see Chapter 2), but are not currently reflected in the BRIDGE typology. Another potential improvement of BRIDGE is to include redox and pH conditions.

These three points are further discussed in the next chapter, where we propose a workflow for defining the HOVER WP3 water families.

5 DEFINING HOVER WP3 GEOLOGICAL/LITHOLOGICAL WATER FAMILIES BY EXTENDING BRIDGE WITH ADDITIONAL VARIABLES

5.1 Proposed methodology

Task 3.2 of Work Package 3 is about examining and proposing a new general methodology that can relate trace element concentrations to lithological/geological water families. Both “trace elements” and “lithological/geological families” are open to interpretation, so after we examined the literature (Chapter 2) and the VMM master dataset in (Chapter 3 and 4), we decided to target a number of specific trace elements in the workflow demonstration. We selected four trace elements (As, Mn, Ni, Zn) that had different distributions (Appendix 1), but also performed differently in the KW and PW tests. These trace elements had also relatively few censored values (< detection limit), and are possibly controlled by different geochemical processes.

In Chapter 4, we demonstrated that BRIDGE typology or the HOVER-Lithology classification alone are insufficient for distinguishing between water families with different concentration levels of trace elements. In this Chapter, we are testing if extending the BRIDGE typology with additional variables leads to a clearer definition of water families with respect to the selected trace elements.

For this part of the report, we work with a sub-set of the VMM master dataset: the four trace elements (As, Mn, Ni, Zn) and the 5 categorical variables we define next. This sub-set was cleaned from the missing values (n=56), so for each ID there is a single value for As, Mn, Ni, Zn. No other data pre-treatment has been done. We are using the VMM dataset as a starting point for developing a harmonized methodology and to demonstrate how this workflow can be implemented. We have intentionally chosen a simplistic approach to this complex issue with a foresight of applying it on pan-European scale. It is important to recognize the challenges of working on this scale: e.g. different data availability, different conventions in working with the data, incl. used programs and methodologies, and highly variable geological and geochemical conditions.

Thus, in this Chapter, we test the potential of extending the BRIDGE typology with:

1. **HOVER-Lithology** – Ten different lithologies represented throughout Europe have been selected at the workshop between GEUS and BRGM in February 2019 (see Appendix 3). These lithology classes are combined with the BRIDGE typologies (n=3), resulting in 12 new groups (Table 7).

Table 7: BRIDGE and HOVER-Lithology combination and number of samples in each group (see Table 18 and Appendix 2 for statistical summary)

BRIDGE	*HOVER-Lithology*	*n*
Fluviatile deposits of major streams	Sedimentary: gravel	222
	Sedimentary: other	191
	Sedimentary: sand	140
Marine deposits	Others	159
	Sedimentary: carbonates (limestone, chalk)	81
	Sedimentary: clays and/or marls	244
	Sedimentary: other	324
	Sedimentary: sand	1689
Others	Metamorphic rocks	77
	Others	1821
	Sedimentary: other	458
	Sedimentary: sand	20

2. **Redox water types** – even though Eh is included in most suits of geochemical analysis, its interpretation is not straightforward, so we decided to use a different approach of defining redox water types. This method is widely applied in Denmark and is included in the national guidelines for the groundwater mapping programs (Hansen & Thorling, 2018). It is based on the concept of redox zone transition in groundwater (i.e., on the redox reactions occurring within it) and their effect on the concentrations of few redox-sensitive major ions. The classification uses data on NO_3, Fe, SO_4, and O_2 and defines the following classes (see also Table 8 and Figure 4):
    a. **A type**: Oxic water (Oxic zone)
    b. **B type**: Nitrate-reducing anoxic water (Anoxic zone)
    c. **C type**: Weakly reduced water (Fe and SO_4 zone); in the original methodology the C type is split into C_1 and C_2 (based on SO_4 levels), but for the purposes of this report we are omitting this step.
    d. **D type**: Strongly reduced (CH_4 and H_2S zone)
    e. **X type**: not classified, according to the algorithm; It may indicate that there is mixing of different water types. In the original method, there are two different groups for such samples, but for the purposes of this report, we have joined them.

    We further refer to the presented redox water types as HOVER-Redox classification. Each of the BRIDGE categories (n=3) was split into sub-categories based on the HOVER-Redox classification (A, B, C, D, X), resulting in 15 groups of observations (see Table 19 and Appendix 2 for statistical summary and number of samples).

3. **Acid/Base water types** – pH is another chemical parameter which is widely available. As a first attempt at extending BRIDGE with pH, we decided to test two classifications with different number of groups, in order to decide how to define pH-water families:
    a. **3 groups**, based on the classic definition:
        i. Acidic: $pH<7$
        ii. Basic: $pH>7$
        iii. Neutral: $pH=7$
    b. **5 groups,** combining the classic definition and the drinking water limits (DWL) given in EU Directive 98/83/EC (Reimann & Birke, 2010):
        iv. Acidic, below DWL: $pH <6.5$
        v. Acidic: $pH \in [6.5, 7)$
        vi. Neutral: $pH=7$
        vii. Basic: $pH \in (7, 9.5]$
        viii. Basic, above DWL: $pH>9.5$

    We further refer to the presented pH water types as HOVER-pH classification. Similarly, the BRIDGE categories were split into sub-categories based on 3a. and 3b. The resulting groups can be found in Table 20 and Table 21 (Appendix 2).

Table 8: Definition of HOVER-Redox types used in this report (modified from Hansen & Thorling, 2018)

Redox type	*Redox condition*	*NO_3^-* mg/l	*Fe* mg/l	*O_2* mg/l	*SO_4^{2+}* mg/l
A	Oxic water	>1	<0.2	≥1	-
B	Nitrate-reducing anoxic water	>1	<0.2	<1	-
C	Weakly reduced water	≤1	≥0.2	-	≥20
D	Strongly reduced	≤1	≥0.2	-	<20
X	Unclassified samples				

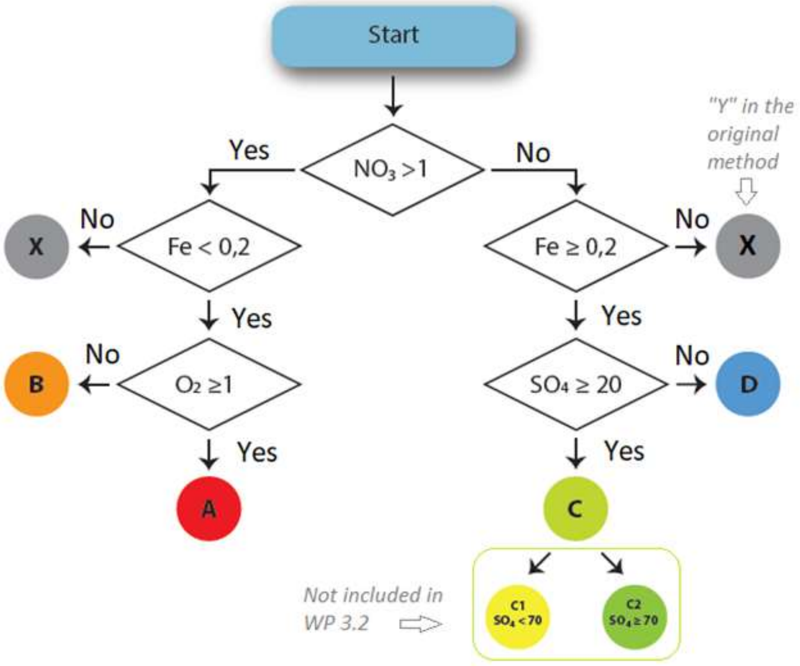

Figure 4: Flowchart of original method and the simplifications introduced in defining the HOVER-redox types for this report (modified from Hansen and Thorling, 2018)

5.2 HOVER Redox-pH water families

Before looking at the results of the extended BRIDGE in relation to the selected trace elements, we examined the HOVER-pH and HOVER-Redox categories and how As, Mn, Ni, and Zn concentrations are distributed throughout these groups (Figure 5).

Figure 5 provides a fast overview of concentrations (low/high) based on the HOVER-redox and HOVER-pH water types, while at the same time visualizing the sample density within each group (each dot represents a unique ID).

Such types of visualization can help with the initial assessment of the variable importance for extending the BRIDGE methodology. For example, Figure 5 reveals that there are very few samples with neutral pH (by definition: only if pH=7). The samples are also unevenly distributed within the HOVER-redox water types: A and C types have generally more samples than B and D. By looking at the color variation for each element, we see that:

- The HOVER-redox and HOVER-pH grouping does not distinguish well high from low As concentrations, but we can find the highest As concentrations in acidic and weakly reduced waters (C type).
- Most of the high Mn concentrations are in weakly reduced waters (both in acidic and basic waters), but the lowest concentrations seem to be found in basic and oxidized (A type) waters.
- Higher Ni and Zn concentrations are found in acidic waters of all redox categories, but for Zn the contrast between high and low concentrations is stronger.

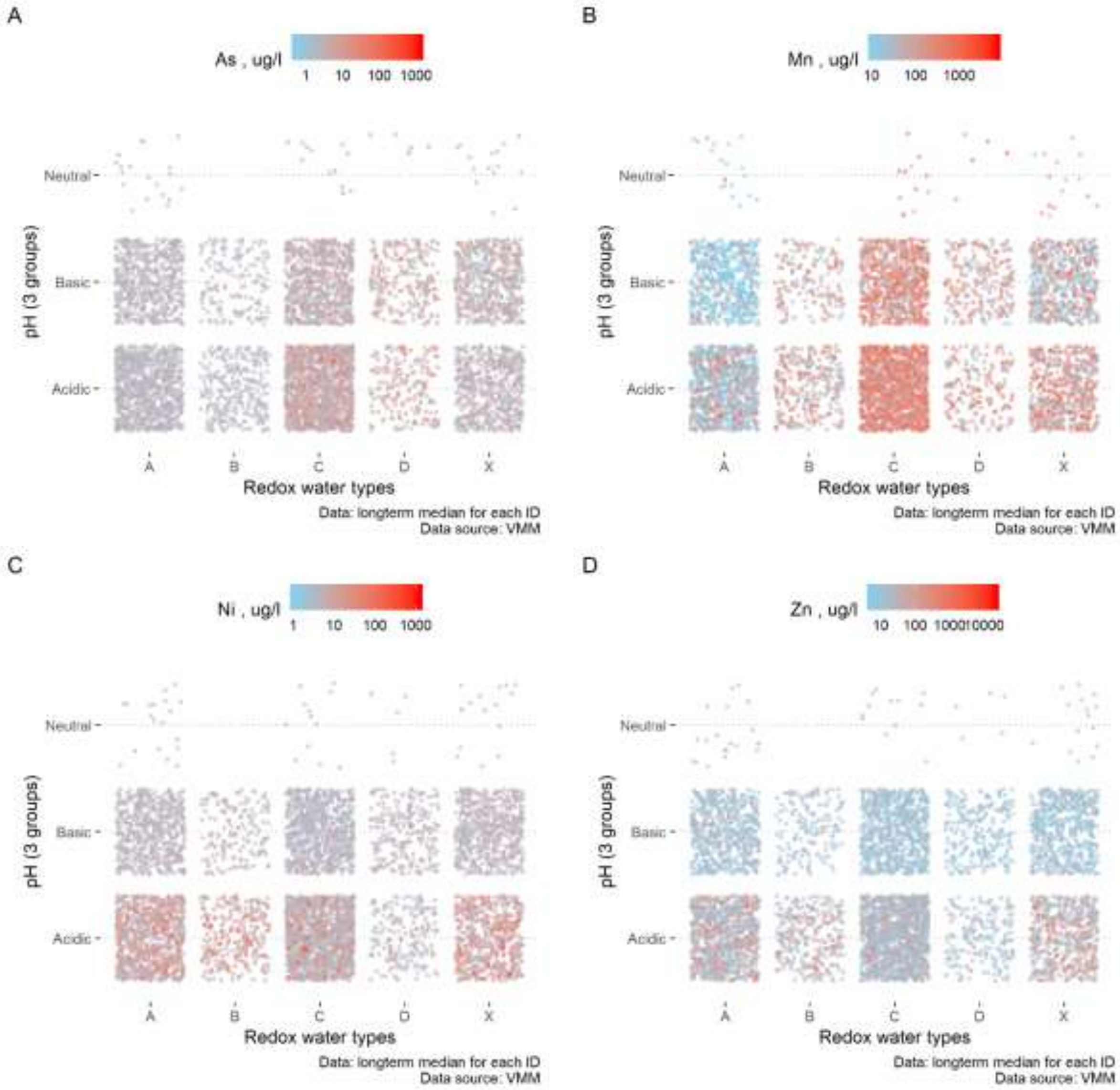

Figure 5: Sample grouping by HOVER-Redox and HOVER-pH water types; As concentrations (A), Mn concentrations (B), Ni concentrations (C), and Zn concentrations (D) are shown with a log-transformed color palette. The palette transitions smoothly from low (blue) into high (red) concentrations. The palette was log-transformed for visualization purposes, the boundaries are relative to the concentration range of each element.

Traditional statistical summary tables (see Appendix 2) add precision to our initial visual screening and minimize the subjectivity of figure interpretations. We use robust indicators, e.g. median instead of mean, median absolute deviation (MAD) instead of standard deviation (SD), and 75th and/or 95th percentiles (Q75 & Q95) instead of the maximum value. That way we can minimize the negative effect of extreme outliers or potential erroneous values on the summary statistics. When working with large and complex datasets, however, it becomes very challenging to identify patterns (e.g. groups with high/low values) in such tables. A way to simplify further the results is to rank the water types based on the median ±MAD, Q75, and Q95 and to prepare a "Top 3" overview table. For example, Table 9 shows the "Top 3" based on the HOVER Redox-pH water families (same data as in Table 17 and Figure 5). The water families are abbreviated, where the 1st letter is for the HOVER-Redox water type, 2nd letter is for the HOVER-pH type (A is for Acid, B for Basic). Additionally, different colors are associated with each family to assist with recognizing general patterns.

Table 9: "Top 3" of HOVER Redox-pH water families with respect to As, Mn, Ni, Zn concentrations, evaluated based on median (Med), 75th percentile (Q75), and 95th percentile (Q95). The color-coding and the water family abbreviations are provided in the legend below the table; this ranking is based on the statistical summaries from Table 17.

Top 3	***As***			***Mn***			***Ni***			***Zn***		
	Med	Q75	Q95	Med	Q75	Q95	Med	Q75	Q95	Med	Q75	Q95
1	DA	DA	DA	CA	CA	CA	BA	BA	XA	XA	XA	XA
2	DB	CA	DB	CB	CB	XA	XA	XA	BA	AA	AA	BA
3	CA	DB	CA	XA	XA	DA	AA	AA	AA	BA	BA	AA

Legend HOVER Redox-pH water families	AA	AB	BA	BB	CA	CB	DA	DB	XA	XB
	1st letter is for the Redox water types: A, B, C, D, X									
	2nd letter is for pH types: Acid, Basic									

The key points, based on Table 9 are:

- the highest As concentrations are found in both strongly and weakly reduced waters (D > C, D,C >> A, B, X) independent of pH conditions
- the highest Mn concentrations are found mostly in acidic and weakly reduced or mixed type of waters (C>>D>B>>A)
- the highest Ni and Zn concentrations are found in acidic waters with oxic/anoxic or mixed redox conditions.

We have hypothesized that by adding these two variables (HOVER-pH and HOVER-Redox) or HOVER-Lithology to the BRIDGE typology, we may be able to delineate lithological/geological water families with high trace element concentrations. However, a major challenge to expanding the BRIDGE typology in a meaningful way is the use of "trace elements" as a collective term. The overview presented in Table 9 illustrates the different effect and importance these geochemically relevant variables (redox and pH) have. In future work on defining lithological/geological water families on pan-European scale, it would be important to group the trace elements based on their geochemical behavior and to target them separately when defining water families.

5.3 Lithological/Geological water families based on extended BRIDGE typology

An overview of the results of the extended BRIDGE typology are shown here as “Top 3” tables (see the HOVER redox-pH water families, Table 9). The standard statistical summary tables, boxplots, and ECDF plots are also provided in Appendix 2.

Table 10: “Top 3” of BRIDGE-HOVER Lithology water families with respect to As, Mn, Ni, and Zn concentrations; the color-coding and the water family abbreviations are provided in the legend below the table; this ranking is based on the statistical summaries from Table 18.

Top3	*As*			*Mn*			*Ni*			*Zn*		
	Med	Q75	Q95	Med	Q75	Q95	Med	Q75	Q95	Med	Q75	Q95
1	FS	XS	FS	FO	FO	FO	MC	FG	FS	MO	XS	FS
2	XS	FS	MO	MO	XO	XO	-	MO	FG	XS	FG	FG
3	MO	MO	XS	XO	MO	MO	-	XS	MO	MC	FS*	XS

Legend BRIDGE & HOVER Lithology	FG	FS	FO	MC	MO	XS	XO	*MO = FS (Zn)
	1st letter: BRIDGE (Fluviatile, Marine, Other: X)							
	2nd letter: HOVER-Lithology (Gravel, Sand, Clay, Other)							

Key points, based on BRIDGE-HOVER Lithology water families (Table 10):

- the highest As concentrations are dominating in sandy and other lithology, deposited both by fluvial, marine, or other processes
- the highest Mn concentrations are found in other sedimentary lithology (different from gravel, sand, or clay), deposited both by fluvial, marine, or other processes
- the median Ni concentration is not a good indicator for difference, since all BRIDGE-Lithology families have very similar median Ni with slight enrichment in the marine clays/marls (MC family). Based on the Q75 and Q95, fluvial gravels and sands and other marine deposits have highest Ni
- for Zn, Q75 and Q95 show different results from the median; if we look at the medians the high Zn concentrations are in marine clays and other than sand of gravel lithology, but if we look at Q75 and Q95, then fluvial and other sands and gravels (not marine ones) dominate the top 3.

Table 11: “Top 3” of BRIDGE and HOVER-Redox water families (legend below the table); this ranking is based on the statistical summaries from Table 19.

Top 3	*As*			*Mn*			*Ni*			*Zn*		
	Med	Q75	Q95	Med	Q75	Q95	Med	Q75	Q95	Med	Q75	Q95
1	FD	XD	MD	XC	XC	XC	FB	FX	FX	FA	FX	FX
2	MD	MD	FD	FC	FC	XD	FX	FB	FB	FX	FA	FA
3	FC	FC	XD	MC	XD	FX	MB	FA	FA	XA	FB	FB

Legend BRIDGE & HOVER-Redox	FA	FB	FC	FD	FX	1st letter: BRIDGE (Fluviatile, Marine, Other: X)
		MB	MC	MD		
	XA		XC	XD		2nd letter: HOVER-Redox (A,B,C,D,X)

Key points, based on the BRIDGE and HOVER-Redox water families (Table 11):

- the highest As concentrations are found in strongly reduced sediments of all 3 types depositional environments (fluvial, marine, other);
- the highest Mn concentrations are found in weakly reduced sediments of other depositional type, high concentrations can be found also in fluvial and marine weakly reduced sediment as well as in strongly reduced other depositional types and in fluvial mixed redox type;
- the highest Ni concnetrations are found in anoxic fluvial and other deposits followed by the oxic fluvial deposits.
- The highest Zn concentrations are found in oxic and mixed redox type fluvial deposits, followed by anoxic fluvial deposits in third position.

Table 12: “Top 3” of BRIDGE and HOVER-pH water families (legend below the table); this ranking is based on the statistical summaries from Table 20.

Top 3	As			Mn			Ni			Zn		
	Med	Q75	Q95	Med	Q75	Q95	Med	Q75	Q95	Med	Q75	Q95
1	FA	-	FA	FB	FB	XA	-	FA	FA	XA	FA	FA
2	-	-	XA	XA	XA	FB	-	MA	MA	MA	XA	XA
3	-	-	MA	FA	XB	MA	-	XA	XA	FA	MA	MA

Legend BRIDGE & HOVER-pH		FA	FB	MA	MB	XA	XB	
	1st letter: BRIDGE (Fluviatile, Marine, Other: X)							
	2nd letter: HOVER-pH (Acid, Base), Neutral excluded							

Key points, based on BRIDGE and HOVER-pH families (Table 12):

- Median and Q75 are not good indicators for determining BRIDGE-pH water families with high As concentrations; based on Q95, acidic conditions for the 3 depositional environments favor high As concentrations.
- High Mn concentrations are found in mostly fluvial deposits with pH>7 and in other deposits with pH<7
- Similarly to As, the median is not a good indicator; if using only Q75 and Q95, the highest concentrations are found in only acidic environments (Fluvial > Marine > Other)
- For Zn, the highest concentrations are also found in acidic environments, but Fluvial > Other > Marine.

In the following chapter, we present a proposal for combining BRIDGE typology, HOVER-Lithology, HOVER-redox, and HOVER-pH together and a workflow for applying this methodology on a pan-European dataset.

6 PERSPECTIVES AND PROPOSED WORKFLOW

From the tested extended BRIDGE versions, BRIDGE and HOVER-pH seems to be the least suited for determining water families with high concentrations of trace elements, based on the VMM sub-set (As, Mn, Ni, Zn) and our definition of pH classes, which we propose to redefine for the pan-European assessment. BRIDGE and HOVER-pH alone are insufficient to represent the complex hydrogeological and geochemical conditions leading to elevated concentrations of these trace elements. However, a promising future direction for defining geological/lithological classes with high trace elements is to combine the BRIDGE-HOVER Lithology water families with a simplification/modification of the HOVER-pH and HOVER-Redox families (Table 13). It is, however, necessary to test this method proposal with a pan-European dataset, so most of the BRIDGE and HOVER lithology classes are represented (Table 14).

The pan-European redox map that is currently under production as part of WP5 might be used in the HOVER-Redox classification (see Table 13).

Table 13: Proposed modification/simplification of HOVER-pH and HOVER-Redox classes

HOVER-pH (n=3)	***HOVER-Redox (n=3)***
Acidic ($pH < 7$)	Oxic or Anoxic (A, B redox types)
Neutral ($pH \in [7, 7.5]$)	Weakly or Strongly reduced (C, D redox types)
Basic ($pH > 7.5$)	Mixed (X redox type)

Table 14: List of BRIDGE and HOVER lithology classes. The underlined classes are represented in the VMM master dataset;

BRIDGE *(n=17)*	***HOVER Lithology*** *(n=10)*
Karstic limestones	Sedimentary: sand
Limestones and interbedded silicatic/carbonate-rocks	Sedimentary: gravel
Limestones of mountainous areas	Sedimentary: carbonates (limestone, chalk)
Paleozoic limestones	Sedimentary: clays and/or marls
Chalk	Sedimentary: other
Volcanic rocks	Volcanic rocks
Crystalline rocks	Crystalline bedrock
Schists and shales	Metamorphic rocks
Sands with saline/brackish water	Others
Glacial sand and gravel deposits	Unknown
Fluviatile deposits of major streams	
Marine deposits	
Triassic sandstones	
Sandstones and silicatic alternating sequences	
Marls and clays	
Others	
Unknown	

The new geological/lithological families can be defined by combining Table 13 and Table 14 classes, merging the BRIDGE & HOVER Lithology (so there is no redundancy) and abbreviating, e.g. Table 15.

Table 15: Example of HOVER WP3 water family labelling, where KL is for (BRIDGE & HOVER Lithology), B is for Basic, R for reduced

Classification for sampling location ID 123	*HOVER WP3 water family*
BRIDGE: Karstic limestones **HOVER-Lithology**: Sedimentary: carbonates (limestone, chalk) **HOVER-pH**: Basic; **HOVER-Redox**: Reduced	**KL-B-R**

We propose a suitable workflow for defining HOVER WP3 geological/lithological water families with high concentrations of trace elements in Table 16.

