Hydrogeochemical characteristics of groundwater in Latvia using multivariate statistical analysis

Inga Retike [1], Andis Kalvans [2], Janis Bikse [1], Konrads Popovs [1] and Alise Babre [1]

[1] Faculty of Geography and Earth Sciences, Centre of Geological Processes Research and Modelling, University of Latvia, Riga, Latvia (inga.retike@lu.lv)
[2] Faculty of Science and Technology, Institute of Ecology and Earth sciences, University of Tartu, Tartu, Estonia (andis.kalvans@lu.lv)

This poster participates in OSP

Outstanding Student Poster Contest

HYDROGEOLOGICAL SETTING

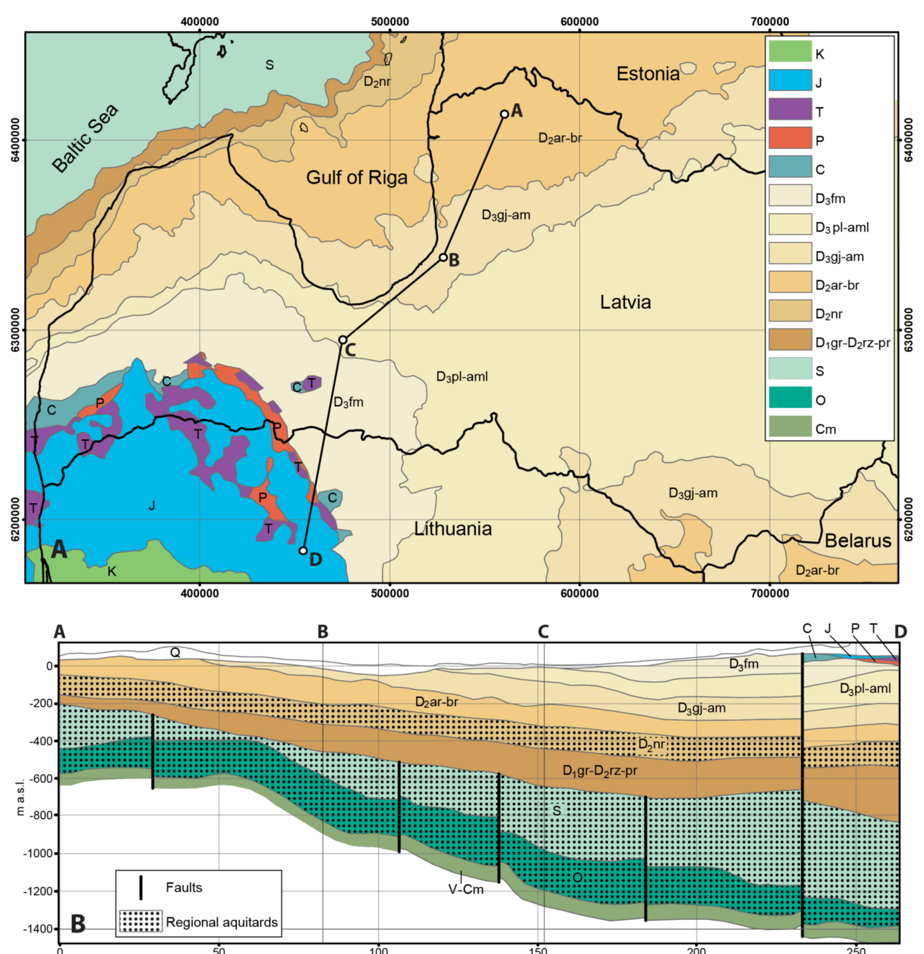

Figure 1. Geological map and geological cross-section of the study region without Quaternary cover (modified after Popovs et al. in print; Virbulis et al. 2013).

