# Hydrogeochemical characteristics of groundwater in Latvia using multivariate statistical analysis

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## HYDROGEOLOGICAL SETTING

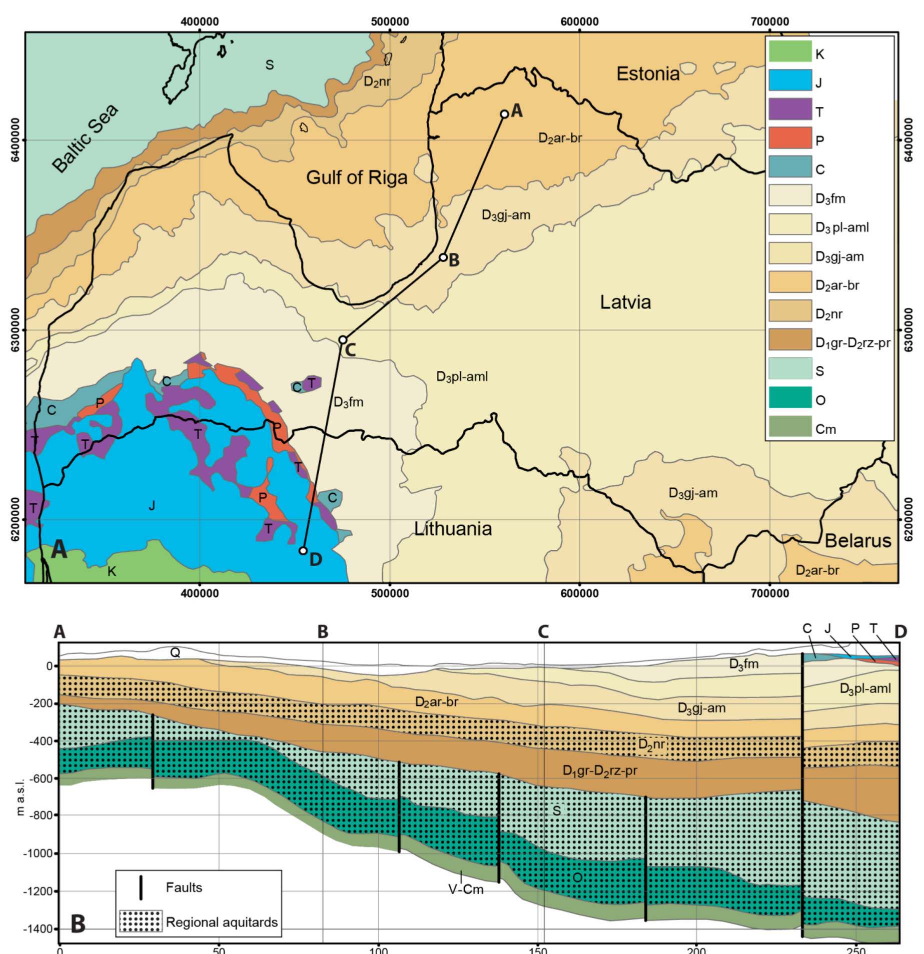

**Figure 1.** Geological map and geological cross-section of the study region without Quaternary cover (modified after Popovs *et al.* in print; Virbulis *et al.* 2013).

Location of cross-section indicated in A. *V-Cm - Ediacaran- Cambrian sequence; O- Ordovician sequence; S- Silurian sequence;* $D_1$*gr-*$D_2$*rz-pr- lower Devonian Gargzdu Fm to middle Devonian Parnu Fm;* $D_2$*nr- middle Devonian Narva formation;* $D_2$*ar-br- middle Devonian Burnieki Fm to Arukila Fm;* $D_3$*gj-am upper Devonian Gauja Fm to Amata Fm;* $D_3$*fm- upper Devonian Famena Fm; C- Carboniferous sequence; P- Permian sequence; T- Triassic sequence; J- Jurassic sequence; K- Cretaceous sequence.*

The study area covers the **central part of the Baltic Artesian Basin.** The thickness of the sedimentary cover varies from about 500m in northern part to more than 2000m in southwestern part of Latvia.