Table 16: Workflow proposal for defining the HOVER WP3 geological/lithological water families

Step	*What*	*Who*
Data preparation	1. Extract data from national databases	HOVER WP3 partners
	2. Quality control the data - assess and exclude chemical analysis based on used laboratory method (too imprecise, inappropriate detection limit) or date (too old)	
	3. Detection limit handling: - there is need to harmonize the treatment of data below detection limits	
	4. Aggregation - calculate long-term median for each ID, so the dataset is a table with each row representing single sampling point, and each column representing a median concentration for the selected period	
	5. Classification - use the supplied classification lists for BRIDGE, Lithology, etc. to add the categorical variables to the dataset	
Descriptive statistics	6. Overview the pan-EU dataset - prepare tables, boxplots, histograms, ECDF plots etc. to get familiar with the dataset	HOVER WP leader
	7. Select target trace element or groups of elements - Preferably the target element(s) should have similar origin and geochemical behavior. - PCA or cluster analysis may help identifying the target elements - Another option is to combine expert knowledge and specific interests by HOVER partners	HOVER partners and HOVER WP leader
HOVER WP3 geological/ lithological water families	8. Extended BRIDGE - formulate the HOVER water family classes (see Table 13, Table 14, and Table 15 for an example) - group the data by the HOVER water families - calculate median, MAD, Q75, and Q95 - rank grouped data by median, Q75, and Q95 - prepare “Top 3” overview to find out which water families are having high concentrations of the target elements - evaluate results with HOVER partners.	HOVER WP leader
	9. Evaluate against alternative approaches, e.g. machine learning approaches	

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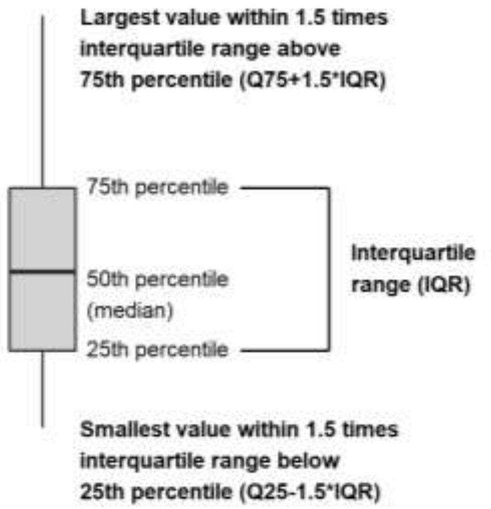
APPENDIX 1 – MAJOR AND TRACE ELEMENT CONCENTRATIONS IN GROUNDWATER GROUPED BY BRIDGE AQUIFER TYPOLOGY OR HOVER LITHOLOGY

Figure Notes:

- All data points are plotted below the boxplot with jitter added to the x coordinate only; the color scheme is same as for the boxplots (see below);
- Boxplot outliers have been suppressed, because the data points are already displayed;
- The color scheme of the empirical cumulative density function (ECDF) plots is the same as for the boxplot (see below);
- The dotted grey line denotes element-specific water action values or guide values for drinking water, according to EU directive 98/83/EC.
- Number of data points in each group differs (see below)
- The group labels were abbreviated to improve readability (see below)

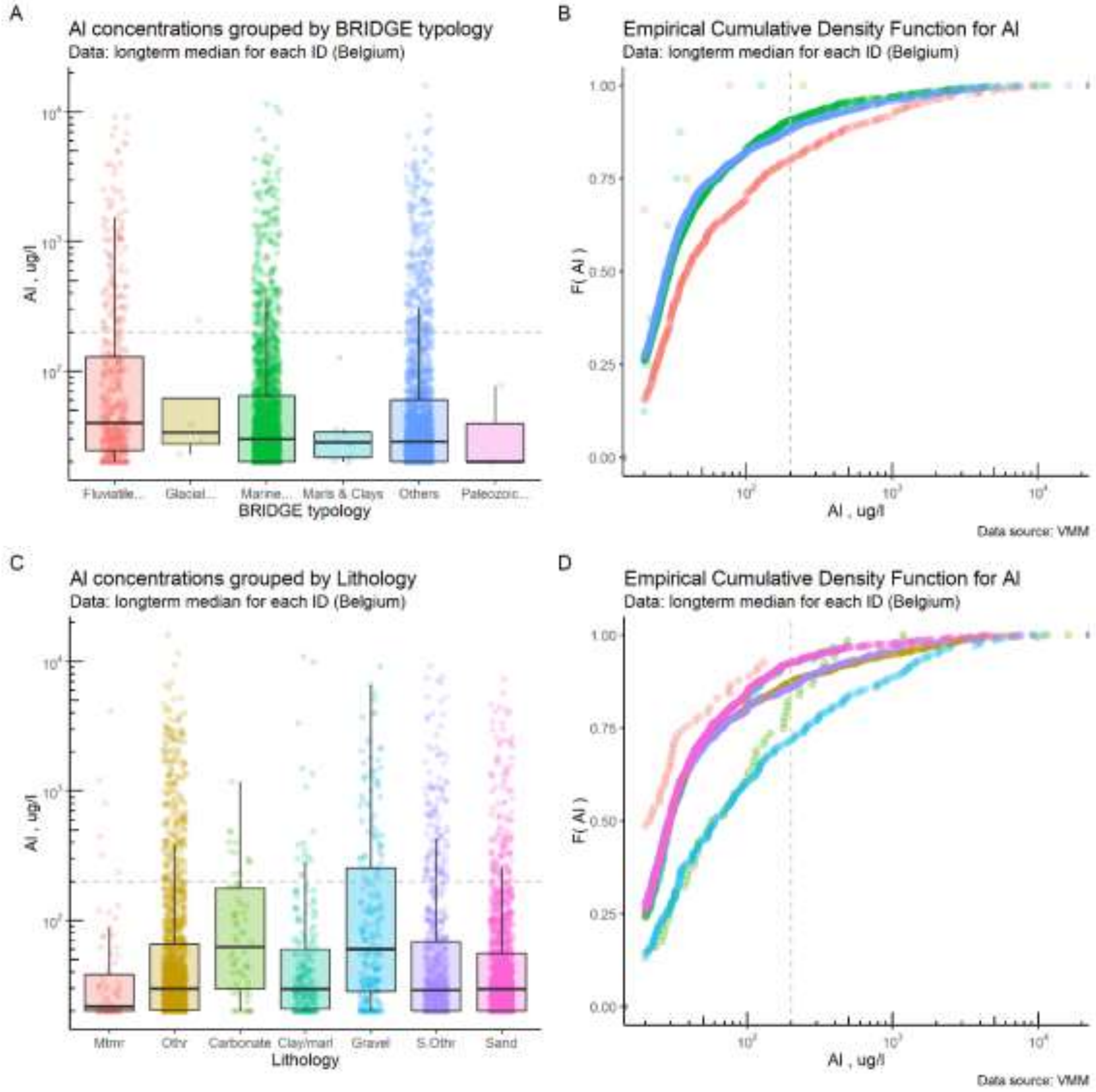


Abbreviations & number of data points (n), BRIDGE:

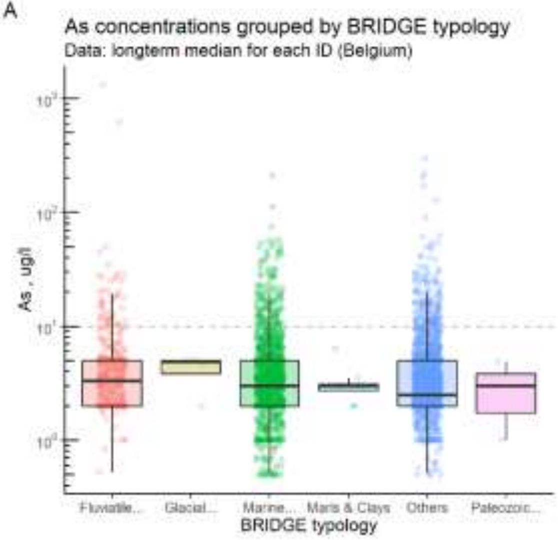
- *"Fluviatile…"* - Fluviatile deposits of major streams (n=569)
- *"Glacial…"* - Glacial sand and gravel deposits (n=4)
- *"Marine…"* - Marine deposits (n=2523)
- Marls and clays (n=8)
- Others (n=2390)
- *"Paleozoic…"* - Paleozoic limestones (n=3)

Abbreviations & number of data points (n), HOVER Lithology:

- *"Mtmr"* - Metamorphic rocks (n=83)
- *"Othr"* - Others (n=1990)
- *"Carbonate"* - Sedimentary: carbonates (limestone, chalk) (n=81)
- *"Clay/Marl"* - Sedimentary: clays and/or marls (n=253)
- *"Gravel"* - Sedimentary: gravel (n=222)
- *"S.Othr"* - Sedimentary: other (n=994)
- *"Sand"* - Sedimentary: sand (n=1874)


A
Al concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
Al , ug/l
10⁴
10³
10²
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for Al
Data: longterm median for each ID (Belgium)
F(Al)
1.00
0.75
0.50
0.25
0.00
10²
10³
10⁴
Al , ug/l
Data source: VMM
C
Al concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
Al , ug/l
10⁴
10³
10²
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for Al
Data: longterm median for each ID (Belgium)
F(Al)
1.00
0.75
0.50
0.25
0.00
10²
10³
10⁴
Al , ug/l
Data source: VMM

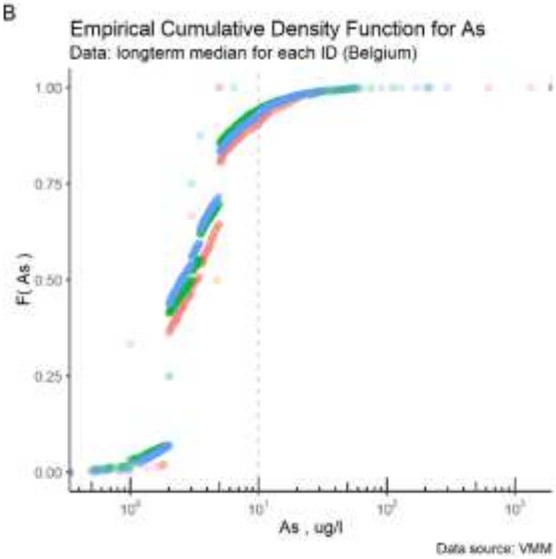
A



As concentrations grouped by BRIDGE typology

Data: longterm median for each ID (Belgium)

B

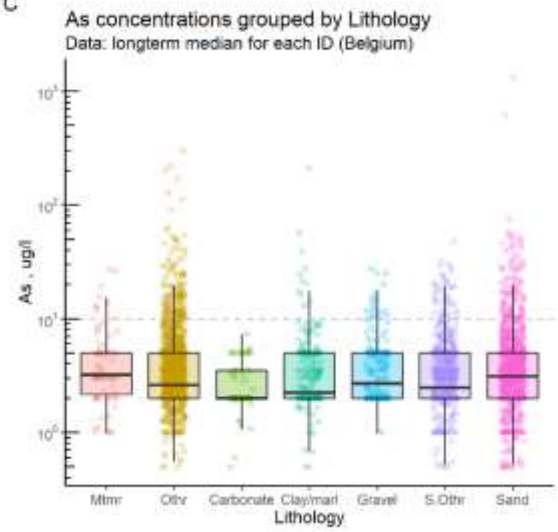


Empirical Cumulative Density Function for As

Data: longterm median for each ID (Belgium)

Data source: VMM

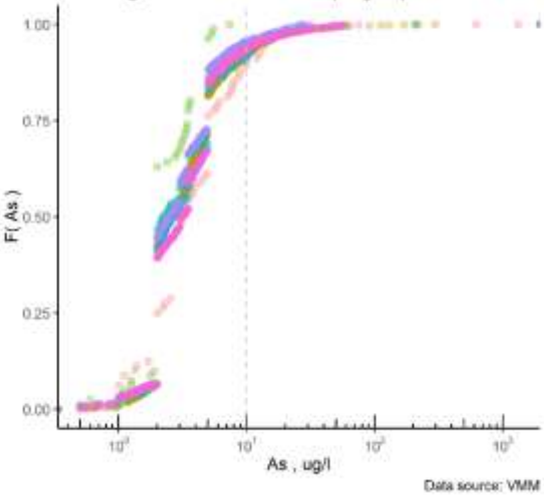
C



As concentrations grouped by Lithology

Data: longterm median for each ID (Belgium)

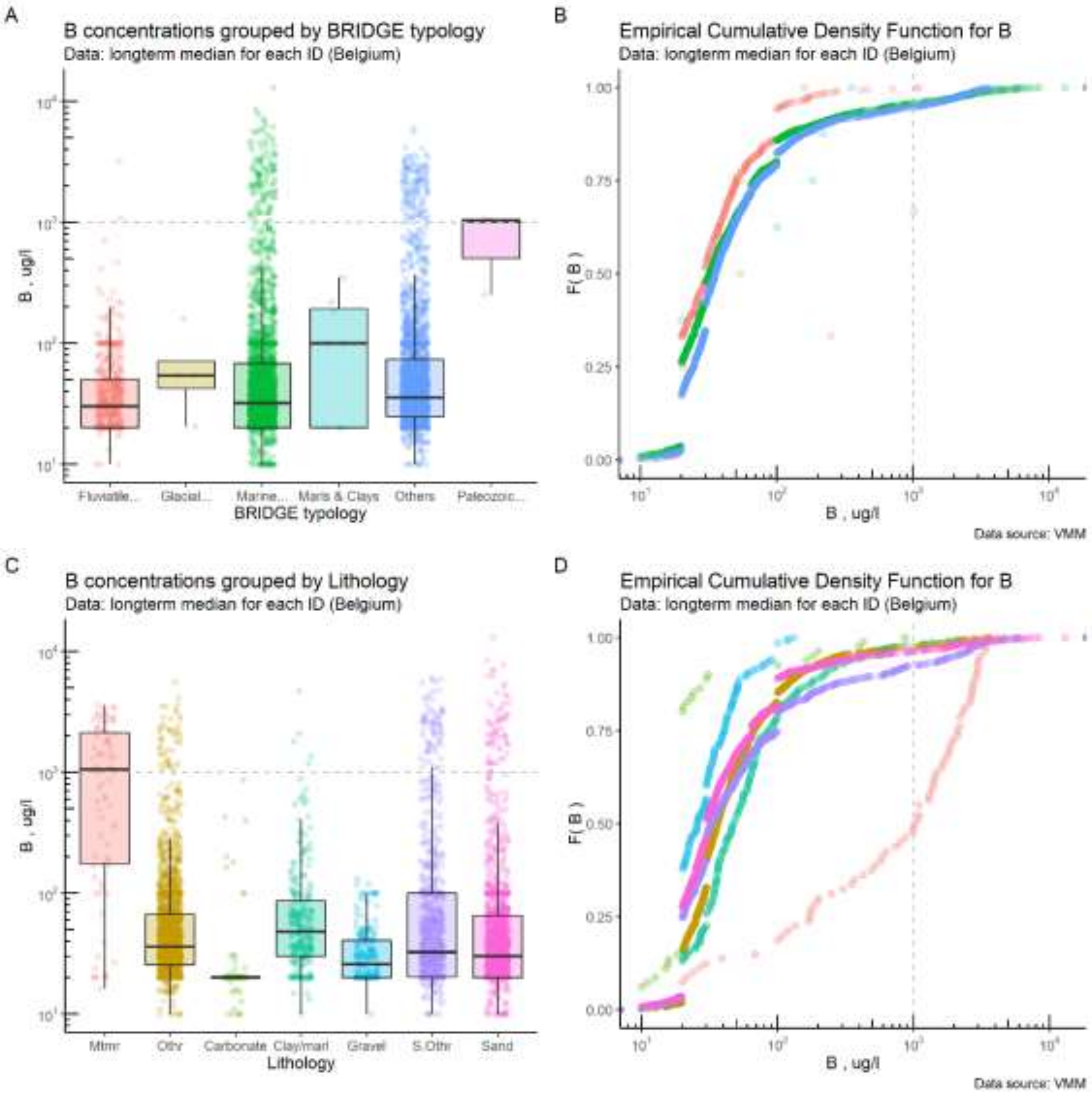
D



Empirical Cumulative Density Function for As

Data: longterm median for each ID (Belgium)

Data source: VMM



B concentrations grouped by BRIDGE typology

Data: longterm median for each ID (Belgium)

Empirical Cumulative Density Function for B

Data: longterm median for each ID (Belgium)

Data source: VMM

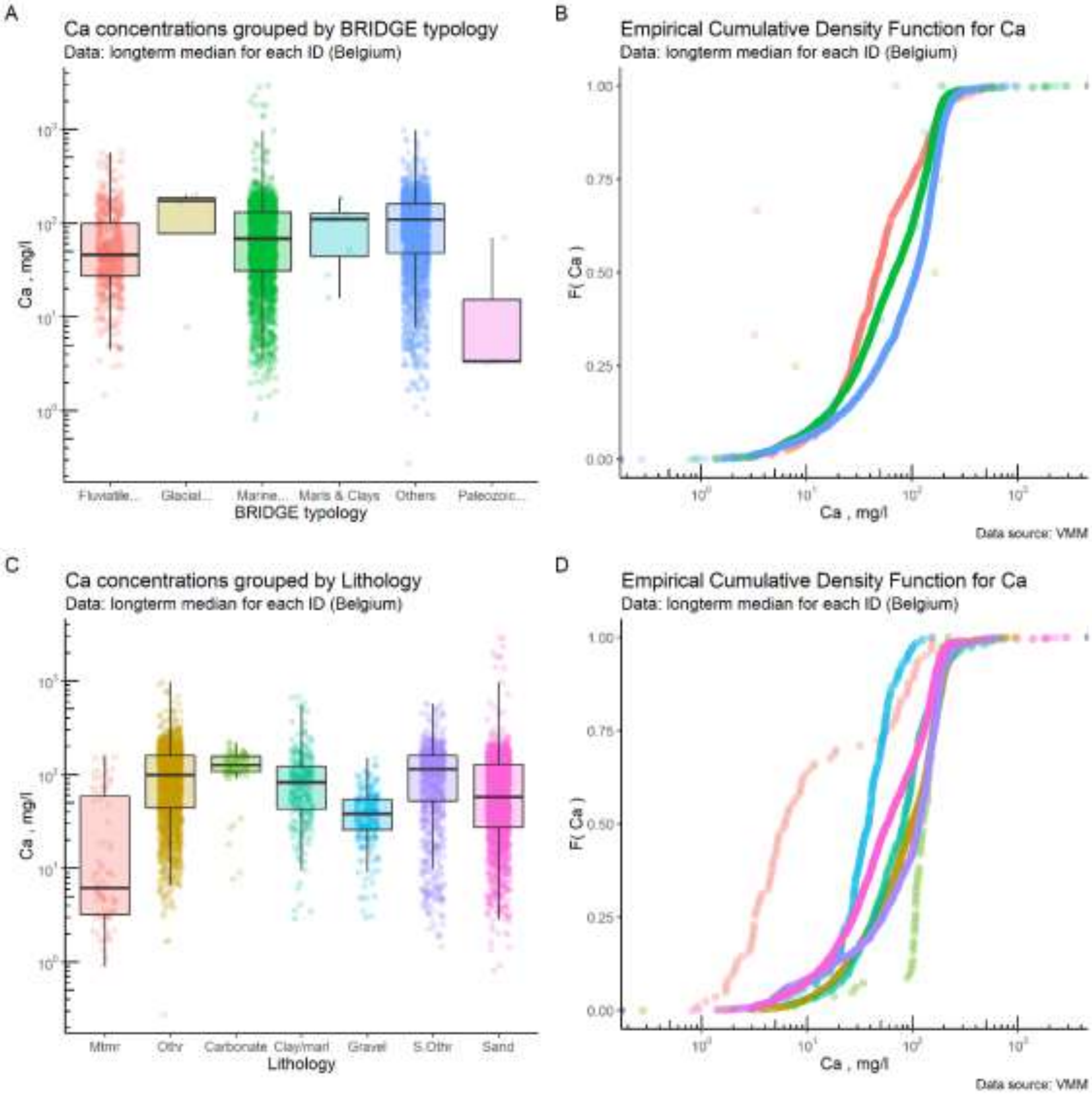
B concentrations grouped by Lithology

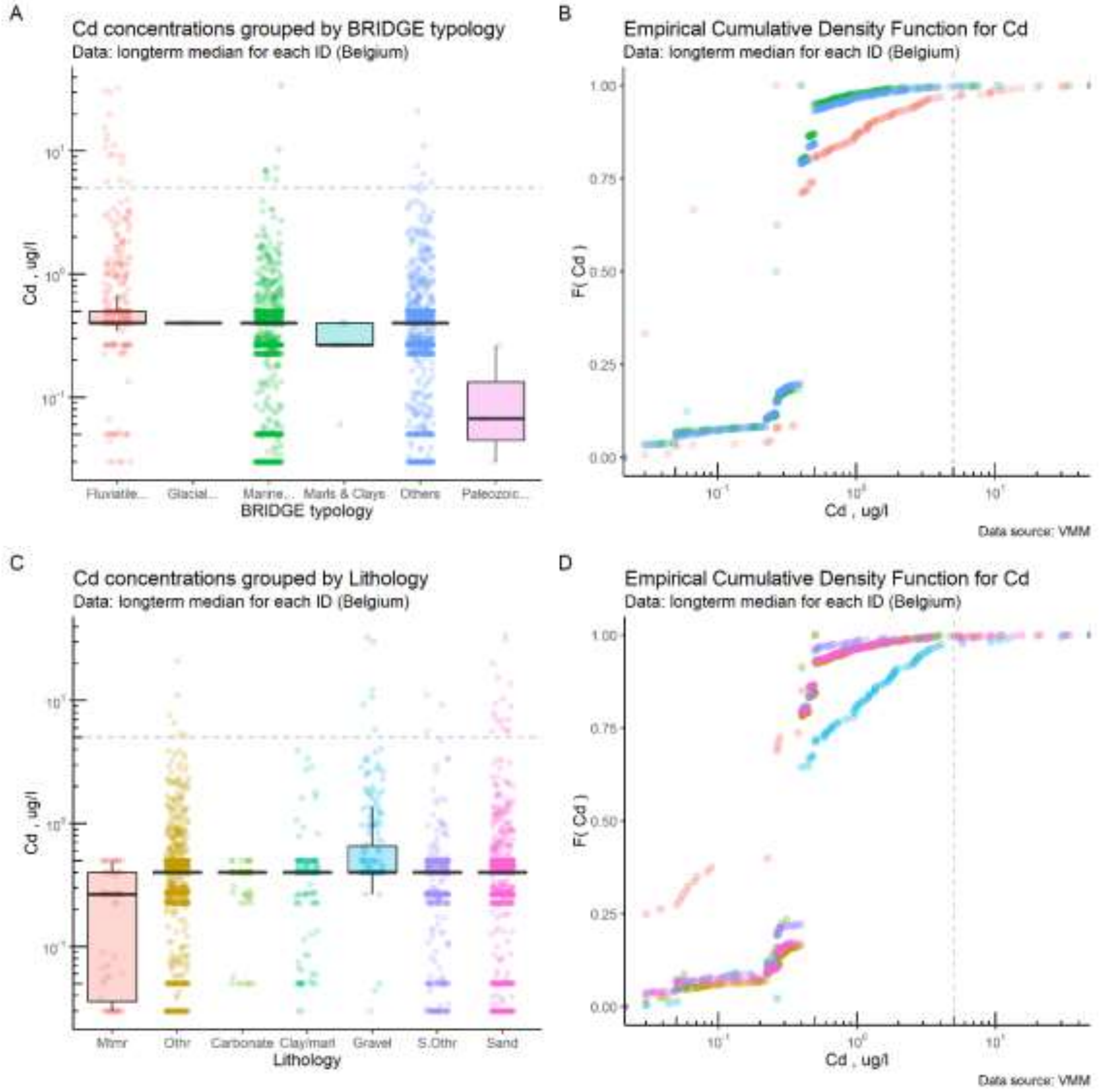
Data: longterm median for each ID (Belgium)