Location of cross-section indicated in A. V-Cm - Ediacaran- Cambrian sequence; O- Ordovician sequence; S- Silurian sequence; D_1gr-D_2rz-pr- lower Devonian Gargzdu Fm to middle Devonian Parnu Fm; D_2nr- middle Devonian Narva formation; D_2ar-br- middle Devonian Burnieki Fm to Arukila Fm; D_3gj-am upper Devonian Gauja Fm to Amata Fm; D_3fm- 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

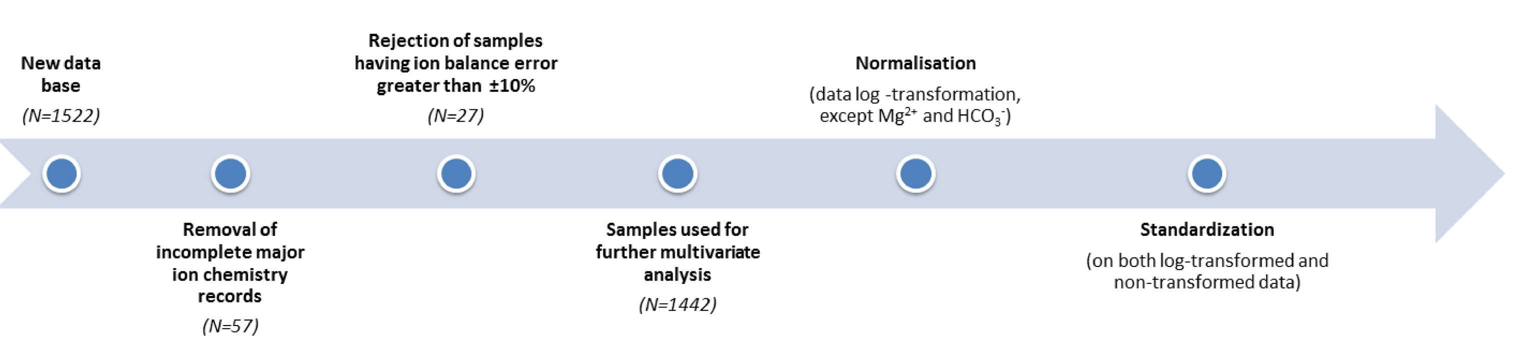

Figure 2. Data preparation for multivariate statistical analysis.

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

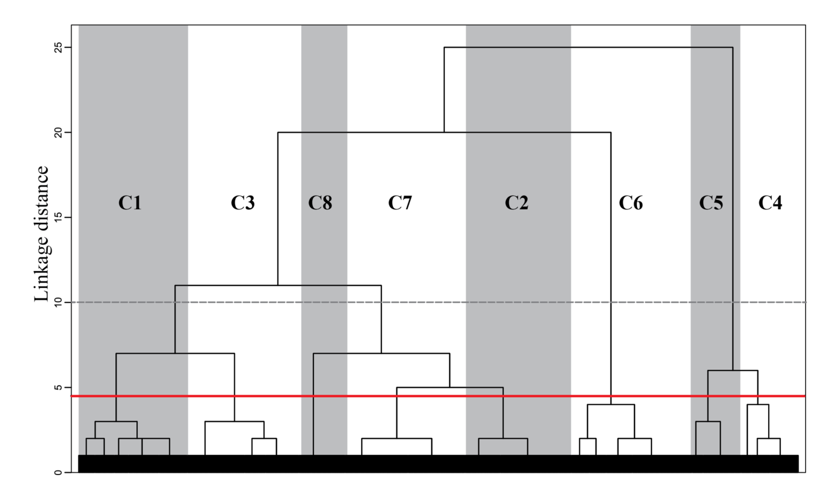

Figure 3. Dendrogram from hierarchical cluster analysis showing division of groundwater samples. Dashed line reflects four major divisions and red line reflects the eight distributed clusters for further analysis.