Three hydrodynamical and hydrochemical zones of groundwater are traditionally identified within study area (Figure 1):

- **stagnation zone**- Ediacaran- Cambrian aquifer complex with brines;
- **passive (slow) water exchange zone** - lower and middle Devonian aquifer complex with brackish groundwater;
- **active water exchange zone**- freshwater aquifers above Narva regional aquitard.

## MATERIALS AND METHODS

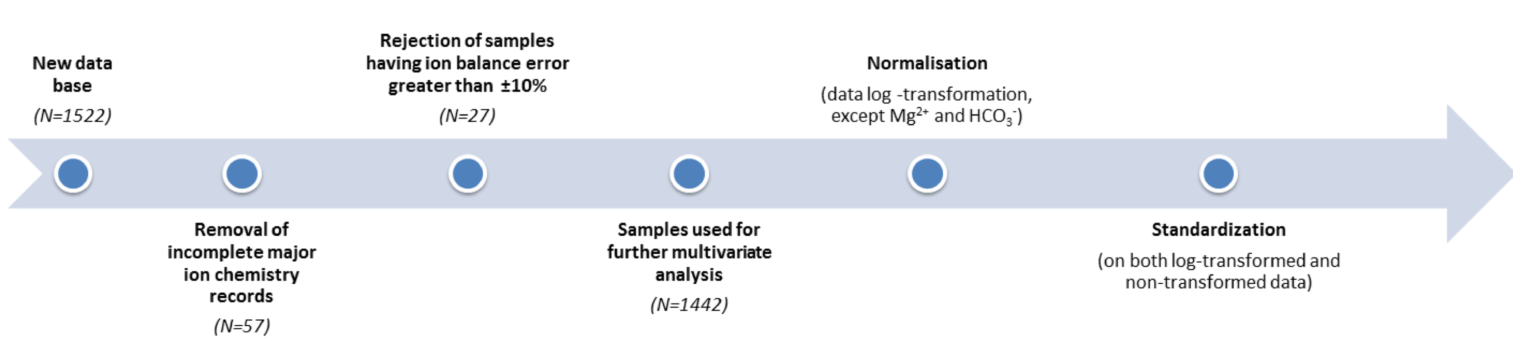


**Figure 2.** Data preparation for multivariate statistical analysis.

Groundwater hydrochemical groups were defined using **hierarchical cluster analysis (HCA)** and **principal component analysis (PCA).** For HCA Euclidean distance as a similarity measure and Ward's method as a linkage method were used. For PCA Varimax rotation was used.

Data pre-treatment, PCA and HCA were performed using SPSS Statistics 22. Electrical balances and saturation indices of calcite, dolomite, gypsum and halite minerals were calculated using software PHREEQC, version 3.

## RESULTS

### HIERARCHICAL CLUSTER ANALYSIS

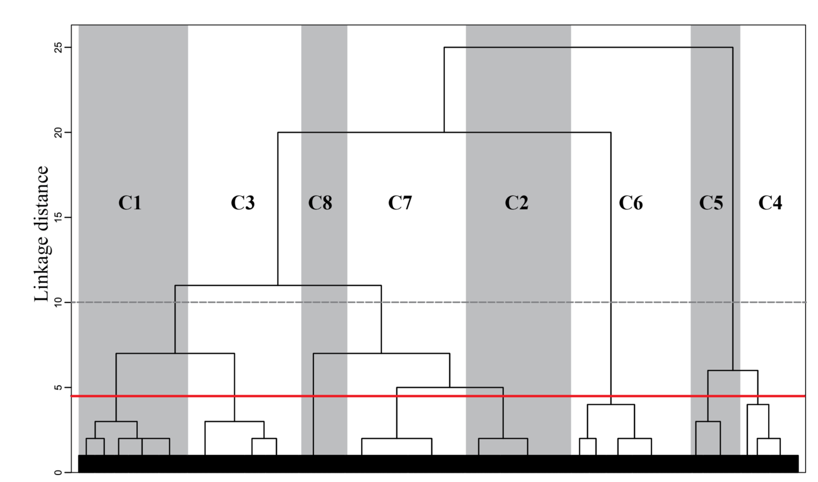


**Figure 3.** Dendrogram from hierarchical cluster analysis showing division of groundwater samples. Dashed line reflects four major divisions and red line reflects the eight distributed clusters for further analysis.