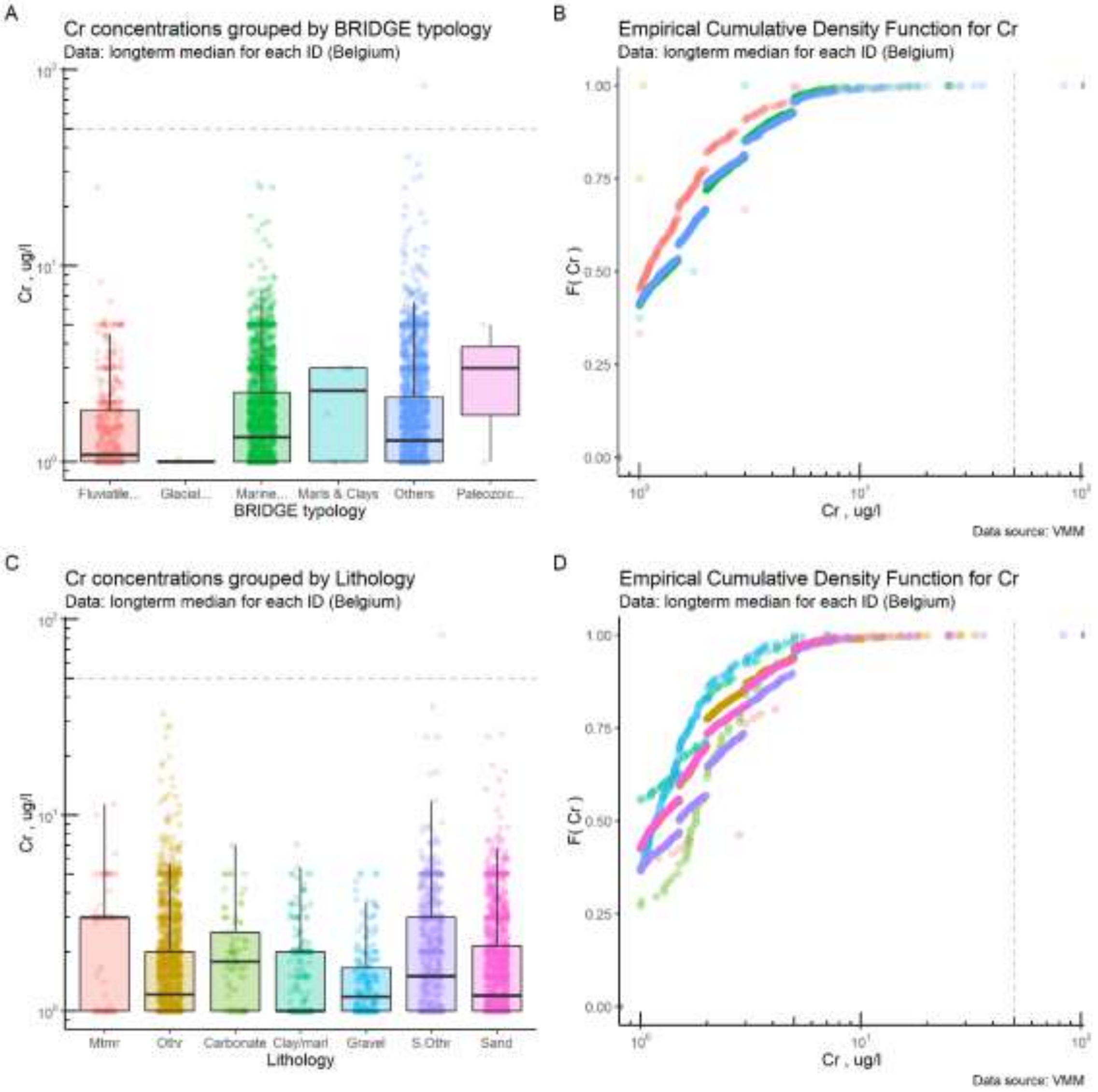
Empirical Cumulative Density Function for B

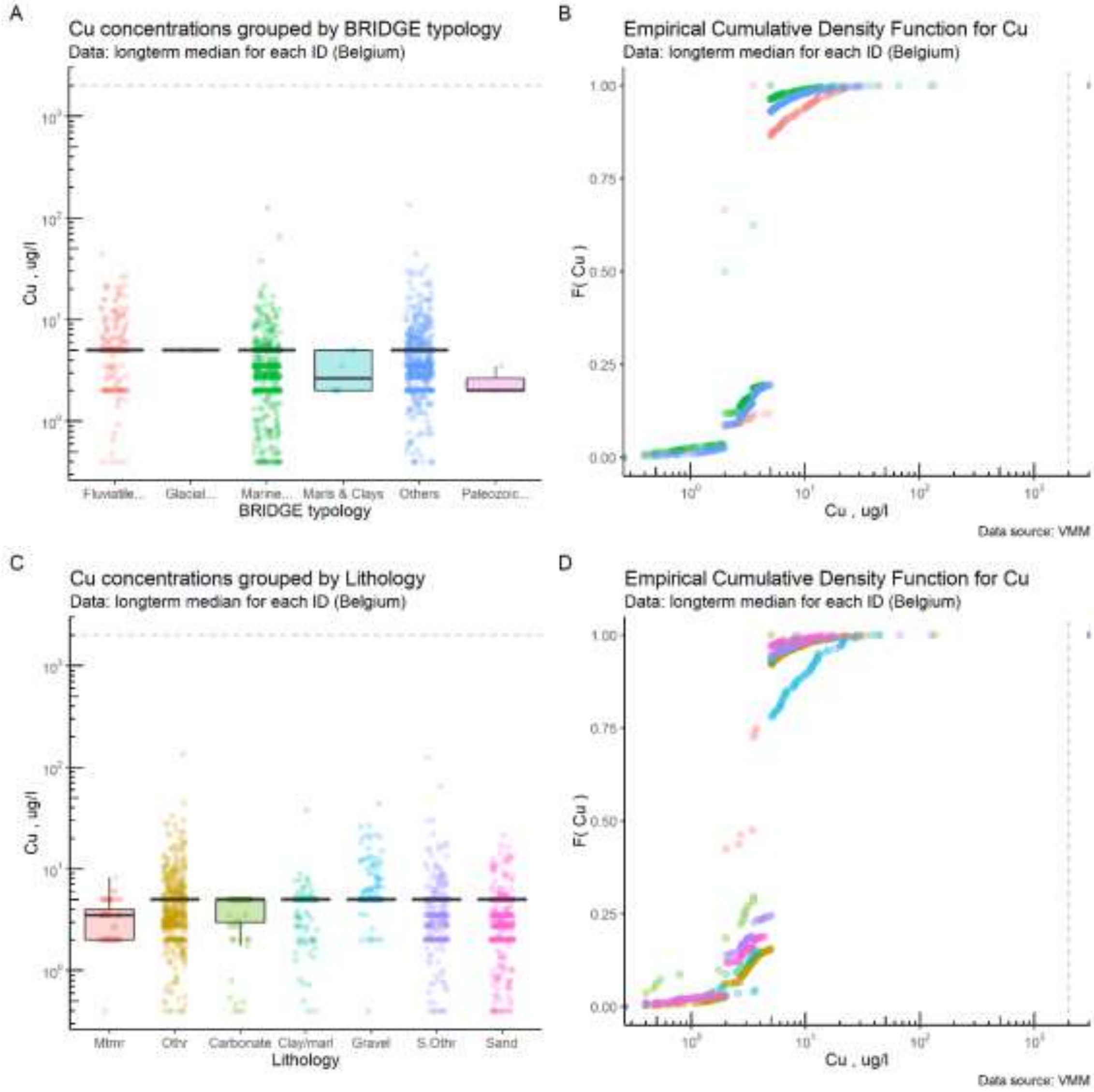
Data: longterm median for each ID (Belgium)

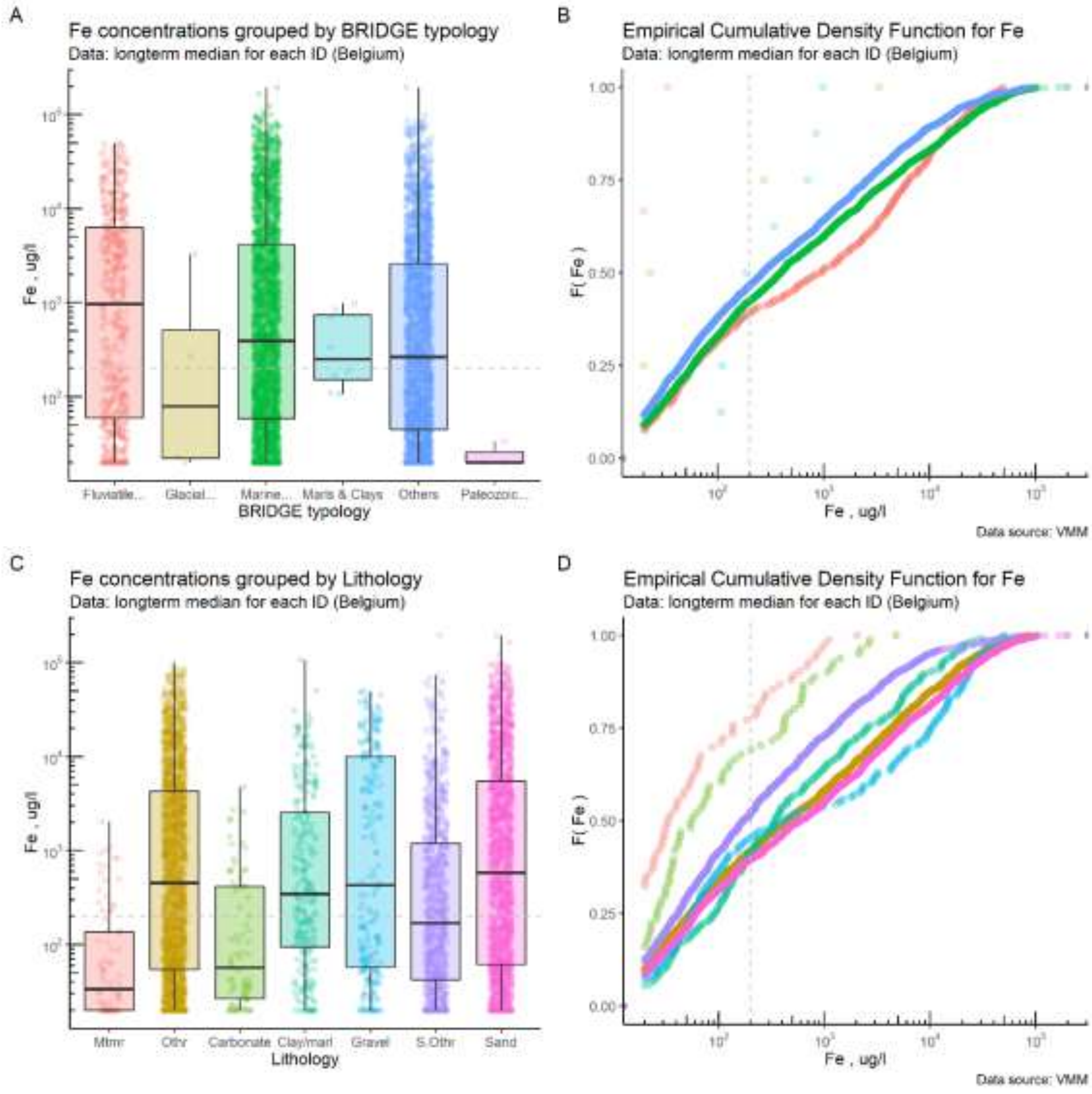
Data source: VMM

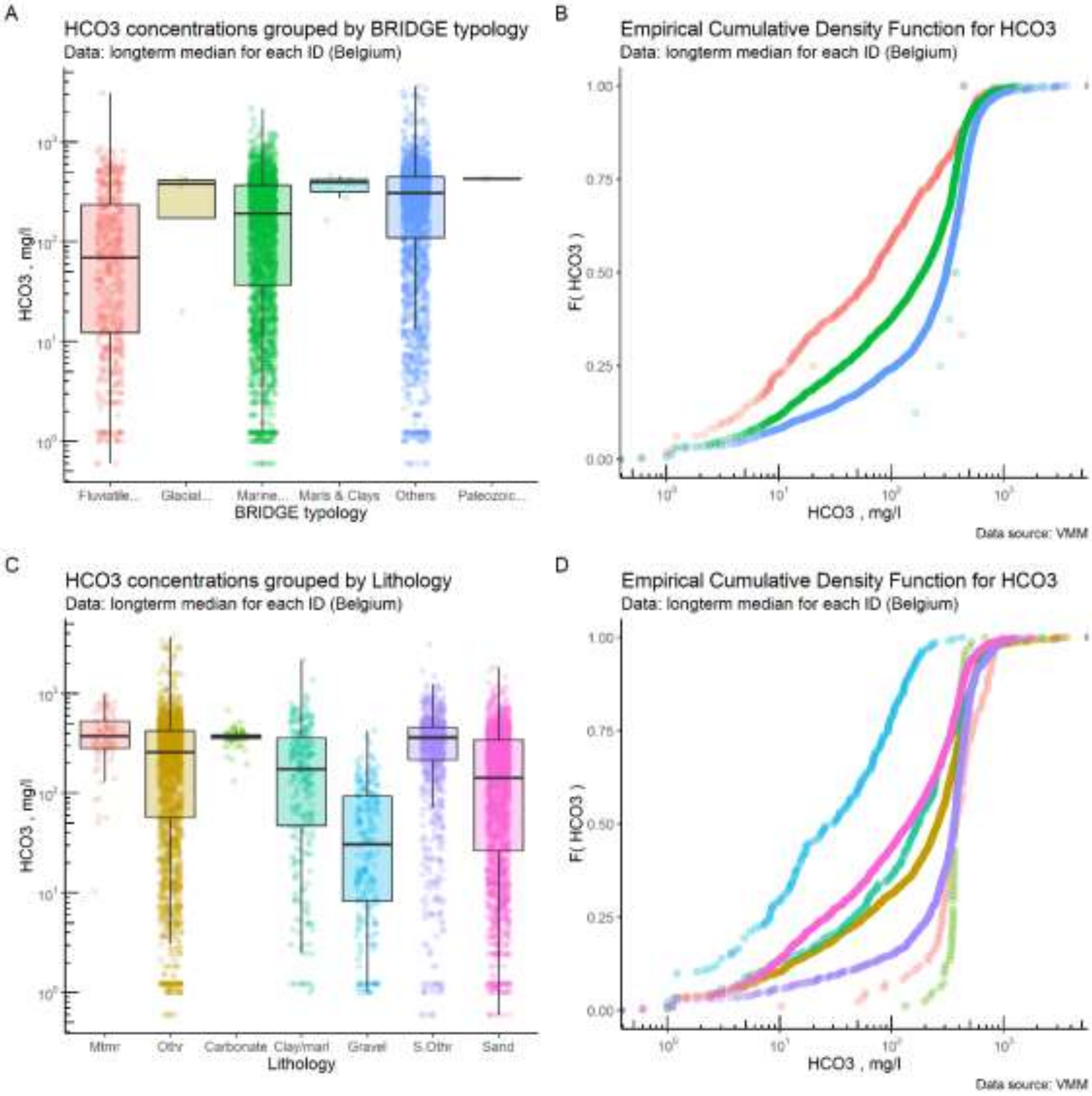

A
Ca concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
Ca , mg/l
10^3
10^2
10^1
10^0
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for Ca
Data: longterm median for each ID (Belgium)
F(Ca)
1.00
0.75
0.50
0.25
0.00
10^0
10^1
10^2
10^3
Ca , mg/l
Data source: VMM
C
Ca concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
Ca , mg/l
10^3
10^2
10^1
10^0
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for Ca
Data: longterm median for each ID (Belgium)
F(Ca)
1.00
0.75
0.50
0.25
0.00
10^0
10^1
10^2
10^3
Ca , mg/l
Data source: VMM


A
Cd concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
Cd , ug/l
10^{1}
10^{0}
10^{-1}
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for Cd
Data: longterm median for each ID (Belgium)
F(Cd)
1.00
0.75
0.50
0.25
0.00
10^{-1}
10^{0}
10^{1}
Cd , ug/l
Data source: VMM
C
Cd concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
Cd , ug/l
10^{1}
10^{0}
10^{-1}
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for Cd
Data: longterm median for each ID (Belgium)
F(Cd)
1.00
0.75
0.50
0.25
0.00
10^{-1}
10^{0}
10^{1}
Cd , ug/l
Data source: VMM

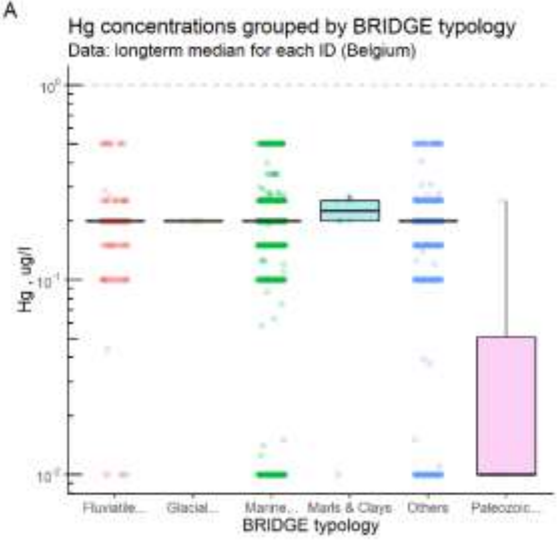

A
Cr concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
Cr , ug/l
10⁰
10¹
10²
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for Cr
Data: longterm median for each ID (Belgium)
F(Cr)
0.00
0.25
0.50
0.75
1.00
10⁰
10¹
10²
Cr , ug/l
Data source: VMM
C
Cr concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
Cr , ug/l
10⁰
10¹
10²
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for Cr
Data: longterm median for each ID (Belgium)
F(Cr)
0.00
0.25
0.50
0.75
1.00
10⁰
10¹
10²
Cr , ug/l
Data source: VMM


A
Cu concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
Cu , ug/l
10^0
10^1
10^2
10^3
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for Cu
Data: longterm median for each ID (Belgium)
F(Cu)
0.00
0.25
0.50
0.75
1.00
10^0
10^1
10^2
10^3
Cu , ug/l
Data source: VMM
C
Cu concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
Cu , ug/l
10^0
10^1
10^2
10^3
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for Cu
Data: longterm median for each ID (Belgium)
F(Cu)
0.00
0.25
0.50
0.75
1.00
10^0
10^1
10^2
10^3
Cu , ug/l
Data source: VMM

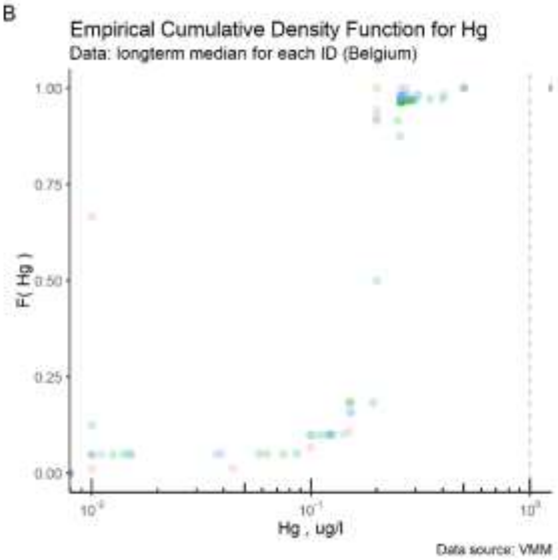

A
Fe concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
Fe , ug/l
10^2
10^3
10^4
10^5
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for Fe
Data: longterm median for each ID (Belgium)
F(Fe)
0.00
0.25
0.50
0.75
1.00
10^2
10^3
10^4
10^5
Fe , ug/l
Data source: VMM
C
Fe concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
Fe , ug/l
10^2
10^3
10^4
10^5
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for Fe
Data: longterm median for each ID (Belgium)
F(Fe)
0.00
0.25
0.50
0.75
1.00
10^2
10^3
10^4
10^5
Fe , ug/l
Data source: VMM


A
HCO3 concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
HCO3 , mg/l
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for HCO3
Data: longterm median for each ID (Belgium)
F(HCO3)
1.00
0.75
0.50
0.25
0.00
HCO3 , mg/l
Data source: VMM
C
HCO3 concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
HCO3 , mg/l
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for HCO3
Data: longterm median for each ID (Belgium)
F(HCO3)
1.00
0.75
0.50
0.25
0.00
HCO3 , mg/l
Data source: VMM

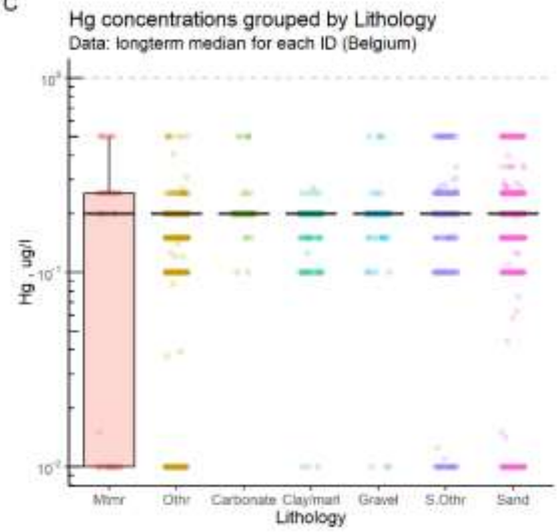
A


Hg concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
Hg , ug/l
10⁰
10⁻¹
10⁻²
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology

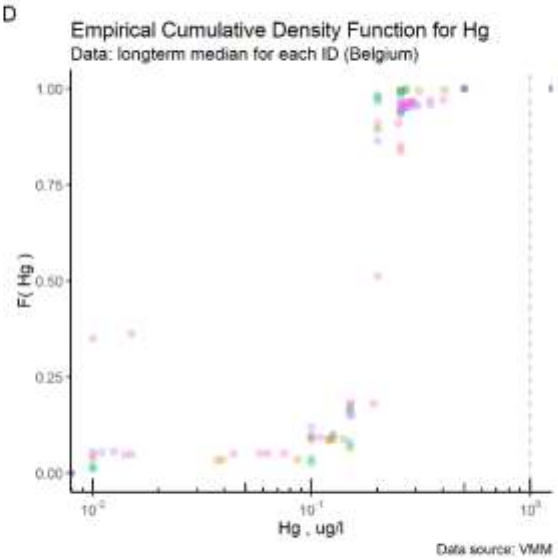
B

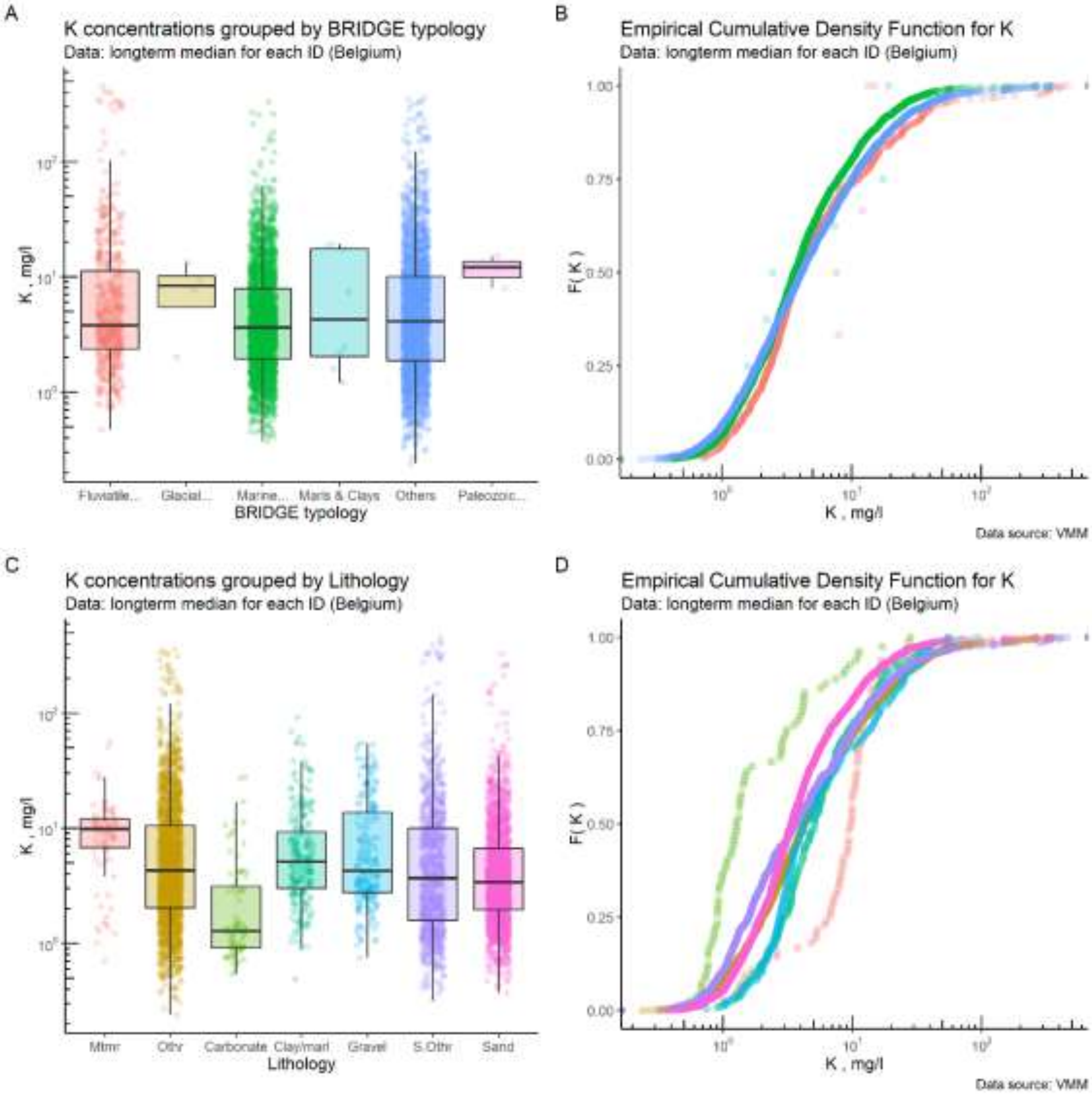

Empirical Cumulative Density Function for Hg
Data: longterm median for each ID (Belgium)
F(Hg)
1.00
0.75
0.50
0.25
0.00
10⁻²
10⁻¹
10⁰
Hg , ug/l
Data source: VMM