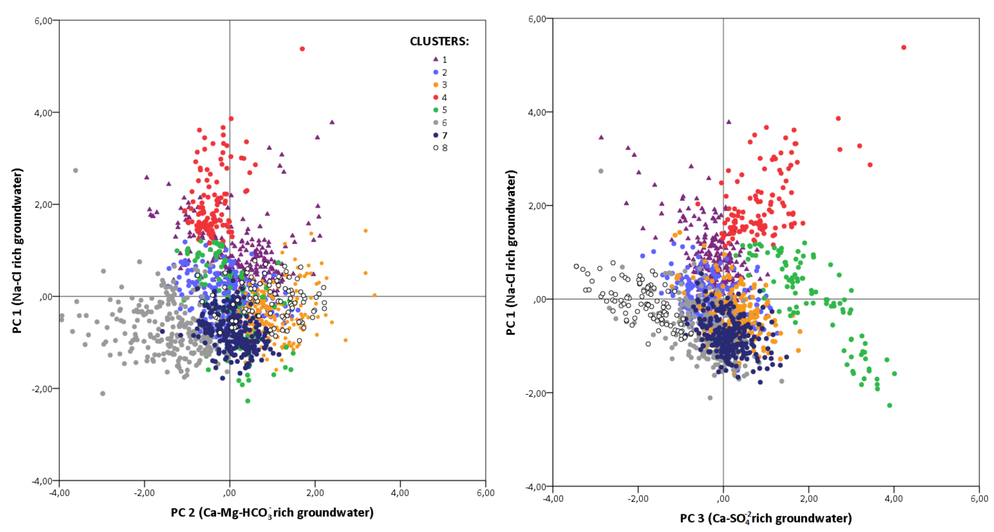

Figure 4. Plot of loadings from PCA for the first and second and first and third PCs. Groundwater samples are grouped according to their clusters from HCA.

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)	▲	PC1 and PC2	4–100	sandstone, sand, dolomite, till	Q, D_3gj, middle Devonian	520–700	elevated Br
C2 (N=213)	●	PC2; PC1 or PC3	4–90	sandstone, sand, dolomite	Q, D_3gj, middle Devonian	400–500	elevated K/Na ratios
C3 (N=223)	●	PC2 and PC3 or PC2 and PC1	2–7	till, sand, dolomite	Q, D_3pl-slp	570–750	elevated NO_3^-, Mn, U
C4 (N=115)	●	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)	●	PC3	15–100	sandstone, dolomite, gypsum	D_3pl-slp, D_3gj	800–2050	high F, B, Rb, Br, Li, Sr (low NO_3^- and Ba)
C6 (N=242)	●	none or PC3	3–15	sand, sandstone	Q, D_3gj, D_2br	170–300	low TDS, elevated Al
C7 (N=240)	●	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)