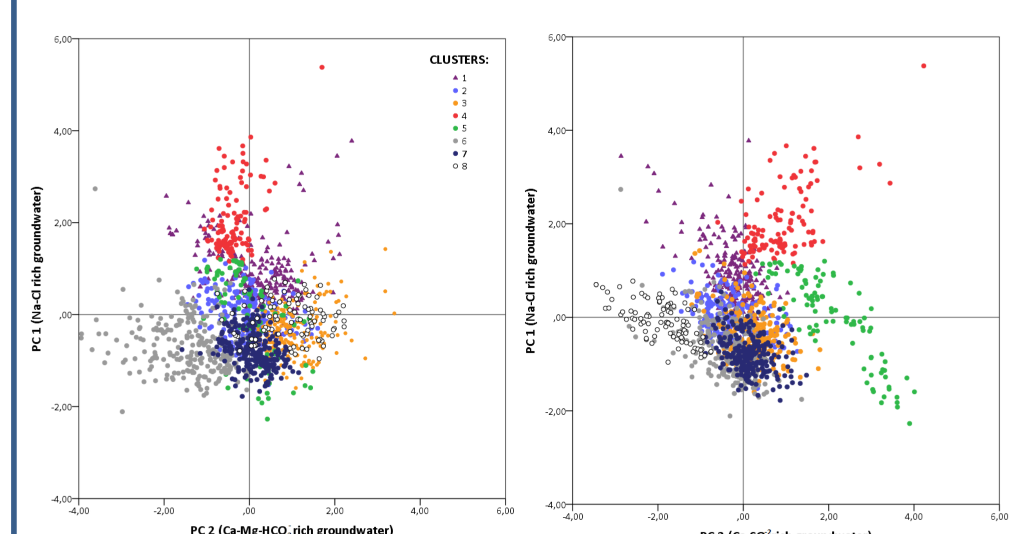

**Figure 4.** Plot of loadings from PCA for the first and second and first and third PCs. Groundwater samples are grouped according to their clusters from HCA.

### PRINCIPAL COMPONENT ANALYSIS

**Table 1.**
Principal component loadings and explained variance for three components with Varimax rotation.

| Parameter | PC 1 | PC 2 | PC 3 |
|---|---|---|---|
| $Ca^{2+}$ | 0.17 | **0.65** | **0.67** |
| $Mg^{2+}$ | 0.52 | **0.63** | 0.43 |
| $Na^{+}$ | **0.92** | 0.10 | 0.18 |
| $K^{+}$ | **0.82** | 0.14 | 0.12 |
| $HCO_3^-$ | 0.01 | **0.93** | -0.14 |
| $Cl^-$ | **0.78** | 0.00 | 0.38 |
| $SO_4^{2-}$ | 0.33 | -0.10 | **0.88** |
| **Eigenvalue** | 3.7 | 1.4 | 0.8 |
| **Explained variance (%)** | 52.7 | 20.1 | 11.3 |
| **Cumulative % of variance** | 52.7 | 72.7 | 84.0 |

**PC 1** reflects the Na-Cl rich groundwater. This type of water is generally found starting from middle-lower Devonian aquifers till Cambrian aquifer. Na-Cl rich groundwater also can be a result of freshwater mixing with saline water in fracture zones and with seawater close to the coastline.

**PC 2** is defined as Ca-Mg-$HCO_3$ water type and is the most common groundwater type in active water exchange zone.

**PC 3** account for gypsum dissolution process and reflects Ca-$SO_4$ water type. This type of water is characteristic to areas where gypsum is encountered in upper and lower Devonian aquifers, however, is also found in other parts of the active water exchange zone.

## MOTIVATION

The main objective was to examine characteristic trace elements in each of the distributed groundwater groups and to propose an insight in major geochemical processes responsible for evolution of each group.