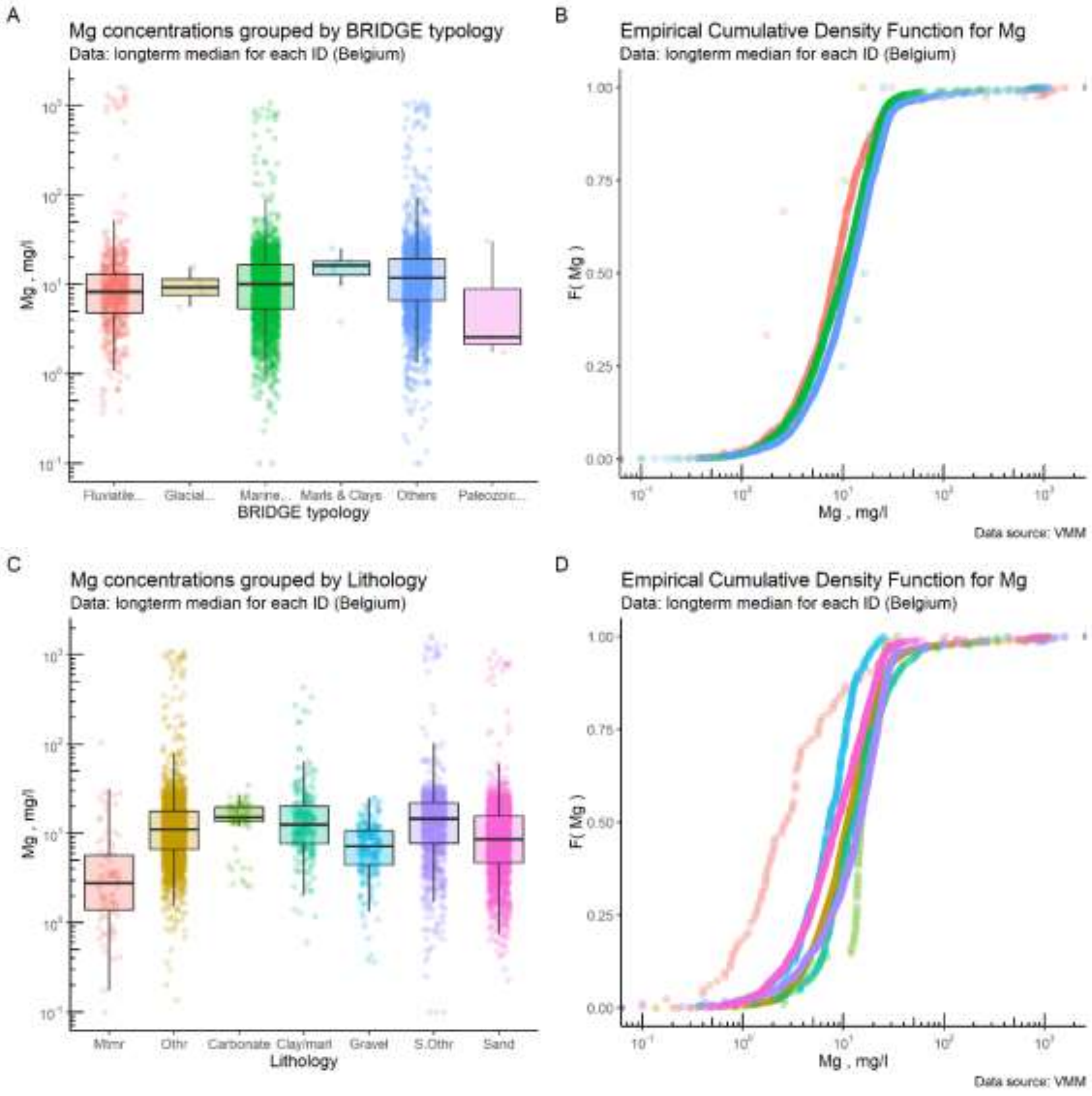
C

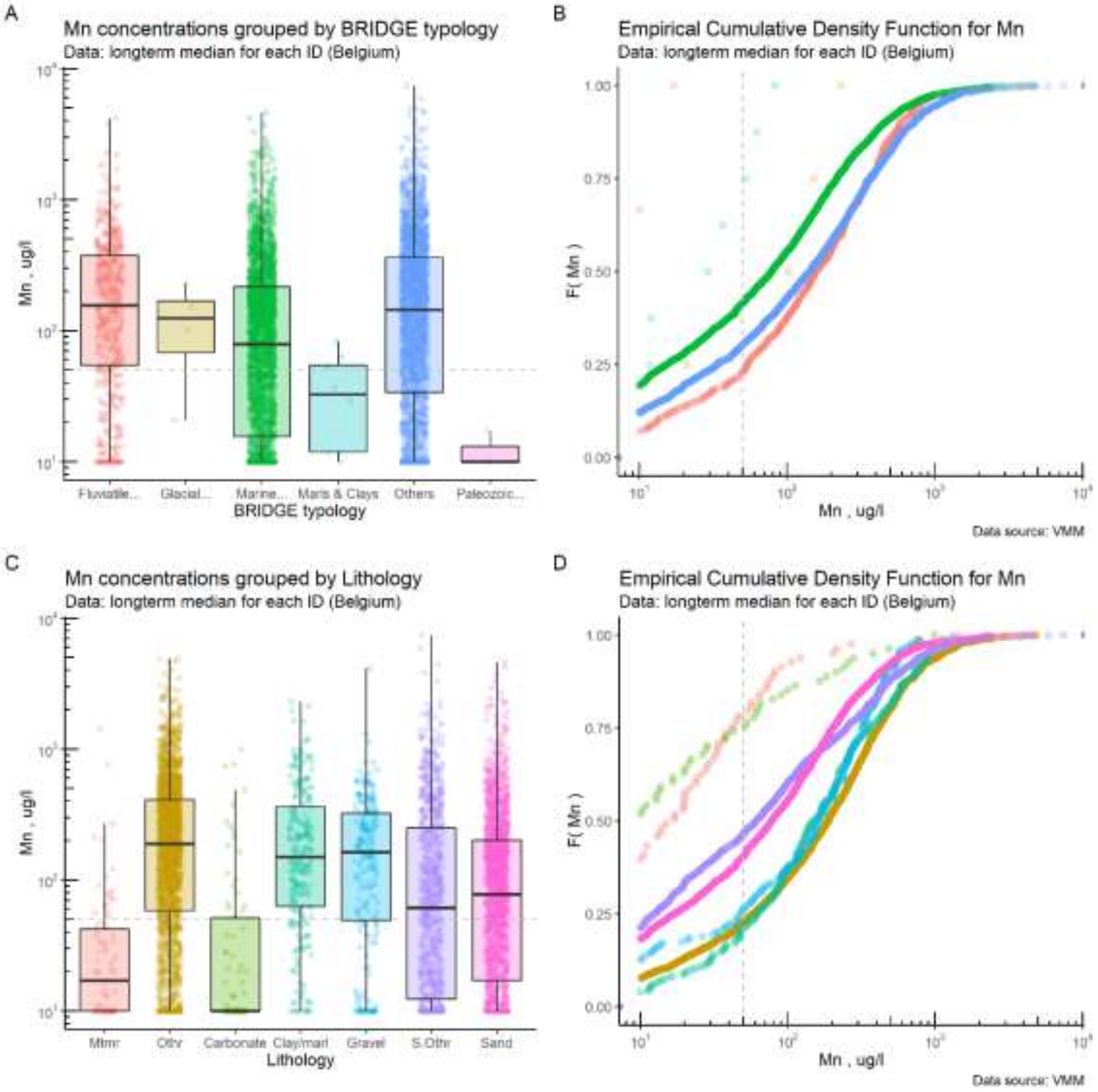

Hg concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
Hg , ug/l
10⁰
10⁻¹
10⁻²
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology

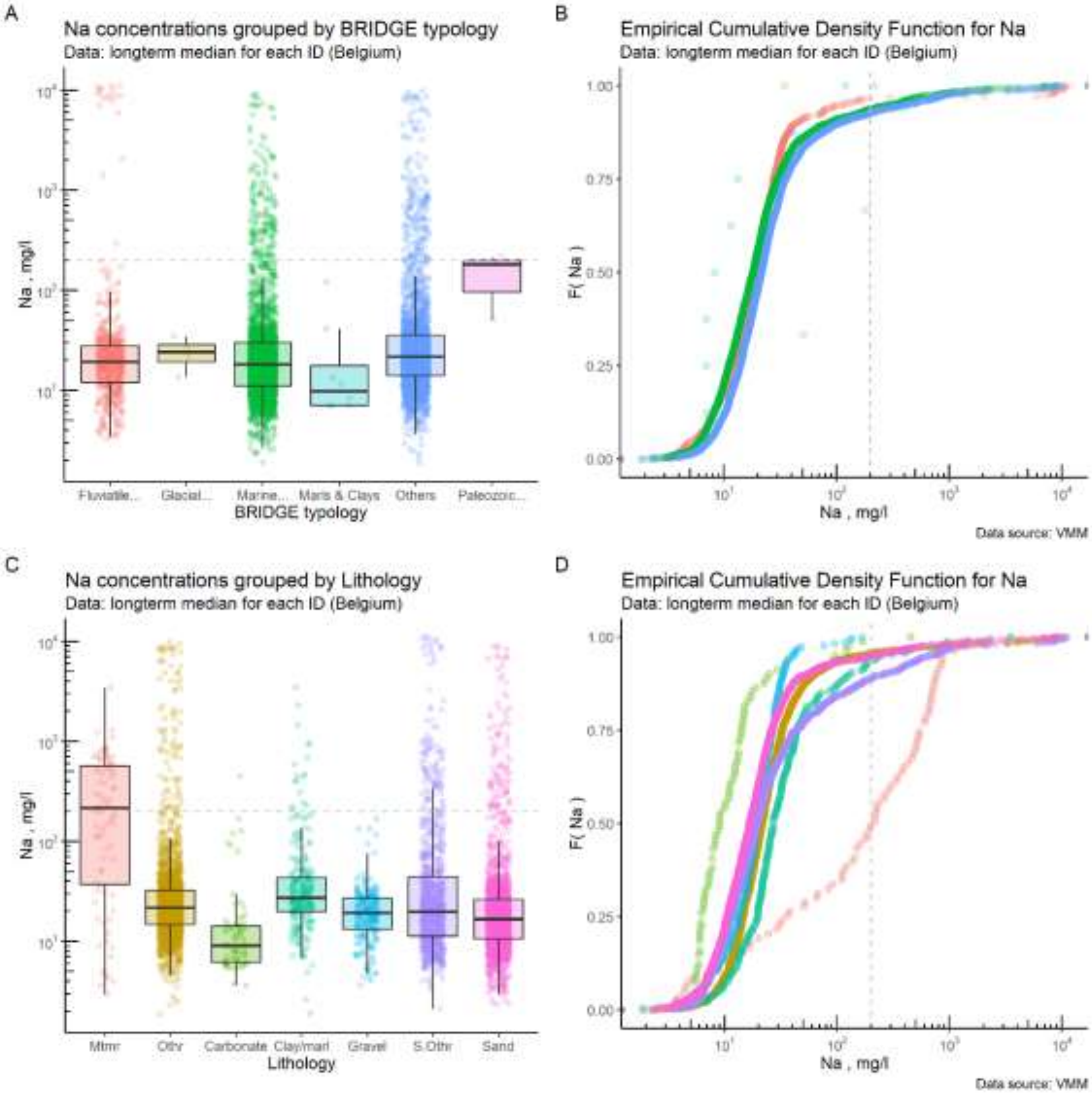
D

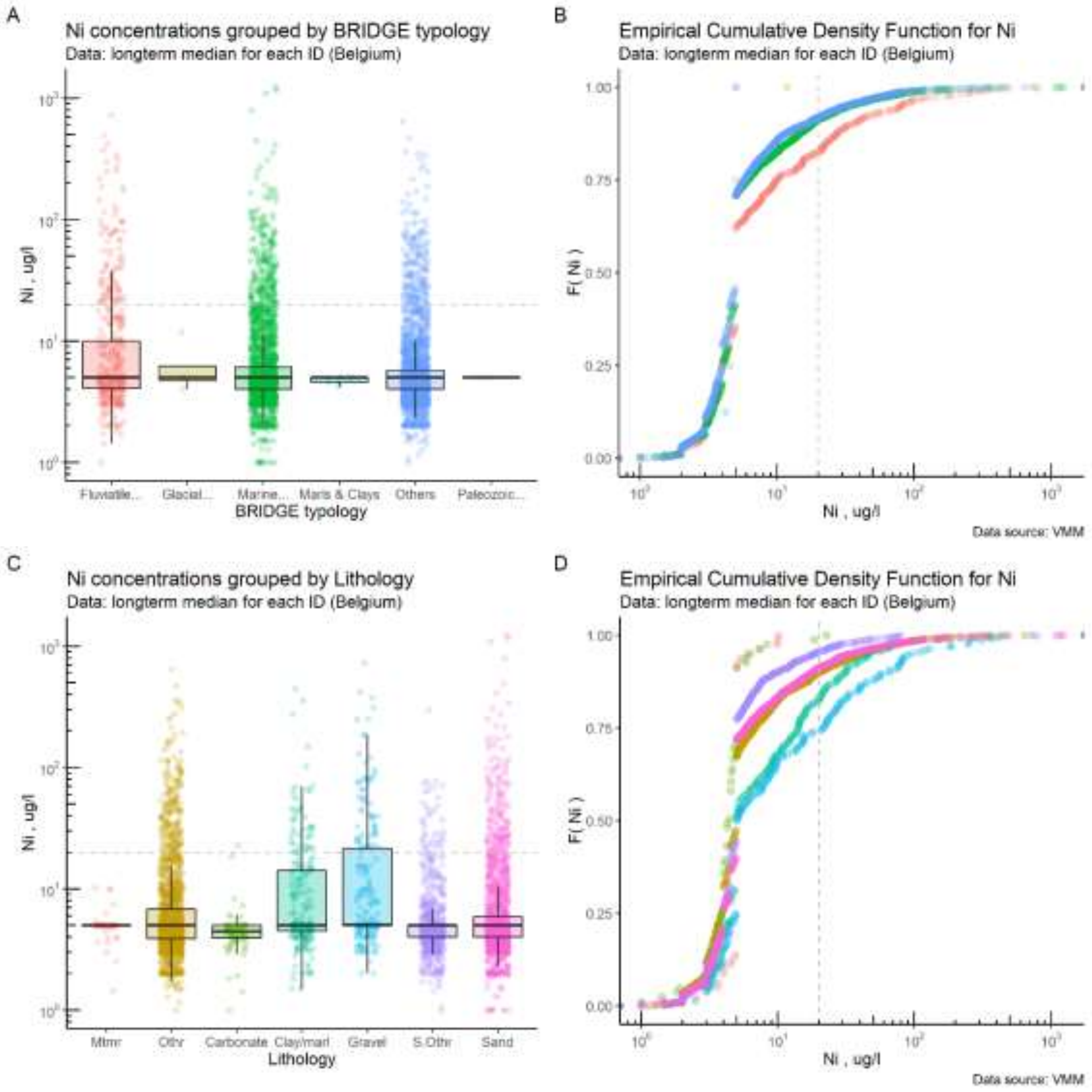

Empirical Cumulative Density Function for Hg
Data: longterm median for each ID (Belgium)
F(Hg)
1.00
0.75
0.50
0.25
0.00
10⁻²
10⁻¹
10⁰
Hg , ug/l
Data source: VMM


A
K concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
K , mg/l
10^2
10^1
10^0
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for K
Data: longterm median for each ID (Belgium)
F(K)
1.00
0.75
0.50
0.25
0.00
10^0
10^1
10^2
K , mg/l
Data source: VMM
C
K concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
K , mg/l
10^2
10^1
10^0
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for K
Data: longterm median for each ID (Belgium)
F(K)
1.00
0.75
0.50
0.25
0.00
10^0
10^1
10^2
K , mg/l
Data source: VMM


A
Mg concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
Mg , mg/l
10⁻¹
10⁰
10¹
10²
10³
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for Mg
Data: longterm median for each ID (Belgium)
F(Mg)
0.00
0.25
0.50
0.75
1.00
10⁻¹
10⁰
10¹
10²
10³
Mg , mg/l
Data source: VMM
C
Mg concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
Mg , mg/l
10⁻¹
10⁰
10¹
10²
10³
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for Mg
Data: longterm median for each ID (Belgium)
F(Mg)
0.00
0.25
0.50
0.75
1.00
10⁻¹
10⁰
10¹
10²
10³
Mg , mg/l
Data source: VMM


A
Mn concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
Mn , ug/l
10⁴
10³
10²
10¹
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for Mn
Data: longterm median for each ID (Belgium)
F(Mn)
1.00
0.75
0.50
0.25
0.00
10¹
10²
10³
10⁴
Mn , ug/l
Data source: VMM
C
Mn concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
Mn , ug/l
10⁴
10³
10²
10¹
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for Mn
Data: longterm median for each ID (Belgium)
F(Mn)
1.00
0.75
0.50
0.25
0.00
10¹
10²
10³
10⁴
Mn , ug/l
Data source: VMM


A
Na concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
Na , mg/l
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for Na
Data: longterm median for each ID (Belgium)
F(Na)
1.00
0.75
0.50
0.25
0.00
Na , mg/l
Data source: VMM
C
Na concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
Na , mg/l
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for Na
Data: longterm median for each ID (Belgium)
F(Na)
1.00
0.75
0.50
0.25
0.00
Na , mg/l
Data source: VMM



Ni concentrations grouped by BRIDGE typology

Data: longterm median for each ID (Belgium)

Empirical Cumulative Density Function for Ni

Data: longterm median for each ID (Belgium)

Data source: VMM

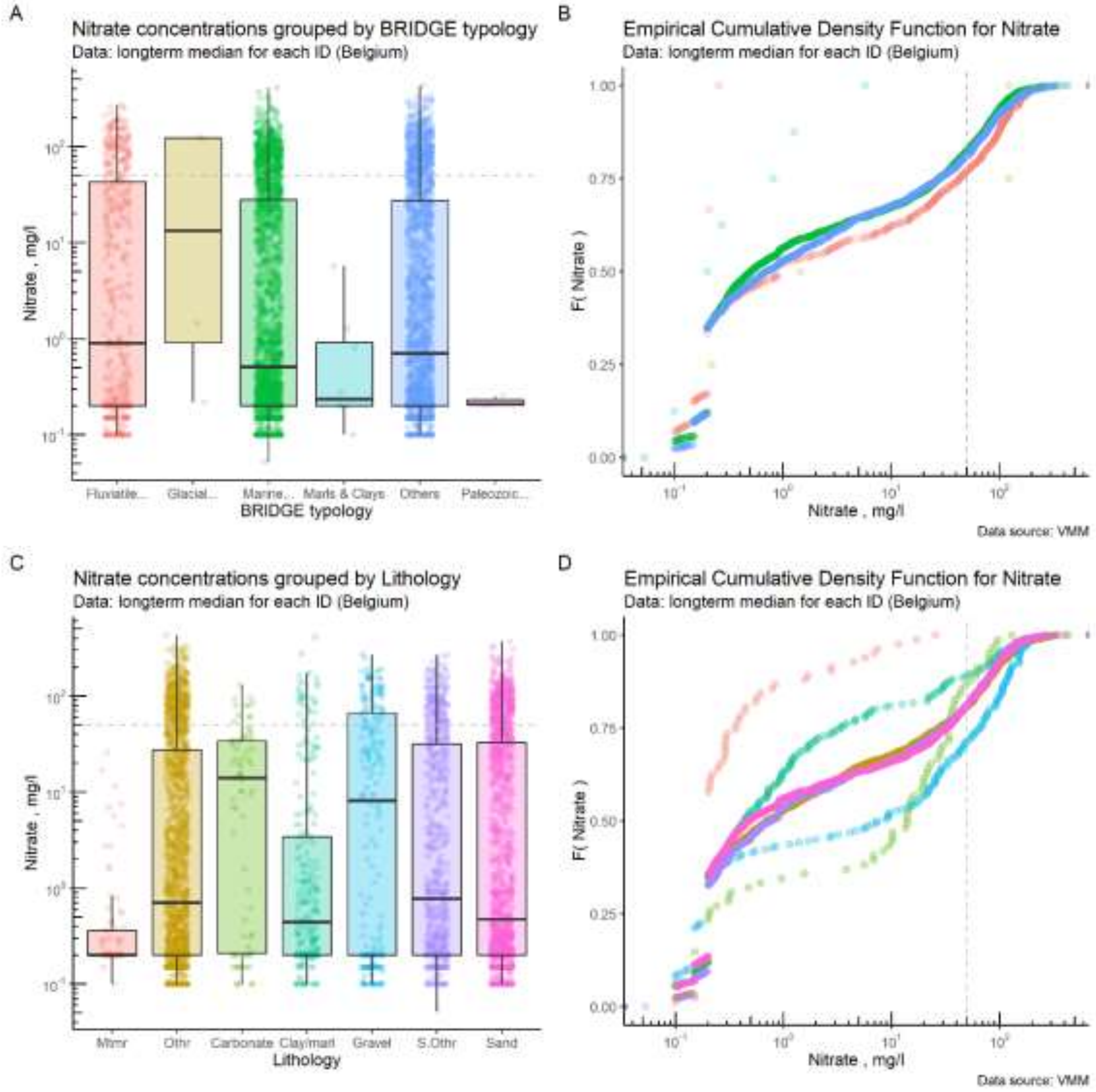
Ni concentrations grouped by Lithology

Data: longterm median for each ID (Belgium)

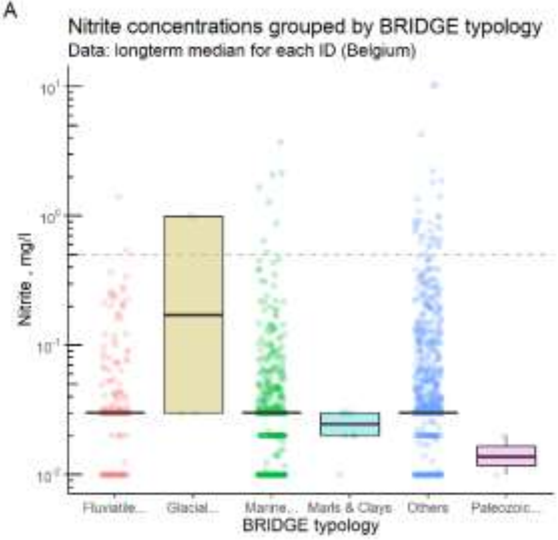
Empirical Cumulative Density Function for Ni