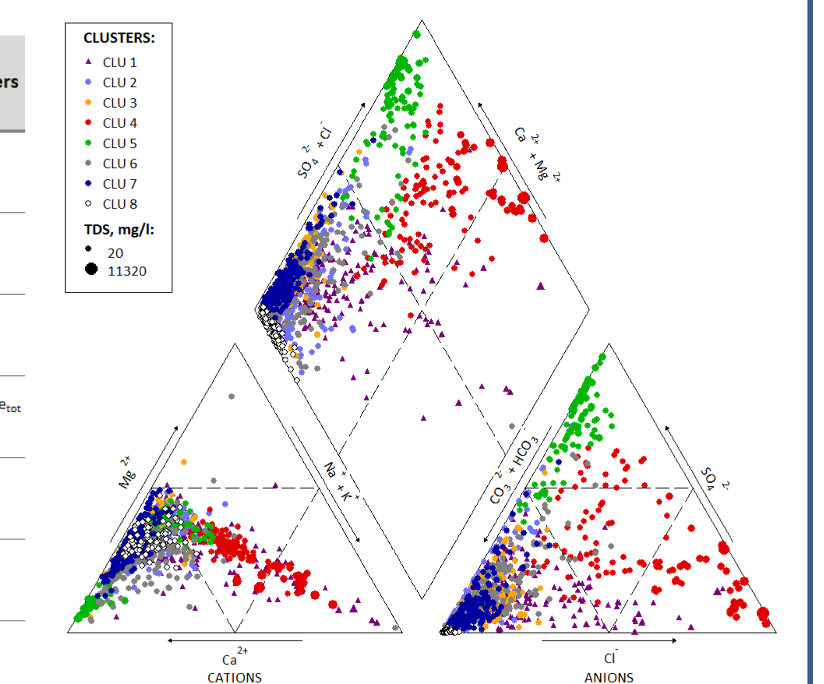

Figure 5. Piper diagram showing the composition of groundwater samples used in this study labeled according to their clusters. Symbol size is associated to TDS.

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.

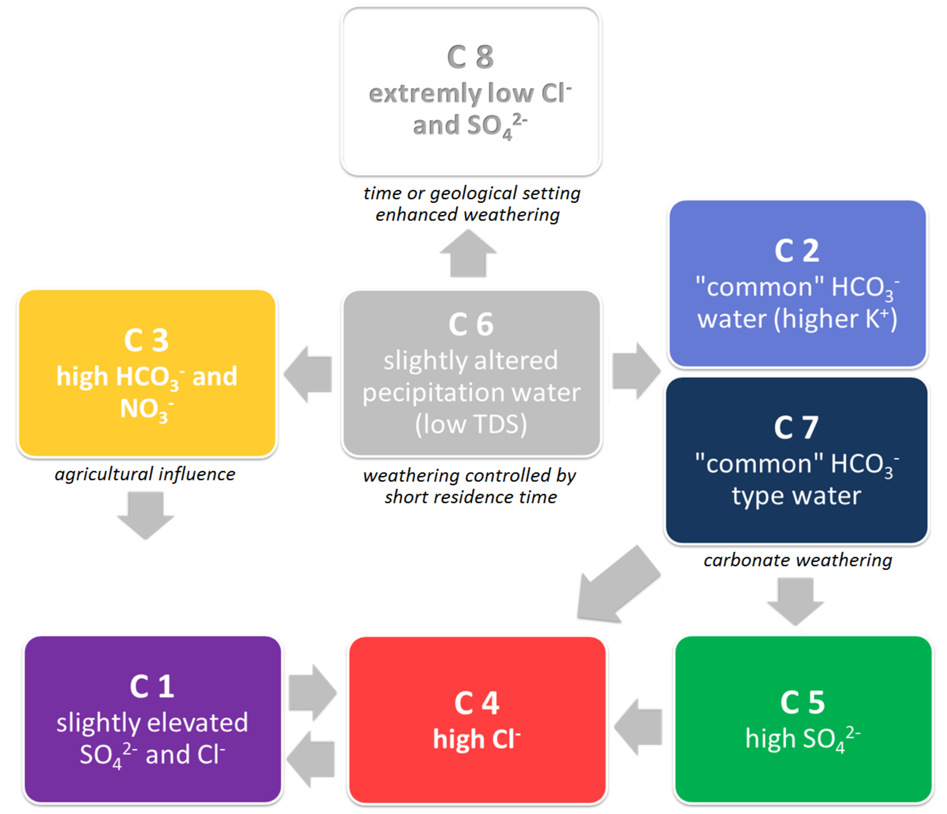

Figure 6. Evolution of groundwater geochemistry.

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.

Euroopa Liit Euroopa Sotsiaalfond

Eesti tuleviku heaks

Mobilitas ESF programm

ERAF EIROPAS REĢIONĀLĀS ATTĪSTĪBAS FONDS

IEGULDĪJUMS TAVĀ NĀKOTNĒ

EIROPAS SAVIENĪBA

LATVIJAS UNIVERSITĀTE ANNO 1919 UNIVERSITY OF LATVIA