**Table 2.**
Main geochemical and hydrogeological characteristics of each cluster.

| Cluster (sample size) |  | Positive PC scores | Average depth, (m) | Aquifer material | Dominant aquifers | Average TDS, (mg/l) | Characteristic parameters |
|---|---|---|---|---|---|---|---|
| **C1 (N=218)** | ▲ (purple) | PC1 and PC2 | 4–100 | sandstone, sand, dolomite, till | Q, $D_3$gj, middle Devonian | 520–700 | elevated Br |
| **C2 (N=213)** | ● (blue) | PC2; PC1 or PC3 | 4–90 | sandstone, sand, dolomite | Q, $D_3$gj, middle Devonian | 400–500 | elevated K/Na ratios |
| **C3 (N=223)** | ● (orange) | PC2 and PC3 or PC2 and PC1 | 2–7 | till, sand, dolomite | Q, $D_3$pl-slp | 570–750 | elevated $NO_3^-$, Mn, U |
| **C4 (N=115)** | ● (red) | PC1 and PC3 | 65–170 | sandstone | middle and lower Devonian | 780–1520 | high B, Br, Rb, Sb, Se, Sr, Li, $Fe_{tot}$ (low $NO_3^-$, Ba, Si) |
| **C5 (N=98)** | ● (green) | PC3 | 15–100 | sandstone, dolomite, gypsum | $D_3$pl-slp, $D_3$gj | 800–2050 | high F, B, Rb, Br, Li, Sr (low $NO_3^-$ and Ba) |
| **C6 (N=242)** | ● (grey) | none or PC3 | 3–15 | sand, sandstone | Q, $D_3$gj, $D_2$br | 170–300 | low TDS, elevated Al |
| **C7 (N=240)** | ● (dark blue) | PC2 or PC2 and PC3 | 3–50 | sand, sandstone, dolomite | Q, upper and middle Devonian | 410–490 | – |
| **C8 (N=93)** | ○ | PC2 or PC2 and PC1 | 25–75 | sandstone, dolomite | upper and middle Devonian | 420–570 | high $NH_4^+$, Ba, $Fe_{tot}$, Sr (low $SO_4^{2-}$ and $Cl^-$, $NO_3^-$ and Mn) |

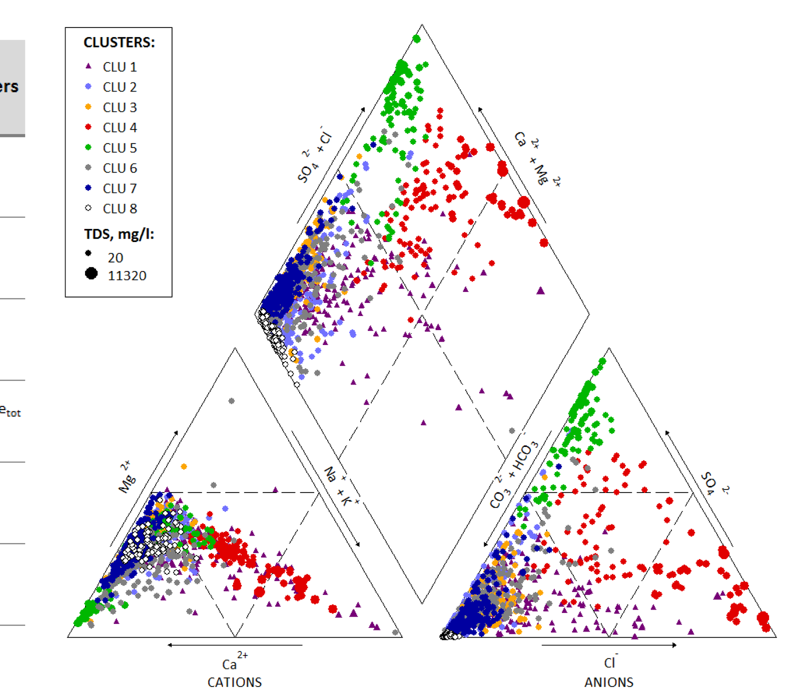


**Figure 5.** Piper diagram showing the composition of groundwater samples used in this study labeled according to their clusters. Symbol size is associated to TDS.