Data: longterm median for each ID (Belgium)

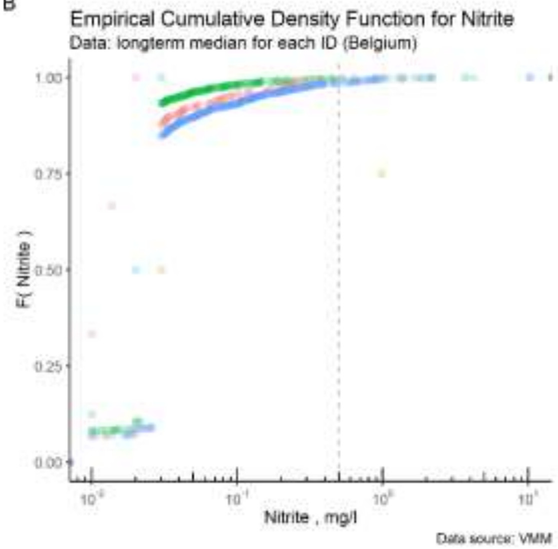
Data source: VMM


A
Nitrate concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
Nitrate , mg/l
10^{-1}
10^{0}
10^{1}
10^{2}
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for Nitrate
Data: longterm median for each ID (Belgium)
F(Nitrate)
0.00
0.25
0.50
0.75
1.00
Nitrate , mg/l
Data source: VMM
C
Nitrate concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
Nitrate , mg/l
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for Nitrate
Data: longterm median for each ID (Belgium)
F(Nitrate)
Nitrate , mg/l
Data source: VMM

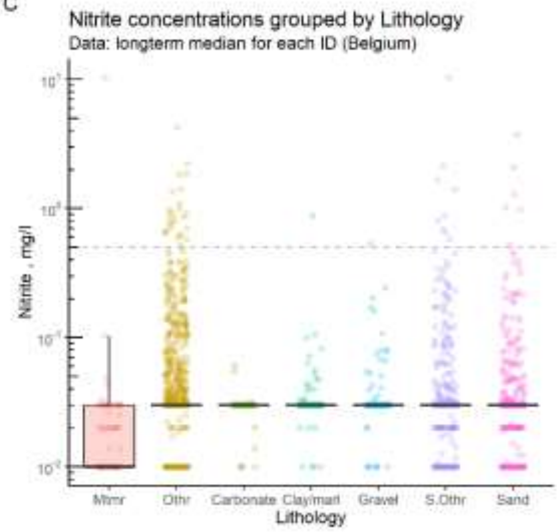
A


Nitrite concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
Nitrite , mg/l
10¹
10⁰
10⁻¹
10⁻²
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology

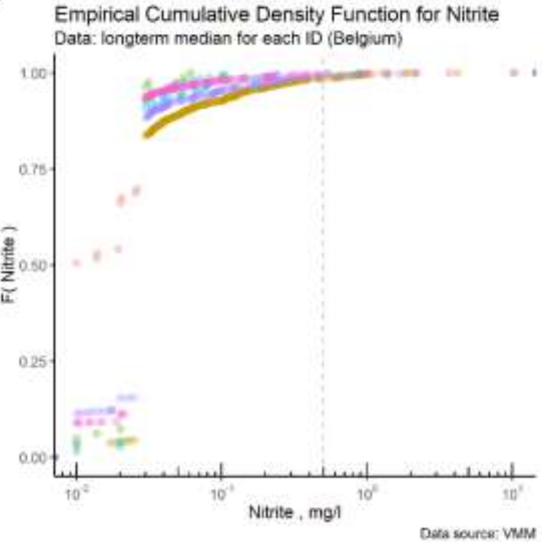
B

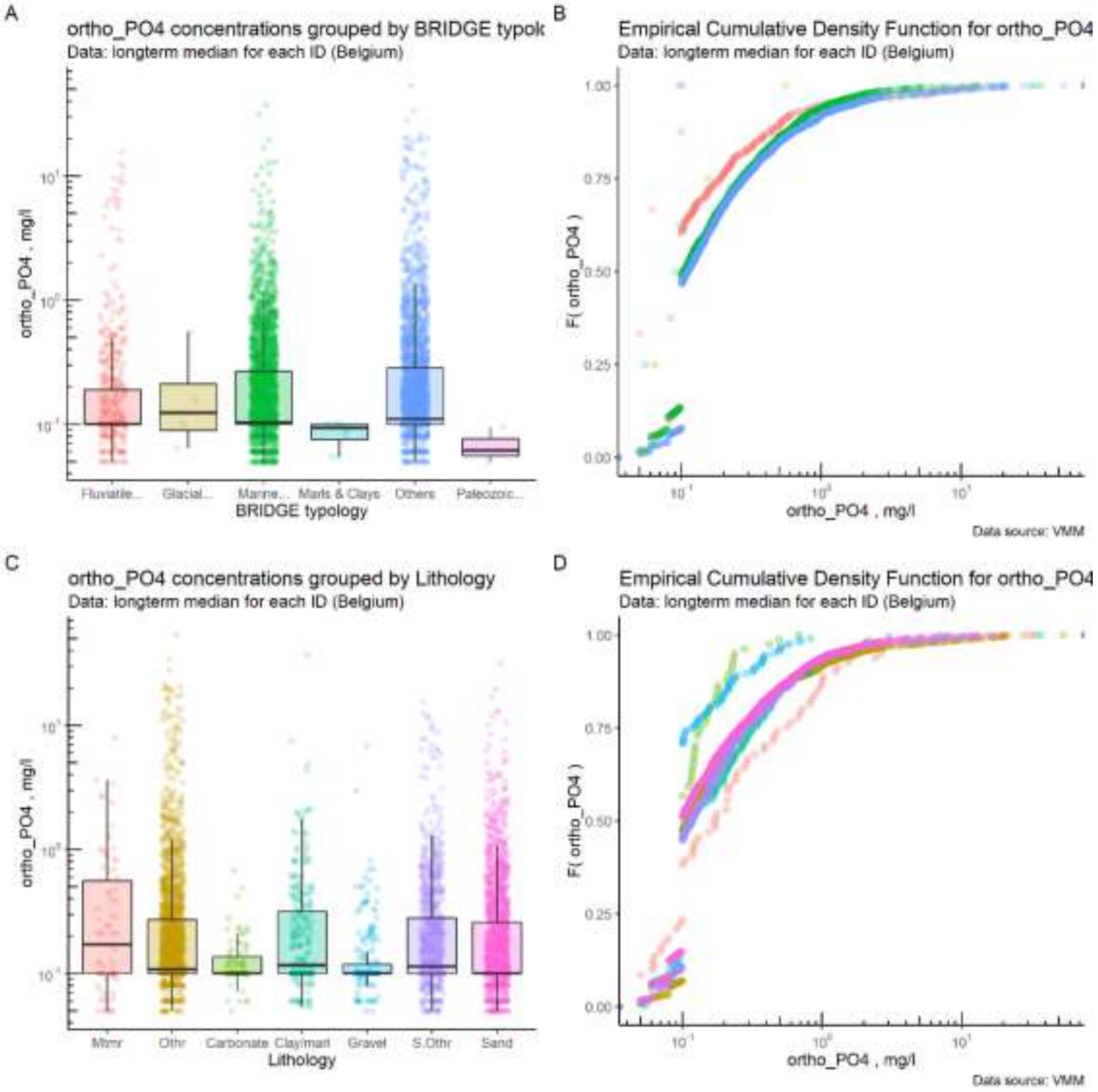

Empirical Cumulative Density Function for Nitrite
Data: longterm median for each ID (Belgium)
F(Nitrite)
1.00
0.75
0.50
0.25
0.00
10⁻²
10⁻¹
10⁰
10¹
Nitrite , mg/l
Data source: VMM

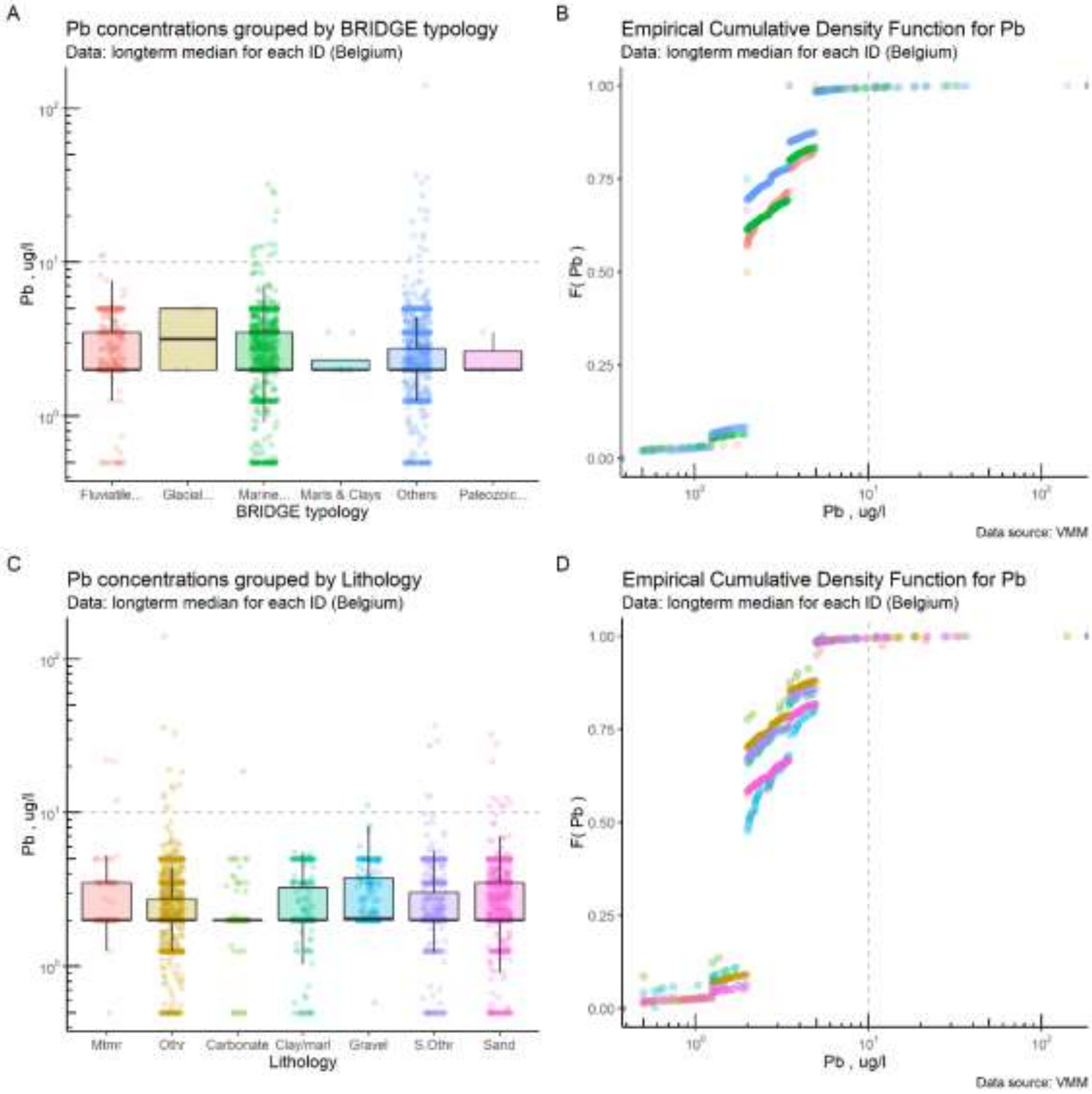
C

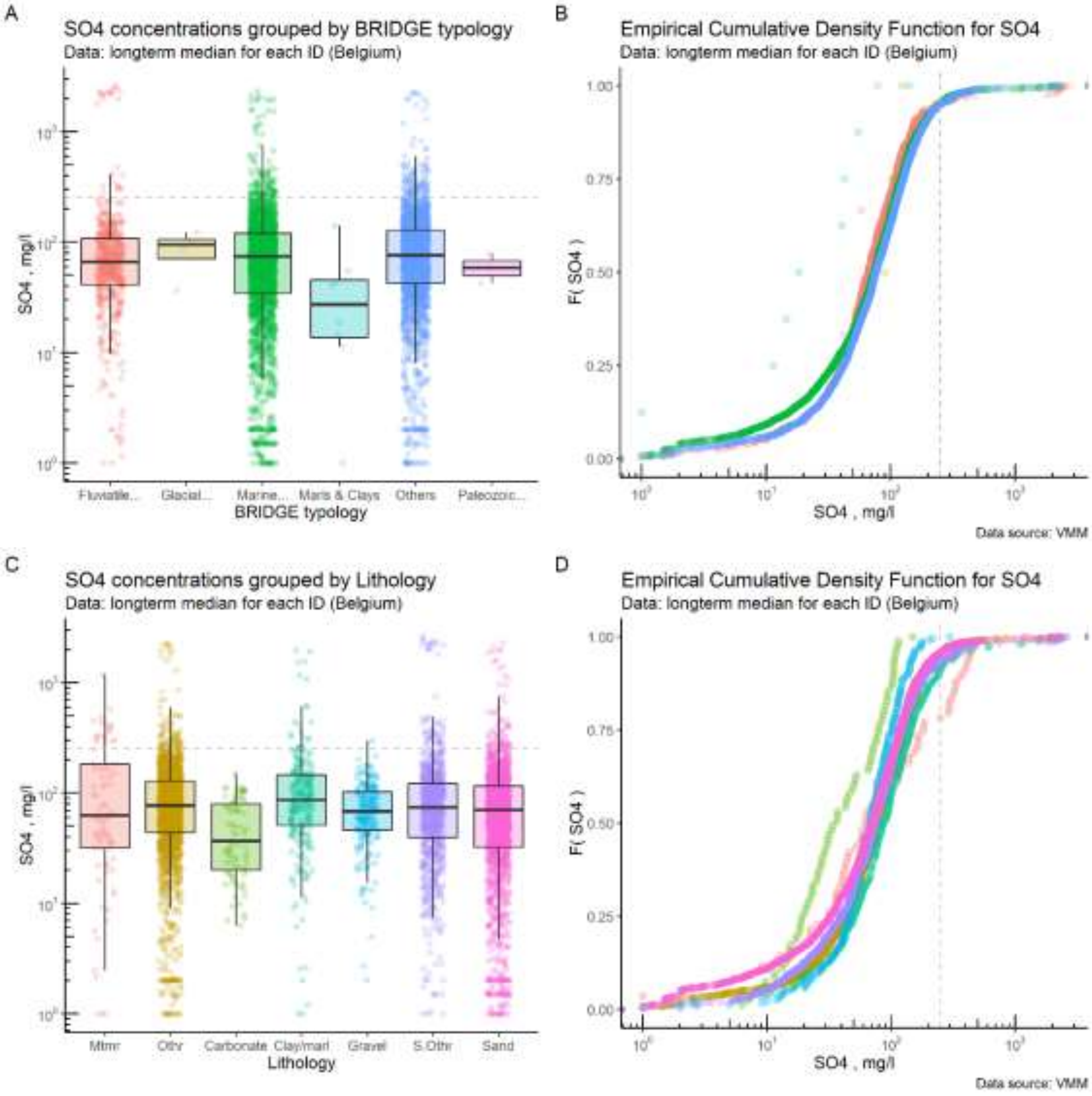

Nitrite concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
Nitrite , mg/l
10¹
10⁰
10⁻¹
10⁻²
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology

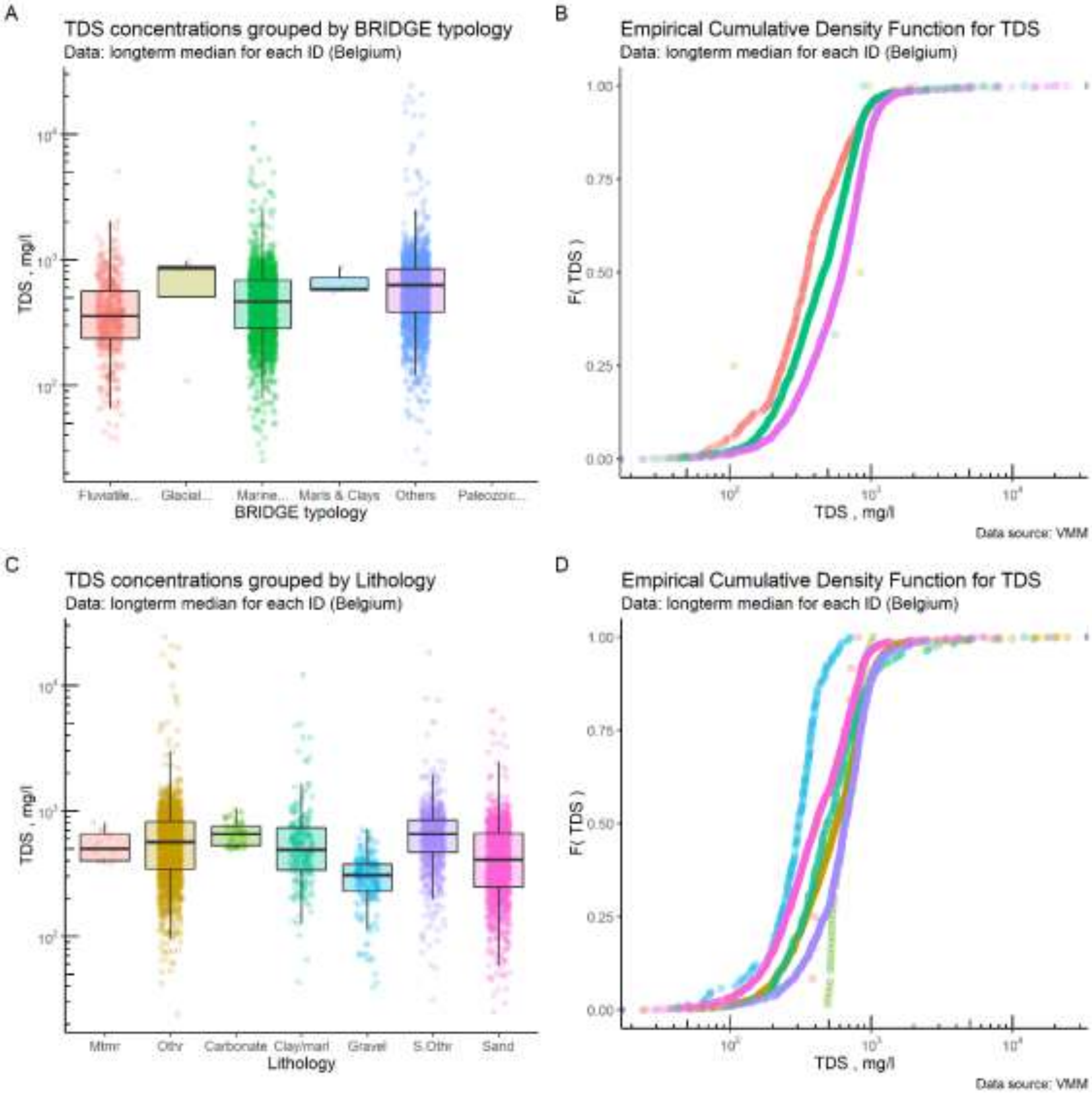
D


Empirical Cumulative Density Function for Nitrite
Data: longterm median for each ID (Belgium)
F(Nitrite)
1.00
0.75
0.50
0.25
0.00
10⁻²
10⁻¹
10⁰
10¹
Nitrite , mg/l
Data source: VMM


A
ortho_PO4 concentrations grouped by BRIDGE typolc
Data: longterm median for each ID (Belgium)
ortho_PO4 , mg/l
10^{1}
10^{0}
10^{-1}
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for ortho_PO4
Data: longterm median for each ID (Belgium)
F(ortho_PO4)
1.00
0.75
0.50
0.25
0.00
10^{-1}
10^{0}
10^{1}
ortho_PO4 , mg/l
Data source: VMM
C
ortho_PO4 concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
ortho_PO4 , mg/l
10^{1}
10^{0}
10^{-1}
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for ortho_PO4
Data: longterm median for each ID (Belgium)
F(ortho_PO4)
1.00
0.75
0.50
0.25
0.00
10^{-1}
10^{0}
10^{1}
ortho_PO4 , mg/l
Data source: VMM


A
Pb concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
Pb , ug/l
10^{2}
10^{1}
10^{0}
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for Pb
Data: longterm median for each ID (Belgium)
F(Pb)
1.00
0.75
0.50
0.25
0.00
10^{0}
10^{1}
10^{2}
Pb , ug/l
Data source: VMM
C
Pb concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
Pb , ug/l
10^{2}
10^{1}
10^{0}
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for Pb
Data: longterm median for each ID (Belgium)
F(Pb)
1.00
0.75
0.50
0.25
0.00
10^{0}
10^{1}
10^{2}
Pb , ug/l
Data source: VMM


A
SO4 concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)
SO4 , mg/l
10^0
10^1
10^2
10^3
Fluviatile...
Glacial...
Marine...
Marls & Clays
Others
Paleozoic...
BRIDGE typology
B
Empirical Cumulative Density Function for SO4
Data: longterm median for each ID (Belgium)
F(SO4)
0.00
0.25
0.50
0.75
1.00
SO4 , mg/l
Data source: VMM
C
SO4 concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)
SO4 , mg/l
Mtmr
Othr
Carbonate
Clay/marl
Gravel
S.Othr
Sand
Lithology
D
Empirical Cumulative Density Function for SO4
Data: longterm median for each ID (Belgium)
F(SO4)
SO4 , mg/l
Data source: VMM



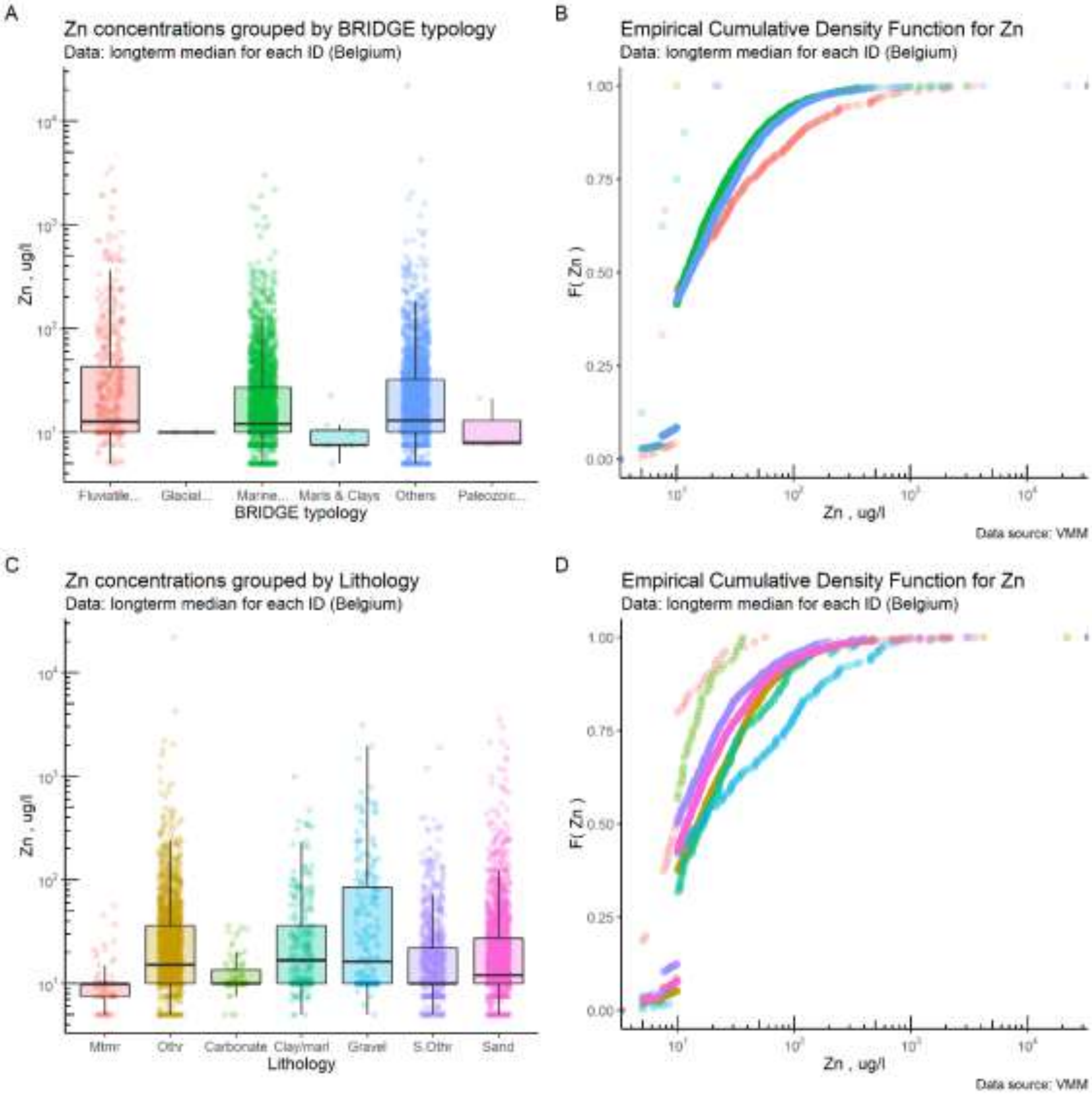
A TDS concentrations grouped by BRIDGE typology
Data: longterm median for each ID (Belgium)

B Empirical Cumulative Density Function for TDS
Data: longterm median for each ID (Belgium)

C TDS concentrations grouped by Lithology
Data: longterm median for each ID (Belgium)

D Empirical Cumulative Density Function for TDS
Data: longterm median for each ID (Belgium)

Data source: VMM


A

Zn concentrations grouped by BRIDGE typology

Data: longterm median for each ID (Belgium)

B

Empirical Cumulative Density Function for Zn

Data: longterm median for each ID (Belgium)

Data source: VMM

C

Zn concentrations grouped by Lithology

Data: longterm median for each ID (Belgium)

D

Empirical Cumulative Density Function for Zn

Data: longterm median for each ID (Belgium)

Data source: VMM

APPENDIX 2 – SUMMARY TABLES AND FIGURES FOR THE EXTENDED BRIDGE

Table 17: Sample distribution (n) and As, Mn, Ni, Zn concentrations grouped by HOVER-Redox water types (A, B, C, D, X) and HOVER-pH (Acidic, Basic, Neutral)

Redox water types	pH water types	n	As , µg/l			Mn µg/l			Ni , µg/l			Zn µg/l		
			median ± MAD	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*
A	Acidic	863	2.0 ±0.0	2.8	5.0	29 ±19	107	428	5.8 ±2.1	14.1	56.1	25.5 ±15.5	61	222
	Basic	561	2.0 ±0.1	3.5	5.0	10 ±0	26	240	4.5 ±0.5	5.0	5.5	10.6 ±0.8	18	37
	Neutral	19	2.0 ±0.0	2.0	3.7	10 ±0	12	152	4.0 ±0.4	4.6	5.5	10.0 ±0.0	23	94
B	Acidic	282	2.0 ±0.0	2.0	5.0	80 ±61	207	740	7.7 ±3.7	19.4	80.4	23.2 ±13.2	57	228
	Basic	156	2.0 ±0.0	3.0	5.0	98 ±82	254	626	4.7 ±0.5	5.0	8.5	10.0 ±1.5	17	31
C	Acidic	1248	4.5 ±2.2	6.2	19.5	265 ±151	500	1293	5.0 ± 1.2	7.1	47.7	15.1 ±5.1	36	143
	Basic	745	3.3 ±1.3	5.0	11.2	204 ±139	388	840	4.4 ±0.7	5.0	5.0	10.0 ±0.0	13	28
	Neutral	12	3.2 ±1.5	5.5	20.8	400 ±315	888	995	4.7 ±0.4	5.0	5.0	10.0 ±2.5	21	34
D	Acidic	186	5.0 ±2.0	10.1	42.7	105 ±63	260	1168	5.0 ±0.5	5.0	8.1	10.0 ±1.5	22	59
	Basic	236	4.5 ±1.5	5.9	21.8	79 ±58	197	598	5.0 ±0.0	5.0	5.1	10.0 ±1.0	11	24
	Neutral	5	11.7 ±5.2	16.3	24.2	856 ±562	1140	1362	4.1 ±0.9	5.0	7.8	10.0 ±0.0	10	18
X	Acidic	551	2.2 ±0.6	4.2	7.1	139 ±108	323	1215	7.6 ±3.4	18.0	96.8	33.0 ±22.6	76	303
	Basic	547	3.2 ±1.5	5.0	10.8	45 ±35	176	599	5.0 ±0.0	5.0	6.4	10.0 ±1.8	12	39
	Neutral	15	2.0 ±0.4	3.0	5.1	97 ±83	410	701	5.0 ±1.3	6.0	13.3	12.0 ±5.6	29	34

Notes: MAD is median absolute deviation, Q75 and Q95 are the 75th and 95th percentile, respectively (used as indication for high concentrations)

Table 18: BRIDGE & HOVER Lithology combination

BRIDGE	Lithology	n	As , µg/l			Mn µg/l			Ni , µg/l			Zn µg/l		
			median ± MAD	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*
Fluviatile deposits of major streams	Sedimentary: gravel	222	2.7 ± 0.7	5.0	11.8	163 ±125	323	571	5.0 ± 1.7	21.4	95	16.3 ±6.3	84	459
	Sedimentary: other	191	2.5 ± 0.5	4.8	15.4	235 ±178	437	1164	4.5 ± 1.1	5.8	25	10.3 ±2.1	26	80
	Sedimentary: sand	140	5.0 ± 1.7	5.8	26.1	100 ±74	213	585	5.0 ± 0.8	9.5	99	13.2 ±5.2	53	701
Marine deposits	Others	159	3.5 ± 1.5	5.6	17.1	194 ±119	371	984	5.0 ± 2.1	18.6	91	27.0 ±17.0	53	207
	Sedimentary: carbonates (limestone, chalk)	81	2.0 ± 0.0	3.5	5.0	10 ± 0	51	375	4.5 ± 0.6	5.0	6	10.0 ±0.4	14	31
	Sedimentary: clays and/or marls	244	2.2 ± 0.6	5.0	9.4	166 ±117	365	900	5.1 ± 1.9	14.3	48	17.2 ±7.2	38	135
	Sedimentary: other	324	3.0 ± 1.0	5.0	9.9	26 ±16	111	498	5.0 ± 0.4	5.0	13	10.0 ±2.5	16	66
	Sedimentary: sand	1689	3.0 ± 1.0	5.0	10.8	74 ±64	199	623	5.0 ± 1.0	5.6	30	11.9 ±2.7	26	99
Others	Metamorphic rocks	77	3.2 ± 1.8	5.0	14.3	20 ±10	43	205	5.0 ± 0.0	5.0	7	9.9 ±2.5	10	24
	Others	1821	2.5 ± 0.6	5.0	12.1	184 ±151	411	1110	5.0 ± 1.1	6.3	34	14.3 ±4.3	34	119
	Sedimentary: other	458	2.1 ± 0.6	5.0	7.6	50 ±40	193	821	5.0 ± 0.7	5.0	22	10.4 ±2.9	26	115
	Sedimentary: sand	20	4.3 ± 2.1	8.9	16.9	147 ±78	298	513	5.0 ± 1.3	18.3	62	17.8 ±7.8	90	184

Table 19: BRIDGE & HOVER-Redox water type

BRIDGE	Redox water type	n	As , µg/l			Mn, µg/l			Ni, µg/l			Zn, µg/l		
			median ± MAD	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*
Fluviatile deposits of major streams	A	150	2.0 ± 0.0	3.2	5.0	50 ±40	158	403	5.2 ±2.3	17.5	73	32.6 ±22.6	89	519
	B	63	2.0 ± 0.0	2.1	5.0	120 ±92	262	571	8.6 ±4.6	23.8	126	21.1 ±11.2	68	502
	C	232	5.0 ± 2.1	6.7	20.2	263 ±159	450	874	5.0 ±1.0	5.0	37	10.0 ±0.0	18	109
	D	41	5.0 ± 1.6	6.2	28.2	105 ±60	211	882	5.0 ±0.0	5.0	5	10.8 ±2.0	17	50
	X	67	2.8 ± 0.8	5.0	7.6	184 ±136	347	1103	6.1 ±2.7	29.6	266	30.7 ±20.7	116	700
Marine deposits	A	701	2.0 ± 0.0	3.5	5.0	10 ±0	32	212	5.0 ±1.0	6.3	36	12.1 ±2.1	24	123
	B	118	2.0 ± 0.0	2.0	4.7	88 ±71	175	495	5.5 ±2.0	14.5	56	17.3 ±7.3	40	172
	C	942	3.0 ± 1.5	5.0	14.3	194 ±121	380	903	5.0 ±1.0	5.0	28	12.1 ±3.0	27	87
	D	224	5.0 ± 2.0	7.2	31.4	67 ±43	133	513	5.0 ±0.0	5.0	5	10.0 ±1.4	15	42
	X	512	3.2 ± 1.2	5.0	8.5	62 ±52	171	696	5.0 ±0.9	9.5	41	13.7 ±6.2	38	129
Others	A	592	2.0 ± 0.0	3.2	5.0	29 ±19	104	481	5.0 ±1.0	7.7	33	22.0 ±12.0	49	136
	B	257	2.0 ± 0.0	2.0	5.0	84 ±66	251	721	5.0 ±1.3	8.9	45	15.1 ±5.1	29	118
	C	831	3.9 ± 1.9	5.8	16.6	302 ±17	565	1279	4.5 ±0.6	5.0	29	10.0 ±2.5	24	111
	D	162	4.7 ± 1.8	8.3	26.1	160 ±117	408	1273	4.4 ±0.6	5.0	9	10.0 ±0.0	14	42
	X	534	2.5 ± 0.7	5.0	10.0	102 ±92	304	1004	5.0 ±1.0	6.8	40	12.5 ±5.0	33	117

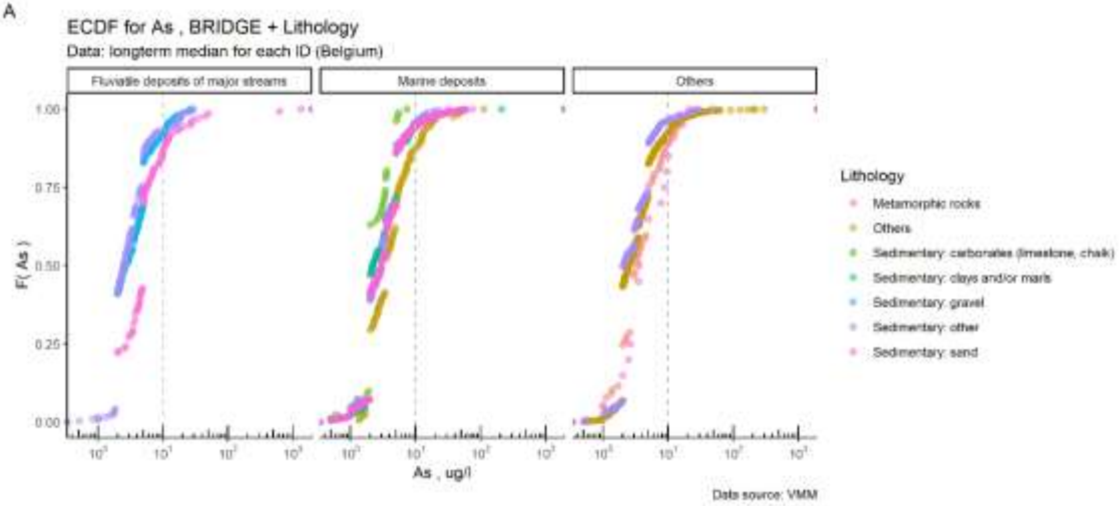
Table 20: BRIDGE & HOVER-pH (3classes)

BRIDGE	pH water types	n	As , µg/l			Mn µg/l			Ni , µg/l			Zn µg/l		
			median ± MAD	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*
Fluviatile deposits of major streams	Acidic	442	3.5 ±1.5	5.0	16.1	145 ±115	310	718	5.0 ±1.5	15.2	95.0	15.6 ±5.7	60.7	470
	Basic	107	3.0 ±1.0	5.0	7.0	235 ±179	428	937	4.0 ±0.9	4.9	5.8	10.0 ±0.0	16.1	37
	Neutral	4	2.0 ±0.0	2.8	4.7	241 ±200	448	538	4.5 ±1.2	5.4	6.2	17.9 ±9.7	27.0	30
Marine deposits	Acidic	1436	2.9 ±0.9	5.0	12.0	127 ±104	280	812	5.0 ±1.5	11.9	56.0	19.1 ±9.1	44.0	157
	Basic	1046	3.0 ±1.0	5.0	10.0	32 ±22	120	470	4.8 ±0.3	5.0	6.1	10.0 ±1.1	13.6	29
	Neutral	15	2.0 ±0.4	2.9	14.6	17 ±7	293	960	4.2 ±0.8	4.9	14.7	10.0 ±0.6	11.0	47
Others	Acidic	1252	2.1 ±0.3	5.0	14.0	163 ±141	426	1292	5.0 ±1.7	10.4	54.0	23.3 ±13.3	52.7	175
	Basic	1092	3.0 ±1.0	5.0	10.3	116 ±106	317	770	4.5 ±0.5	5.0	5.8	10.0 ±0.9	15.4	37
	Neutral	32	2.0 ±0.7	4.9	15.6	99 ±88	423	1014	4.1 ±0.8	5.0	6.2	11.0 ±1.0	28.1	49

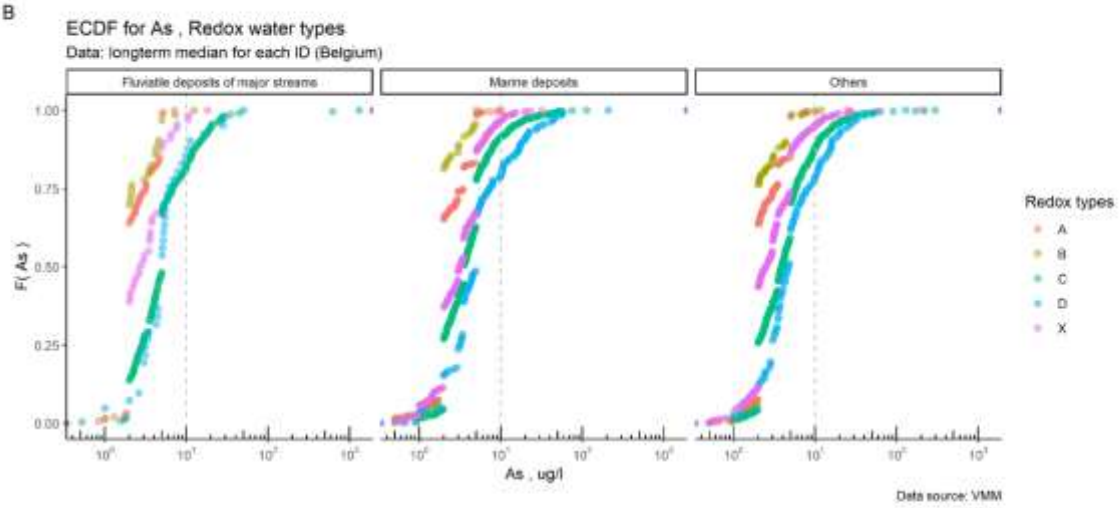
Table 21: BRIDGE and HOVER-pH (5 classes)

BRIDGE	pH water types	n	As , µg/l			Mn µg/l			Ni , µg/l			Zn µg/l		
			median ± MAD	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*	*median ± MAD*	*Q75*	*Q95*
Fluviatile deposits of major streams	Acidic	105	3.1 ±1.1	5.0	15.8	115 ±101	378	943	5.0 ±0.5	5.0	24.3	10.0 ±0.0	20.8	60
	Acidic, <DWL	337	3.5 ±1.5	5.0	16.0	152 ±111	295	625	5.9 ±2.2	21.3	115.0	22.2 ±12.2	92.0	553
	Basic	107	3.0 ±1.0	5.0	7.0	235 ±179	428	937	4.0 ±0.9	4.9	5.8	10.0 ±0.0	16.1	37
	Neutral	4	2.0 ±0.0	2.8	4.7	241 ±200	448	538	4.5 ±1.2	5.4	6.2	17.9 ±9.7	27.0	30
Marine deposits	Acidic	382	3.0 ±1.0	5.0	10.8	98 ±88	294	1487	5.0 ±0.9	5.3	13.4	14.6 ±4.6	29.6	79
	Acidic, below DWL	1054	2.9 ±0.9	5.0	12.3	133 ±104	280	727	5.4 ±2.2	15.9	73.0	21.0 ±11.0	48.9	196
	Basic	1044	3.0 ±1.0	5.0	10.	32 ±22	120	470	4.8 ±0.3	5.0	6.1	10.0 ±1.0	13.6	29
	Basic, above DWL	2	12.0 ±7.0	15.5	18.3	12 ±2	12	13	5.0 ±0.0	5.0	5.0	6.3 ±1.2	6.9	7
	Neutral	15	2.0 ±0.4	2.9	14.6	17 ±7	293	960	4.2 ±0.8	4.9	14.7	10.0 ±0.6	11.0	47
Others	Acidic	573	2.1 ±0.4	5.0	14.6	194 ±180	560	1460	5.0 ±1.0	5.5	10.6	15.2 ±5.2	33.0	81
	Acidic, below DWL	679	2.0 ±0.3	5.0	13.9	142 ±113	336	954	8.1 ±4.1	21.4	75.0	36.0 ±25.0	80.0	308
	Basic	1083	3.0 ±1.0	5.0	10.1	118 ±108	320	770	4.5 ±0.5	5.0	5.8	10.0 ±0.9	15.5	37
	Basic, above DWL	9	5.0 ±2.0	5.0	14.9	10 ±0	10	11	5.0 ±0.0	5.0	5.1	7.5 ±2.5	10.0	13
	Neutral	32	2.0 ±0.7	4.9	15.6	99 ±89	423	1014	4.1 ±0.8	5.0	6.2	11.0 ±1.0	28.1	49

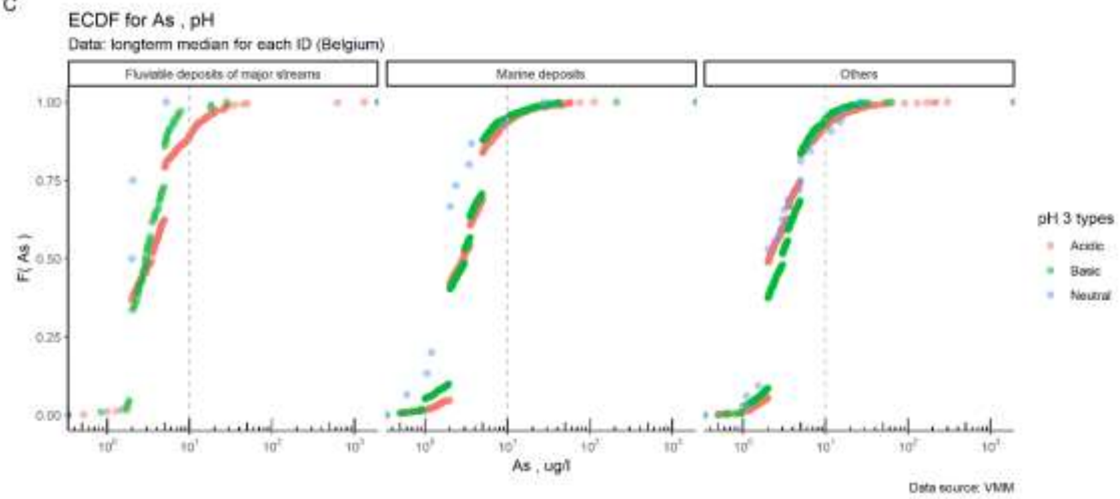
A


ECDF for As , BRIDGE + Lithology
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
F(As)
1.00
0.75
0.50
0.25
0.00
10^0
10^1
10^2
10^3
As , ug/l
Lithology
Metamorphic rocks
Others
Sedimentary: carbonates (limestone, chalk)
Sedimentary: clays and/or marls
Sedimentary: gravel
Sedimentary: other
Sedimentary: sand
Data source: VMM

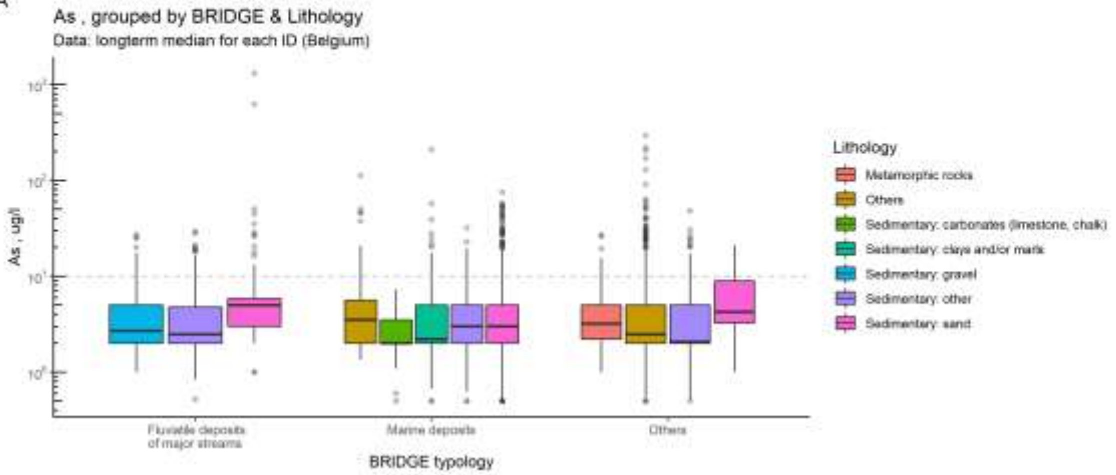
B


ECDF for As , Redox water types
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
F(As)
1.00
0.75
0.50
0.25
0.00
10^0
10^1
10^2
10^3
As , ug/l
Redox types
A
B
C
D
X
Data source: VMM

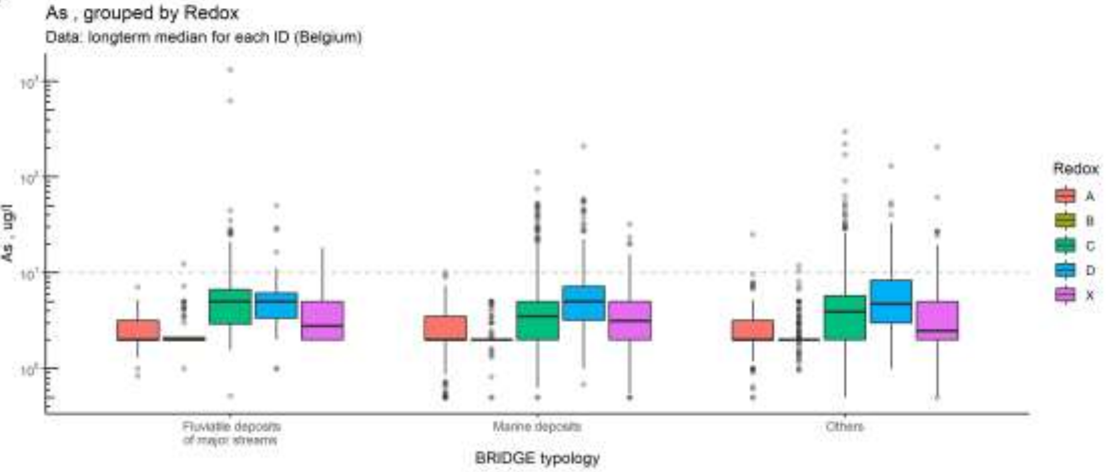
C


ECDF for As , pH
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
F(As)
1.00
0.75
0.50
0.25
0.00
10^0
10^1
10^2
10^3
As , ug/l
pH 3 types
Acidic
Basic
Neutral
Data source: VMM