## CONCLUSIONS

**Eight geochemically distinct groundwater groups (C1- C8) can be observed characterised by particularly elevated or depressed major ion, trace elements and $NO_3^-$ and $NH_4^+$ concentrations:**

- ✓ **C6 is interpreted as recharge water not yet equilibrated with most of the sediment forming minerals.**
- ✓ **C3 is interpreted as groundwater form water table aquifers affected by diffuse agricultural pollution.**
- ✓ **Groundwater in C4 reflects brine or seawater mixing with fresh bicarbonate groundwater.**
- ✓ **C5 corresponds to gypsum dissolution in the active water exchange zone.**
- ✓ **C7 and C2 belong to typical bicarbonate groundwater resulting from calcite and dolomite weathering with slightly elevated $K^+$ concentrations in case of C2.**
- ✓ **Extremely low $Cl^-$ and $SO_4^{2-}$ are observed in C8 and interpreted as pre-industrial groundwater or solely carbonate weathering result.**
- ✓ **C1 seems to be a poorly definite subgroup resulting from mixing between other groups.**

**The results show that although trace elements and nitrogen compounds were not included in multivariate statistical analysis, their variance in groundwater can be observed by analyzing their composition within each of the subdivided groups based on major ion chemistry.**

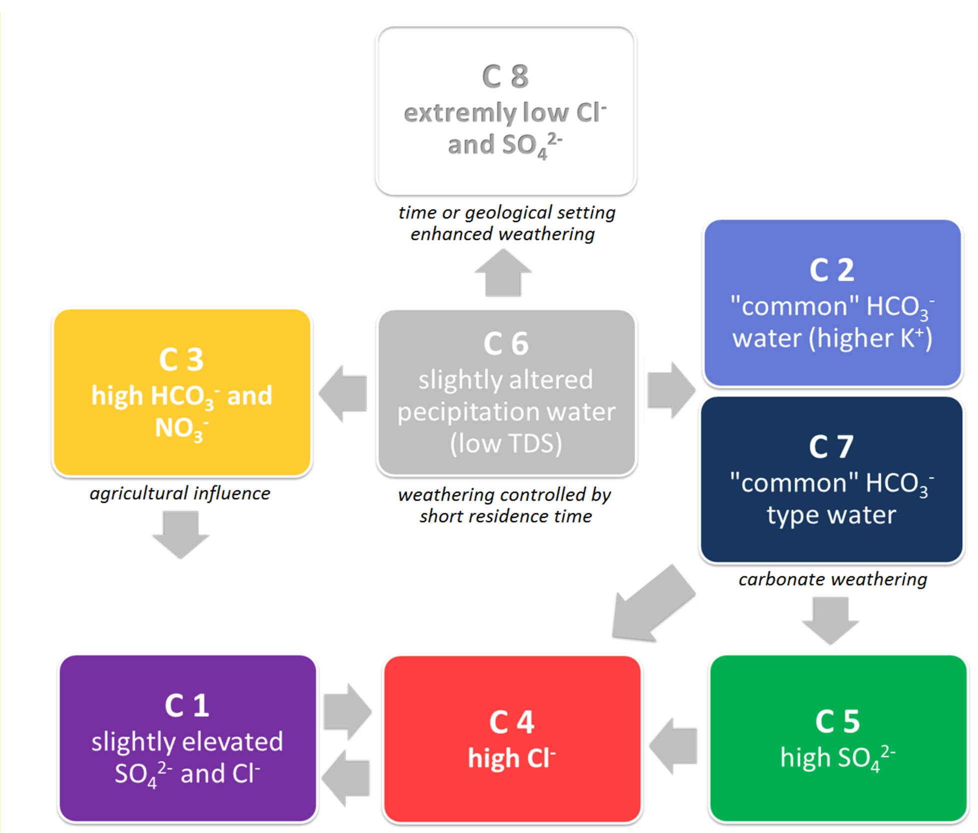


**Figure 6.** Evolution of groundwater geochemistry.

### Acknowledgement

This research is supported by the European Union through the ESF Mobilitas grant No MJD309 and the European Regional Development Fund project Nr.2013/0054/2DP/2.1.1.1.0/13/APIA/VIAA/007.

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