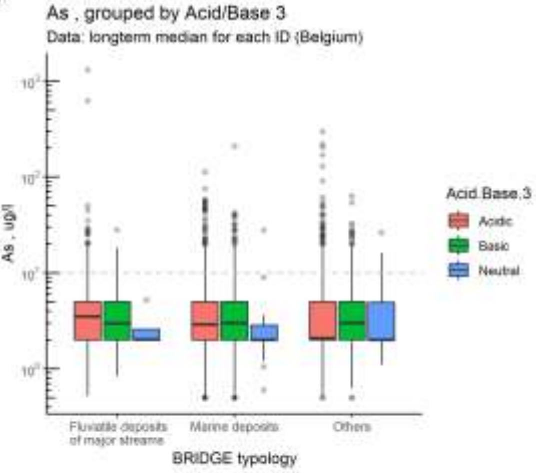
A


As , grouped by BRIDGE & Lithology
Data: longterm median for each ID (Belgium)
As , ug/l
10^3
10^2
10^1
10^0
Fluviatile deposits of major streams
Marine deposits
Others
BRIDGE typology
Lithology
Metamorphic rocks
Others
Sedimentary: carbonates (limestone, chalk)
Sedimentary: clays and/or marls
Sedimentary: gravel
Sedimentary: other
Sedimentary: sand

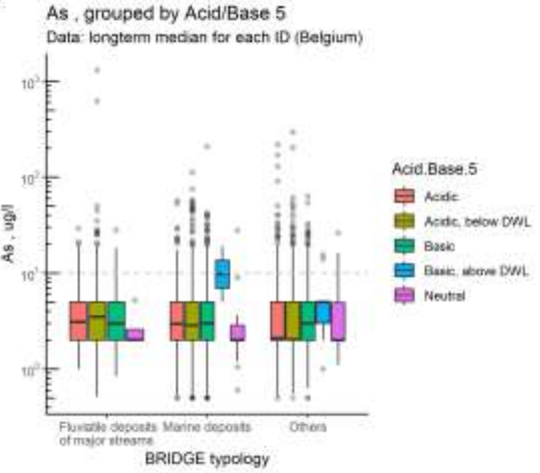
B


As , grouped by Redox
Data: longterm median for each ID (Belgium)
As , ug/l
10^3
10^2
10^1
10^0
Fluviatile deposits of major streams
Marine deposits
Others
BRIDGE typology
Redox
A
B
C
D
X

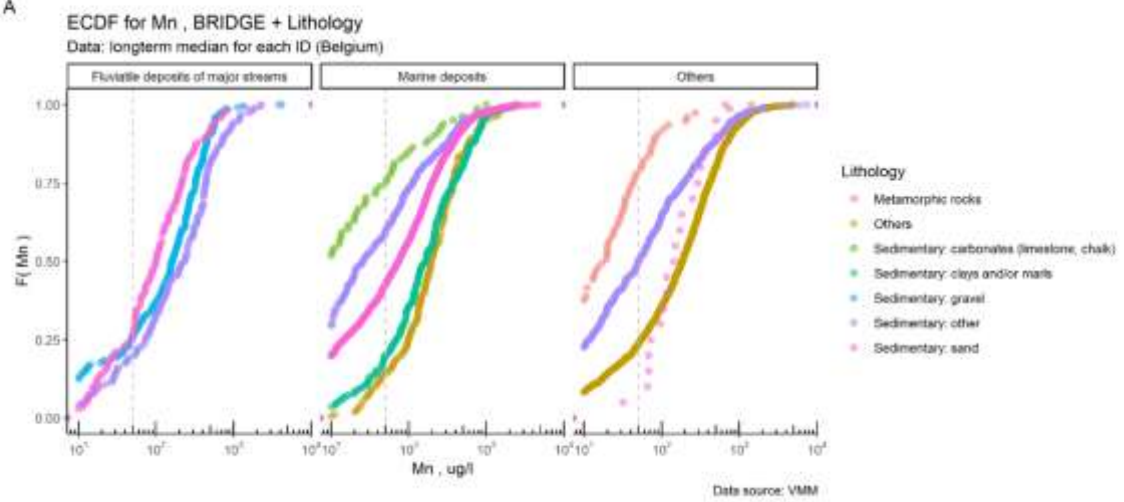
C


As , grouped by Acid/Base 3
Data: longterm median for each ID (Belgium)
As , ug/l
10^3
10^2
10^1
10^0
Fluviatile deposits of major streams
Marine deposits
Others
BRIDGE typology
Acid.Base.3
Acidic
Basic
Neutral

D

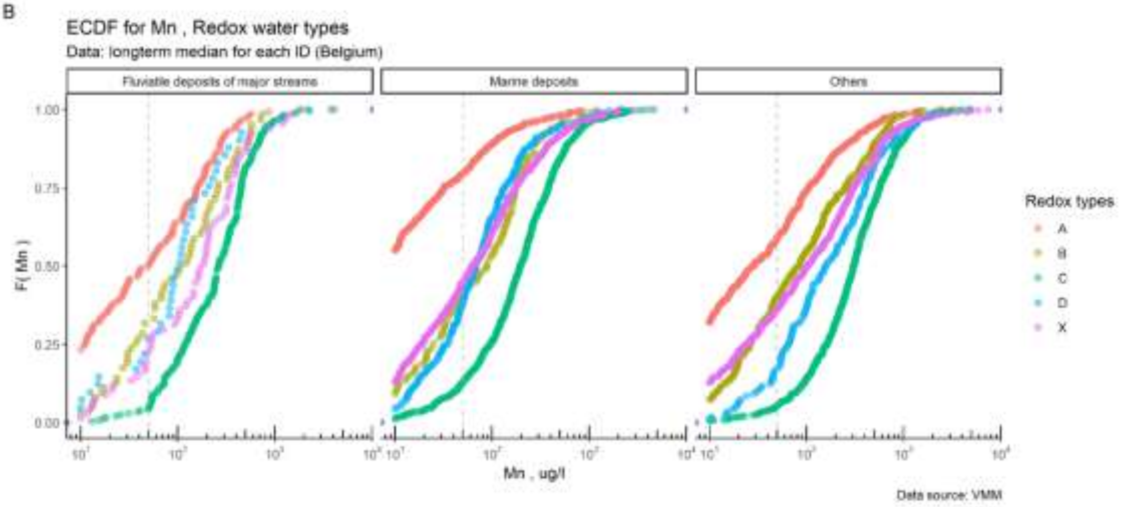

As , grouped by Acid/Base 5
Data: longterm median for each ID (Belgium)
As , ug/l
10^3
10^2
10^1
10^0
Fluviatile deposits of major streams
Marine deposits
Others
BRIDGE typology
Acid.Base.5
Acidic
Acidic, below DWL
Basic
Basic, above DWL
Neutral

A



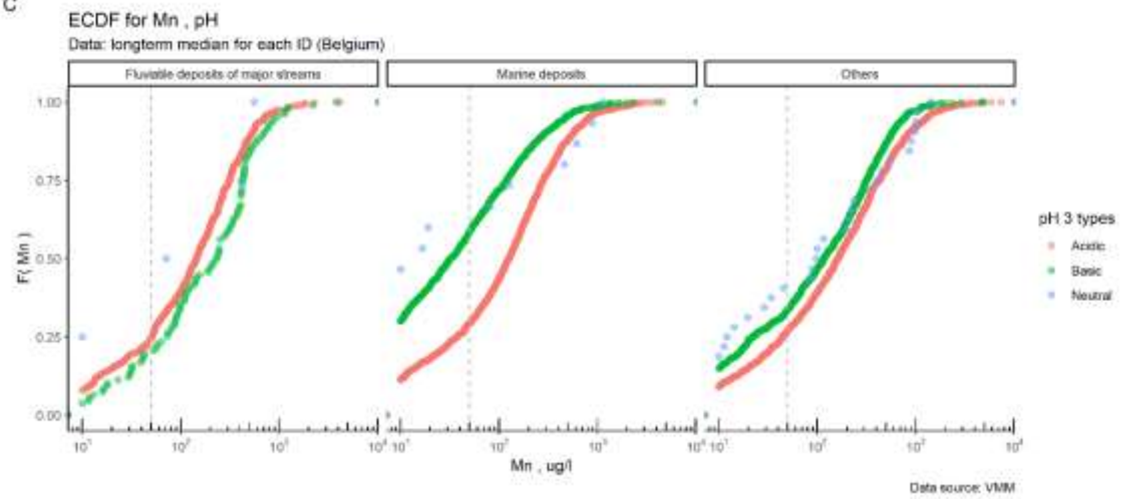
ECDF for Mn , BRIDGE + Lithology
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
F(Mn)
1.00
0.75
0.50
0.25
0.00
Mn , ug/l
Lithology
Metamorphic rocks
Others
Sedimentary: carbonates (limestone, chalk)
Sedimentary: clays and/or marls
Sedimentary: gravel
Sedimentary: other
Sedimentary: sand
Data source: VMM

B



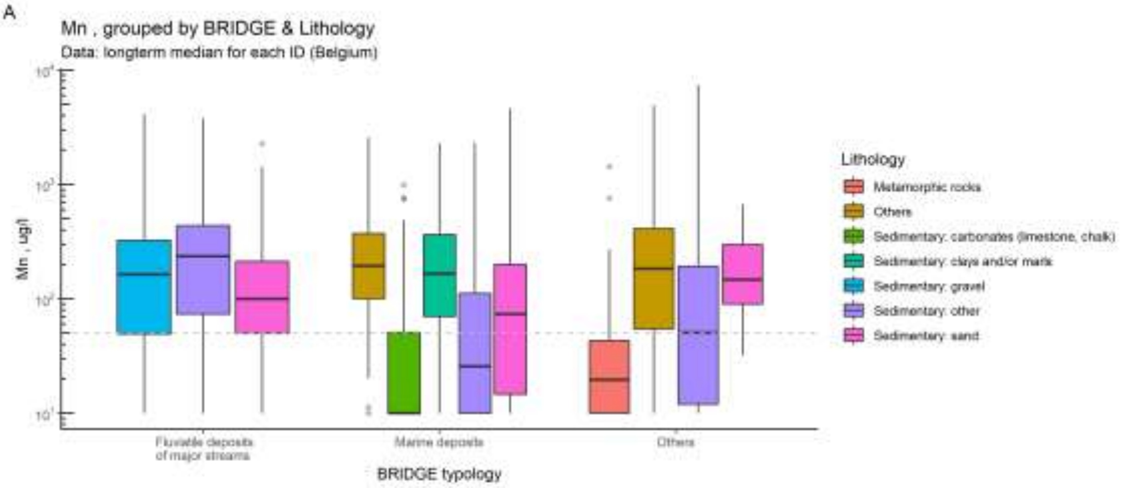
ECDF for Mn , Redox water types
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
F(Mn)
1.00
0.75
0.50
0.25
0.00
Mn , ug/l
Redox types
A
B
C
D
X
Data source: VMM

C

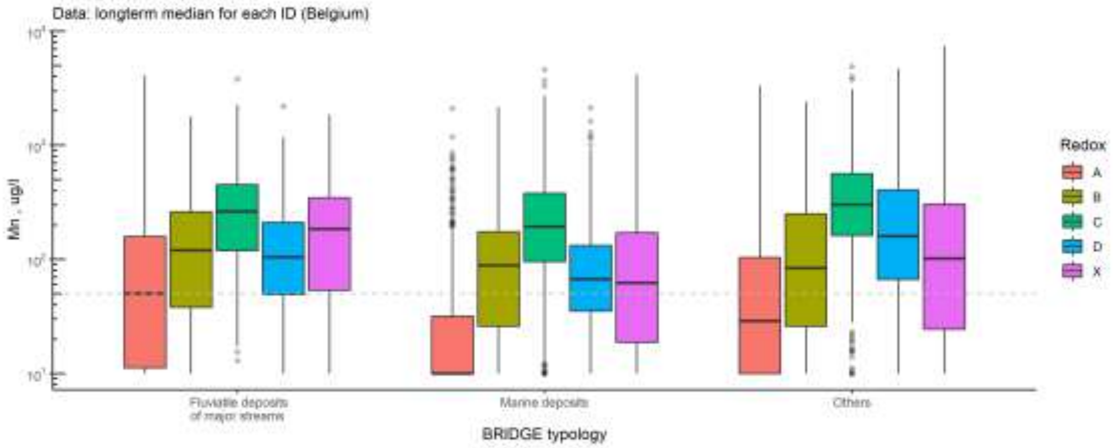


ECDF for Mn , pH
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
F(Mn)
1.00
0.75
0.50
0.25
0.00
Mn , ug/l
pH 3 types
Acidic
Basic
Neutral
Data source: VMM

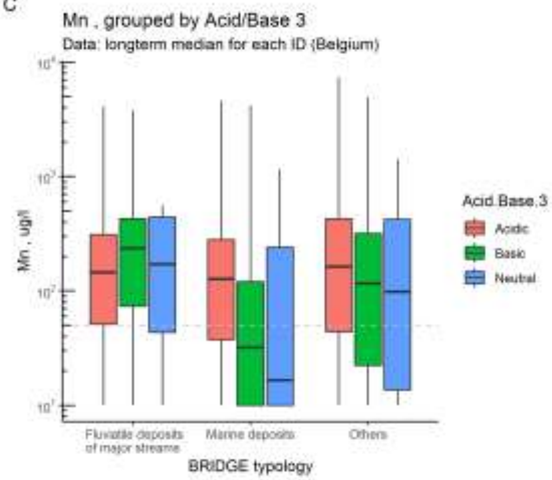
A


Mn , grouped by BRIDGE & Lithology
Data: longterm median for each ID (Belgium)
Mn , ug/l
10^1
10^2
10^3
10^4
Fluviatile deposits of major streams
Marine deposits
Others
BRIDGE typology
Lithology
Metamorphic rocks
Others
Sedimentary: carbonates (limestone, chalk)
Sedimentary: clays and/or marls
Sedimentary: gravel
Sedimentary: other
Sedimentary: sand

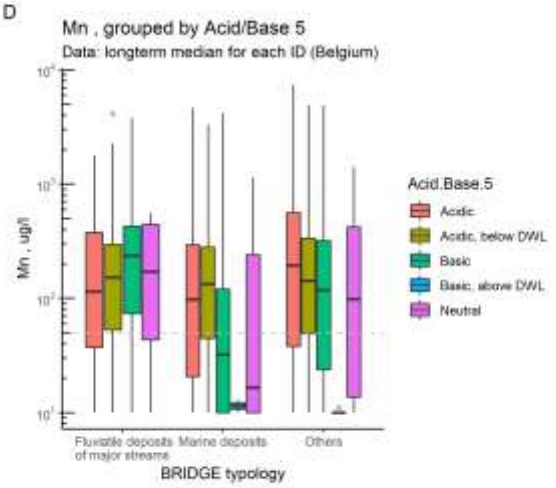
B


Mn , grouped by Redox
Data: longterm median for each ID (Belgium)
Mn , ug/l
10^1
10^2
10^3
10^4
Fluviatile deposits of major streams
Marine deposits
Others
BRIDGE typology
Redox
A
B
C
D
X

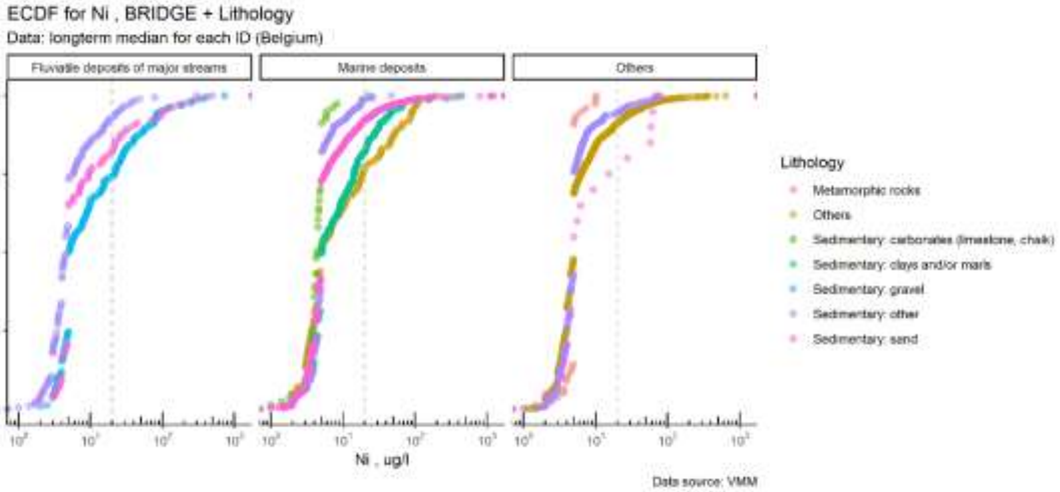
C


Mn , grouped by Acid/Base 3
Data: longterm median for each ID (Belgium)
Mn , ug/l
10^1
10^2
10^3
10^4
Fluviatile deposits of major streams
Marine deposits
Others
BRIDGE typology
Acid.Base.3
Acidic
Basic
Neutral

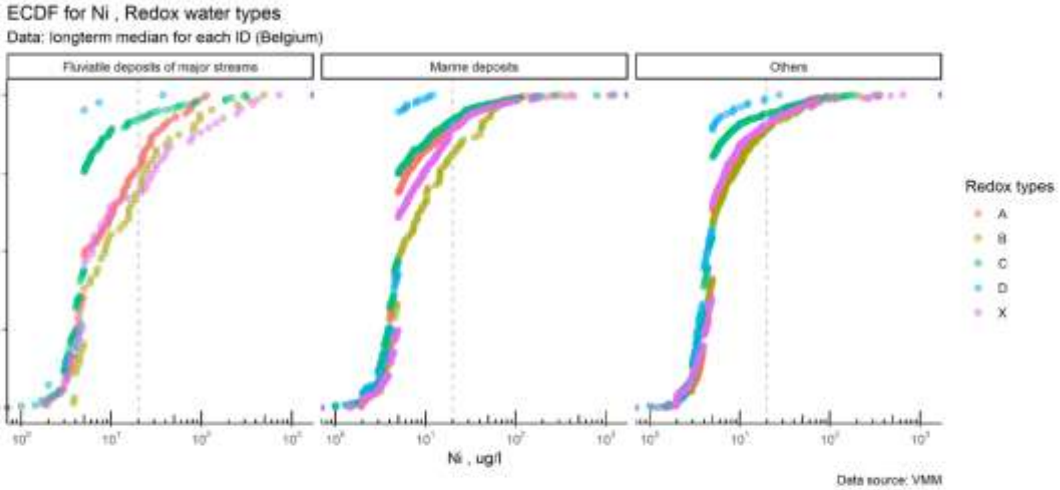
D


Mn , grouped by Acid/Base 5
Data: longterm median for each ID (Belgium)
Mn , ug/l
10^1
10^2
10^3
10^4
Fluviatile deposits of major streams
Marine deposits
Others
BRIDGE typology
Acid.Base.5
Acidic
Acidic, below DWL
Basic
Basic, above DWL
Neutral

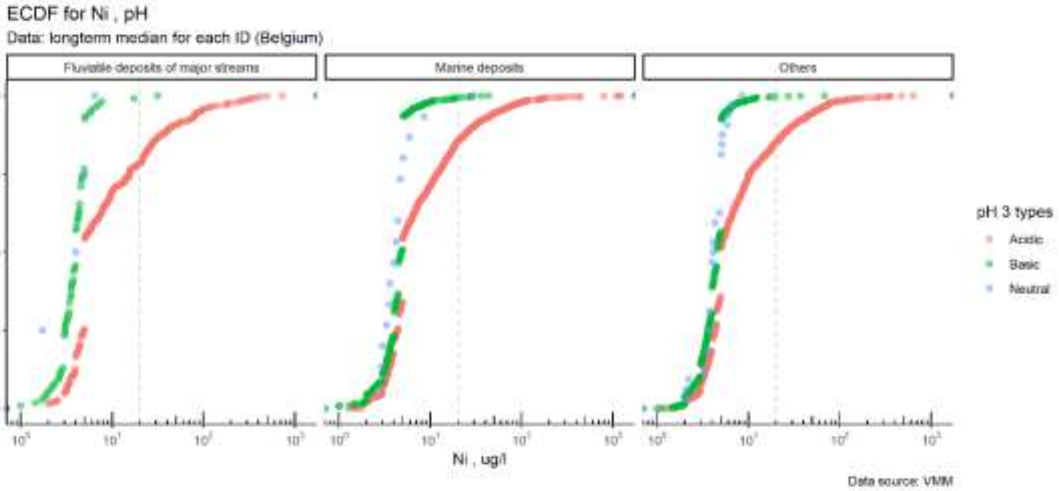
A

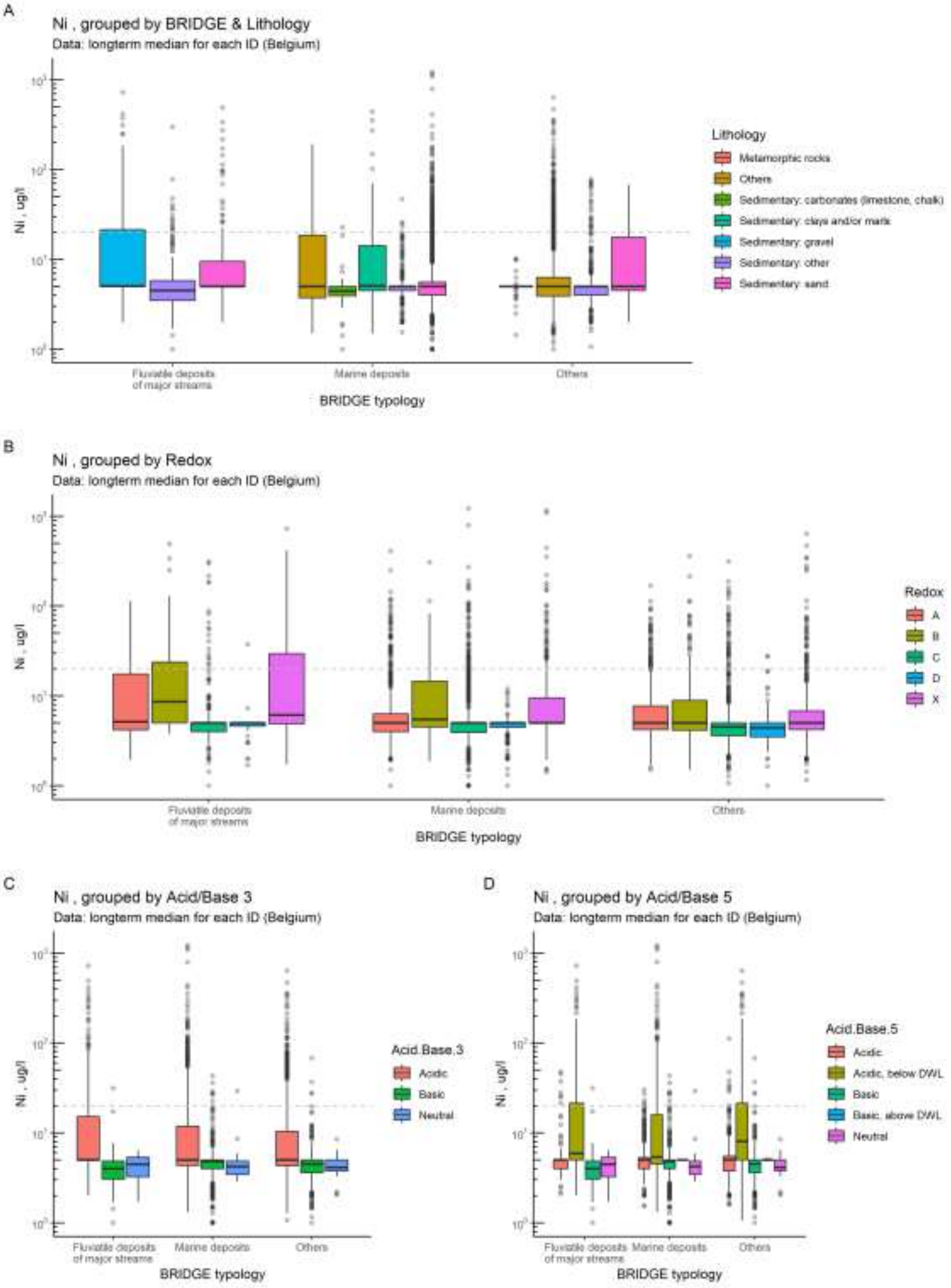

ECDF for Ni , BRIDGE + Lithology
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
F(Ni)
1.00
0.75
0.50
0.25
0.00
Ni , ug/l
Lithology
Metamorphic rocks
Others
Sedimentary: carbonates (limestone, chalk)
Sedimentary: clays and/or marls
Sedimentary: gravel
Sedimentary: other
Sedimentary: sand
Data source: VMM

B

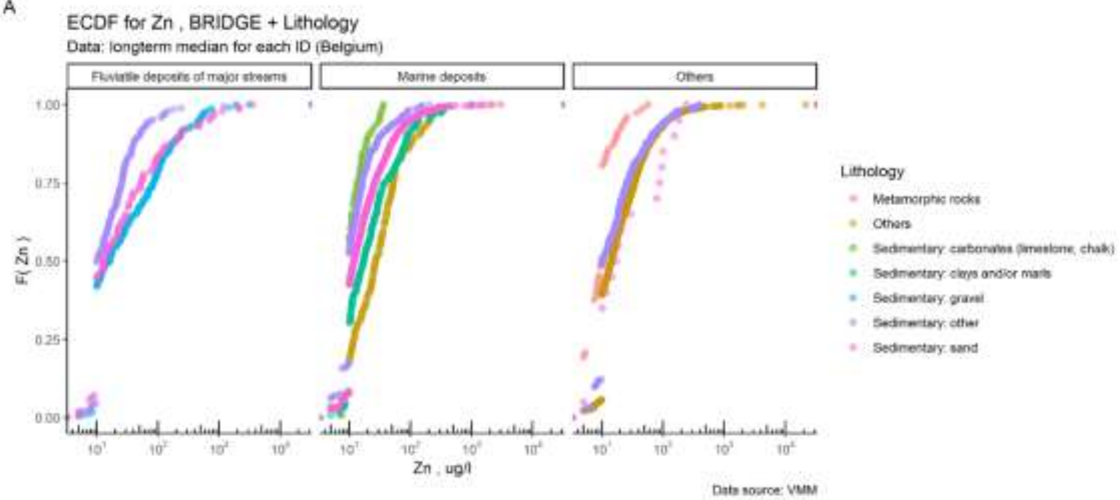

ECDF for Ni , Redox water types
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
F(Ni)
1.00
0.75
0.50
0.25
0.00
Ni , ug/l
Redox types
A
B
C
D
X
Data source: VMM

C

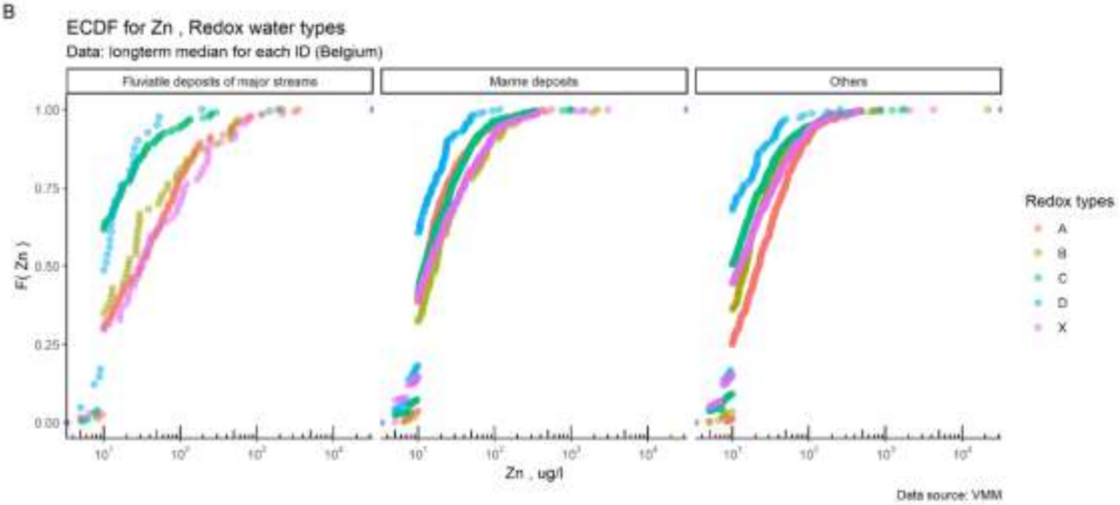

ECDF for Ni , pH
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
F(Ni)
1.00
0.75
0.50
0.25
0.00
Ni , ug/l
pH 3 types
Acidic
Basic
Neutral
Data source: VMM


A
Ni , grouped by BRIDGE & Lithology
Data: longterm median for each ID (Belgium)
Ni , ug/l
10^0
10^1
10^2
10^3
Fluviatile deposits of major streams
Marine deposits
Others
BRIDGE typology
Lithology
Metamorphic rocks
Others
Sedimentary: carbonates (limestone, chalk)
Sedimentary: clays and/or marls
Sedimentary: gravel
Sedimentary: other
Sedimentary: sand
B
Ni , grouped by Redox
Data: longterm median for each ID (Belgium)
Ni , ug/l
Fluviatile deposits of major streams
Marine deposits
Others
BRIDGE typology
Redox
A
B
C
D
X
C
Ni , grouped by Acid/Base 3
Data: longterm median for each ID (Belgium)
Ni , ug/l
Fluviatile deposits of major streams
Marine deposits
Others
BRIDGE typology
Acid.Base.3
Acidic
Basic
Neutral
D
Ni , grouped by Acid/Base 5
Data: longterm median for each ID (Belgium)
Ni , ug/l
Fluviatile deposits of major streams
Marine deposits
Others
BRIDGE typology
Acid.Base.5
Acidic
Acidic, below DWL
Basic
Basic, above DWL
Neutral

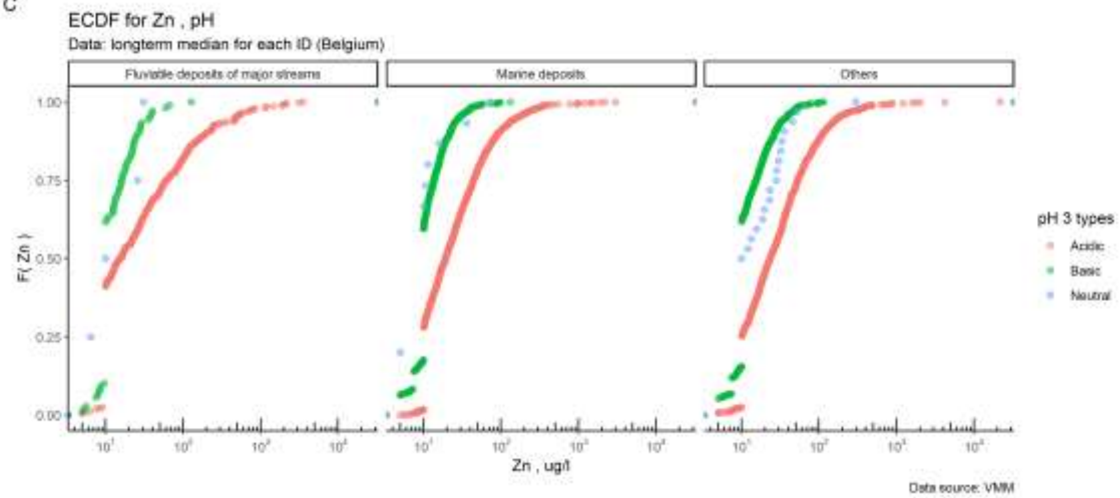
A


ECDF for Zn , BRIDGE + Lithology
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
F(Zn)
1.00
0.75
0.50
0.25
0.00
10^1
10^2
10^3
10^4
Zn , ug/l
Lithology
Metamorphic rocks
Others
Sedimentary: carbonates (limestone, chalk)
Sedimentary: clays and/or marls
Sedimentary: gravel
Sedimentary: other
Sedimentary: sand
Data source: VMM

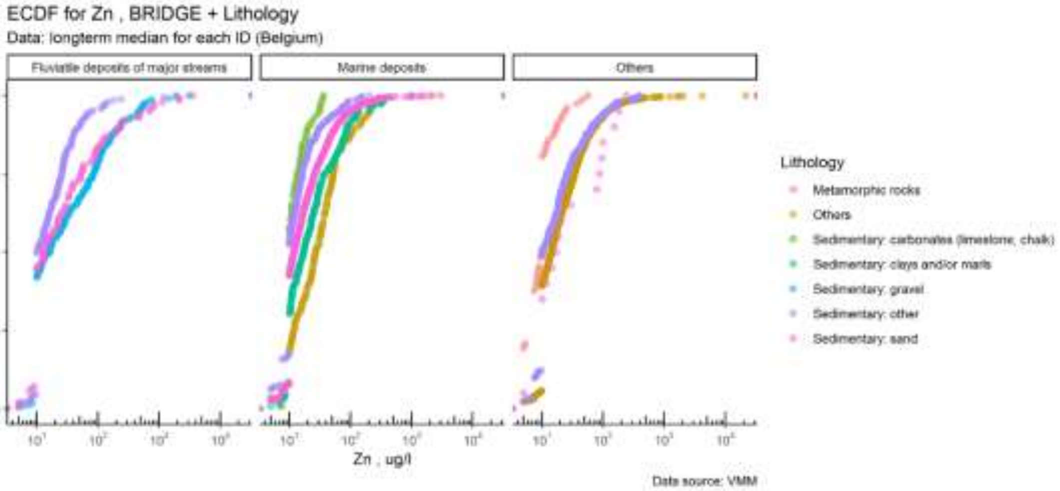
B


ECDF for Zn , Redox water types
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
F(Zn)
1.00
0.75
0.50
0.25
0.00
10^1
10^2
10^3
10^4
Zn , ug/l
Redox types
A
B
C
D
X
Data source: VMM

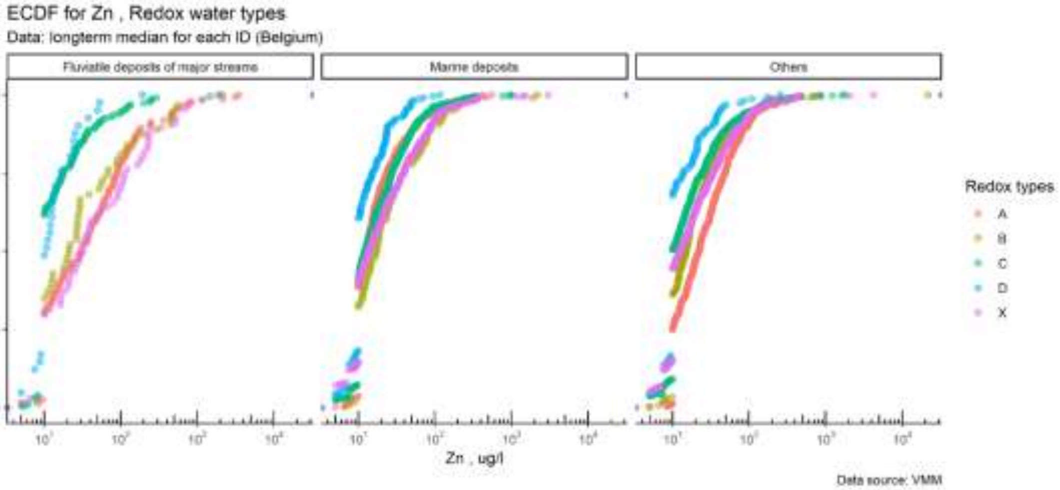
C


ECDF for Zn , pH
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
F(Zn)
1.00
0.75
0.50
0.25
0.00
10^1
10^2
10^3
10^4
Zn , ug/l
pH 3 types
Acidic
Basic
Neutral
Data source: VMM

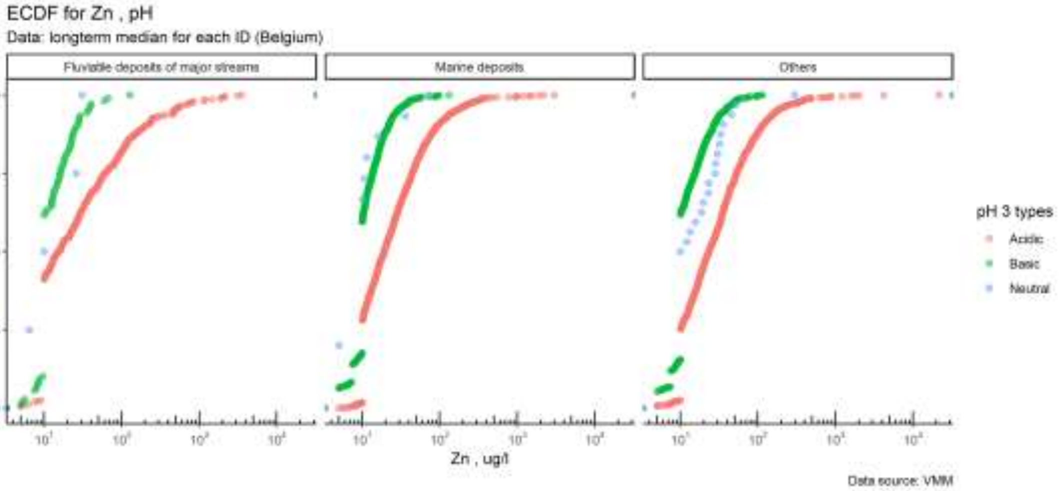
A

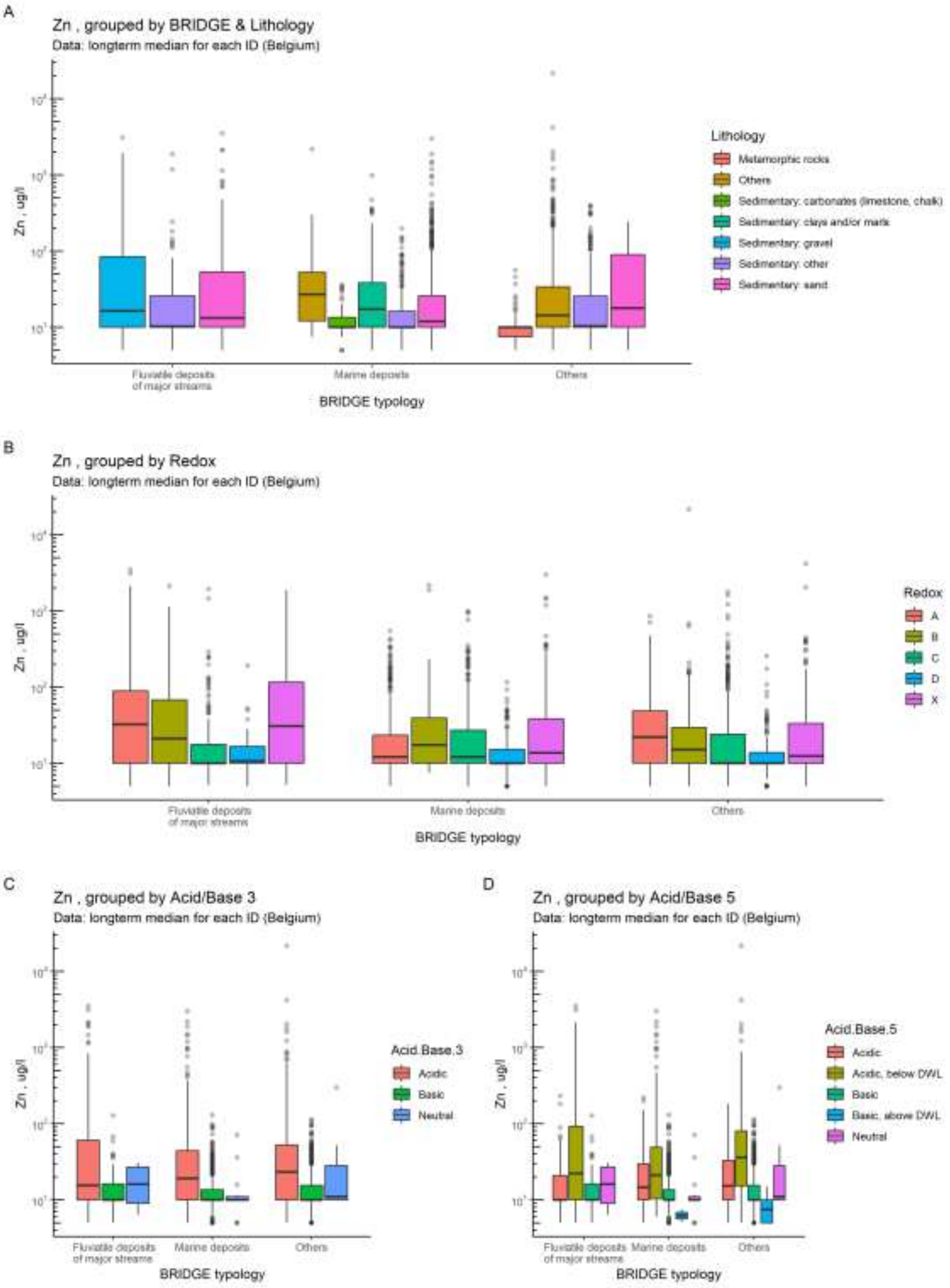

ECDF for Zn , BRIDGE + Lithology
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
1.00
0.75
0.50
0.25
0.00
F(Zn)
10^1
10^2
10^3
10^4
Zn , ug/l
Lithology
Metamorphic rocks
Others
Sedimentary: carbonates (limestone, chalk)
Sedimentary: clays and/or marls
Sedimentary: gravel
Sedimentary: other
Sedimentary: sand
Data source: VMM

B


ECDF for Zn , Redox water types
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
1.00
0.75
0.50
0.25
0.00
F(Zn)
10^1
10^2
10^3
10^4
Zn , ug/l
Redox types
A
B
C
D
X
Data source: VMM

C


ECDF for Zn , pH
Data: longterm median for each ID (Belgium)
Fluviatile deposits of major streams
Marine deposits
Others
1.00
0.75
0.50
0.25
0.00
F(Zn)
10^1
10^2
10^3
10^4
Zn , ug/l
pH 3 types
Acidic
Basic
Neutral
Data source: VMM


A
Zn , grouped by BRIDGE & Lithology
Data: longterm median for each ID (Belgium)
Zn , ug/l
BRIDGE typology
Fluviatile deposits of major streams
Marine deposits
Others
Lithology
Metamorphic rocks
Others
Sedimentary: carbonates (limestone, chalk)
Sedimentary: clays and/or marls
Sedimentary: gravel
Sedimentary: other
Sedimentary: sand
B
Zn , grouped by Redox
Data: longterm median for each ID (Belgium)
Zn , ug/l
BRIDGE typology
Fluviatile deposits of major streams
Marine deposits
Others
Redox
A
B
C
D
X
C
Zn , grouped by Acid/Base 3
Data: longterm median for each ID (Belgium)
Zn , ug/l
BRIDGE typology
Fluviatile deposits of major streams
Marine deposits
Others
Acid.Base.3
Acidic
Basic
Neutral
D
Zn , grouped by Acid/Base 5
Data: longterm median for each ID (Belgium)
Zn , ug/l
BRIDGE typology
Fluviatile deposits of major streams
Marine deposits
Others
Acid.Base.5
Acidic
Acidic, below DWL
Basic
Basic, above DWL
Neutral

APPENDIX 3 – DATA COLLECTION QUESTIONNAIRE

This questionnaire for data collection was conceived during a two-day workshop for tasks 3-2 (lead: GEUS) and 3-3 (lead: BRGM) and send to five HOVER WP3-partners (MBFSZ, GSS, GSI, VMM, and IGME). It consists of an e-mail with questions and a spreadsheet template for data collection.

E-mail:

Dear HOVER WP3 participants,
In tasks 3-2 and 3-3, we will work with data on a European scale. To start with, we are going to use data from selected pilot areas with groundwater quality monitoring, to define lithological/geological water families. For this, we need your help and data!
Please reply to the questions below and fill in the attached Excel template **by April 8th**. Should your data not fit in an Excel file, please contact us, as well if you have any questions.
Pilot areas:

- Belgium
- Hungary
- Ireland
- Serbia
- Spain [added later]

What would we like from you?

1. Please fill out the Excel sheet with the measurement points in your pilot areas and groundwater chemistry. Please choose from the supplied list of answers, if a list is given. Below are explanations for some of the variables you have to fill in:
    a. Have you applied the BRIDGE methodology to determine aquifer typologies for hydrogeochemical characterization? If yes, please enter it in the Excel file under **Aquifer Typology (BRIDGE)**
    b. If no, do you use another method to classify aquifer typologies? If yes, please explain it here and enter the class in the Excel file under **Aquifer Typology (other than BRIDGE)**
    c. **Signs of anthropogenic influence**: if there has been a detection of pesticides or any other anthropogenic pollutants at the sampling point, please answer yes, otherwise no
    d. Do you have data on solid analyses of mineralogical contents at the measurement points? If yes, please fill in the Excel sheet **Minerals**

2. Do you have GIS files (e.g. shapefiles) of the pilot area, the measurement points, and/or hydrogeological groups? If yes, please provide them.

3. Do you have data on anthropogenic pressures (diffuse or point pollution) in the pilot areas?
    a. GIS files
    b. Input from agricultural pressure
    c. Input from industrial activities more specifically mining
    d. Input from urban influence/pressure
    e. Do you have a database linking specific activities to pollutants?

Main spreadsheet

ID of the measuring point	free text
Type	spring, borehole,well
Sample Date	date
X coordinate	number
Y coordinate	number
Coordinate System	text, e.g. UTM32N
Depth of the measuring point	number
Aquifer Typology (BRIDGE)	select from list
Aquifer Typology (other than BRIDGE)	free text
Lithology	select from list
Flow media	select from list
Deposition type	select from list
Age/stratifigraphy	select from list
Aquifer type	confined, semi-confined, unconfined
Signs of anthropogenic influence	yes/no
Redox conditions	oxic, reduced, mixed, unknown
Recharge	mm/year
Recharge (approx)	select from list
Hydraulic conductivity	m/s
Concentrations of the following	**(in correct units)**
Oxygen	mg/L
Nitrate (NO3-)	mg/L
Nitrite (NO2-)	mg/L
Pesticides (sum)	µg/L
Na	mg/L
Mg	mg/L
Ca	mg/L
K	mg/L
SO4	mg/L
HCO3	mg/L
P total	mg/L
ortho-P	mg/L
pH	-
Eh NHE	mV
Conductivity	mS/cm
TDS	mg/L
Temperature	°C
Al	µg/L
Sb	µg/L
As	µg/L
Ba	µg/L
B	µg/L
Br	µg/L
Cd	µg/L
Cr	µg/L
Cu	µg/L
F	µg/L
I	µg/L
Fe	µg/L
Pb	µg/L
Li	µg/L
Mn	µg/L
Hg	µg/L
Ni	µg/L
Se	µg/L
Sr	µg/L
U	µg/L
V	µg/L
Zn	µg/L

Sheet: Minerals

- ID of the measuring point
- Calcite
- Barite
- Pyrite
- Dolomite
- Salts (gypsum, halite, etc.)
- Silica
- Cerusite
- Cuprite
- Fluorite
- Fluoroapatite
- Sphalerite
- Senarmontite
- Chalcocite
- Siderite
- Others minerals identifed: please add here

Classification lists

BRIDGE

- Karstic limestones
- Limestones and interbedded silicatic/carbonate-rocks
- Limestones of mountaineuos areas
- Paleozoic limestones
- Chalk
- Volcanic rocks
- Crystalline rocks
- Schists and shales
- Sands with saline/brackish water
- Glacial sand and gravel deposits
- Fluviatile deposits of major streams
- Marine deposits
- Triassic sandstones
- Sandstones and silicatic alternating sequences
- Marls and clays
- Others
- Unknown

Lithology

- Sedimentary: sand
- Sedimentary: gravel
- Sedimentary: carbonates (limestone, chalk)
- Sedimentary: clays and/or marls
- Sedimentary: other
- Volcanic rocks
- Crystalline bedrock
- Metamorphic rocks
- Others
- Unknown

Deposition type
Marine
Fresh water
Glacial
Aerial (e.g. loess)
Others
Unknown

Age/stratigraphy
Quaternary
Cenozoic/Tertiary
Mesozoic (Cretaceous, Jurassic, Triassic)
Paleozoic
Others

Type
Spring
borehole
well
other

Aquifer
confined
semi-confined
unconfined
unknown

Redox
oxic
reduced
mixed
unknown

Flow media
matrix
fractured
mixed
karst

Recharge
<100 mm
100-300 mm
300-800 mm
800-1500 mm
>1500 mm