

EVOLUTION OF GROUNDWATER CHEMICAL COMPOSITION THROUGH QUATERNARY SEDIMENTS IN LATVIA

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Figure 1. Map of study area

Groundwater chemistry mainly depends on the minerals present in layer of water-bearing rocks through which water moves. The most common Quaternary sediments in Latvia are till, silt, various coarse of sand, clay and peat. They differ in mineral composition and grain size distribution which affect groundwater chemistry as well.

INTRODUCTION

The territory of Latvia is a part of the Baltic Artesian (Sedimentary) basin which considering water chemistry and intensity of water connection between aquifers can be divided into three major water exchange zones: **freshwater** (active water exchange), **saline** (delayed exchange), and **brines** (stagnant water exchange zone).

The chemical composition of unconfined groundwater is influenced by all the processes that take part during their formation and water feeding conditions, which depend on site lithology, have a great importance.

MATERIALS AND METHODS

In this study data (trace element content, major ion chemistry, stable isotope signals (groundwater only) and physical parameters) about **686 groundwater samples from Quaternary sediments and rain water** from Latvian Environment, Geology and Meteorology Centre databases, project "Agricultural Influence on Groundwater in Latvia" (Gosk et al., 2006) and European Social Fund project "Establishment of interdisciplinary scientist group and modelling system for groundwater research" are used.

612 groundwater samples were analyzed by **inductively coupled plasma mass spectrometry (ICPMS)** (data from previous studies) (Gosk et al., 2006). In this research 64 groundwater samples were analyzed by **total x-ray fluorescence (TXRF)** and **atomic absorption spectroscopy** to determine the concentrations of trace and major elements (cations).

Principal component analysis (PCA) with Varimax rotation was performed to determine the distribution of different water types and the processes affecting their formation in Quaternary sediments. **A preliminary cleaning of the data set** included removal of strong outliers, of variables with a poor reproducibility and of variables with missing more than 30% of the data (including non-detects). The observations below detection limit (<DL) were substituted with 50% of DL (Gosk et al., 2006; Olsen et al., 2012). PCA was performed using SPSS Statistics 19.

Samples for **stable isotopes** were taken during years 2010 – 2012, totally **59 samples were collected**, there 44 from **monitoring and production wells** and 15 samples from **springs**. Stable isotopes in precipitation were gained from IAEA/WMO (2006) and GNIP Database from which local meteoric water line for Riga meteorological station were constructed. Only precipitation data, which contained both, e.g., oxygen and deuterium data have been selected. Groundwater samples for stable isotope content were analyzed in the Institute of Geology at Tallinn University of technologies with Picarro Isotopic Water Analyzer.

AIM OF THE STUDY

In this research chemical composition of rainwater and unconfined groundwater in Quaternary sediments is studied to find out the role of different water-bearing rocks in making unconfined groundwater composition.

RESULTS

The first five PC explaining 55% of the total variance of the data set are presented in table 1.

PC 1 is grouping the positive loading of sulphates, calcium, magnesium, electrical conductivity, fluoride, lithium, strontium and silicon. This component can be interpreted as carbonate rock with gypsum layers dissolution or influx of saline sulphate groundwater from deeper aquifers (Gosk et al., 2006).

PC 2 is grouping the positive loading of calcium, alkalinity, magnesium, electrical conductivity, uranium, total nitrogen and nitrate. Previous studies suggest that this factor reflects diffuse contamination of groundwater from agricultural areas (with dolomites used for neutralisation of acid solids, agricultural additives) (Gosk et al., 2006). But this component also can be interpreted as the composition of groundwater in till sediments which contains carbonates and clay. The PCA performed with the data taken only from sand and till sediments showed that in till sediments this is the major PC and explains 25% of the total variance of the data set. But in sand sediments similar PC loadings explains only 5% of the total variance of the data set.

PC 3 is grouping positive loading of electrical conductivity, sodium, chlorine, aluminium and bromine. This factor can be explained by seawater intrusion or groundwater mixing with greather depth chlorine sodium saline groundwater. Less likely this component reflects groundwater contamination with NaCl used for roads de-icing in winter.

PC 4 is grouping the positive loading of total nitrogen, potassium, nitrate and rubidium. This factor reflects groundwater contamination with fertilizers. In minerals almost always rubidium is found together with potassium.

PC 5 is grouping positive loading of rubidium, arsenic, cobalt, iron, silicon, manganese and negative loading of *pH*. This factor explains dissolution of carbonate cement and hydrolysis of aluminium silicate minerals by infiltrating water or as well-known dependence of trace metals on acidity and dissolved organic matter in the solution (Gosk et al., 2006).

Table 2 shows that PCA performed for all samples (taken from till, sand, peat, gravel deposits) (Table 1) and PCA performed only for samples taken from sand deposits are similar and contains similar principal components. The PC loadings show that in sand deposits the main processes affecting groundwater compositions are carbonate with gypsum dissolution (PC 1), diffuse groundwater contamination from agricultural areas, mainly with potassium fertilizers (PC 2), saline water intrusion (PC 3). This can be also explained by data set structure, the groundwater samples were mainly taken from sand and sand-gravel deposits.

The PCA performed with data taken from till sediments showed much smaller anthropogenic influence on groundwater composition. Till composition can be very various therefore the PCA results are strongly influenced by small data set.

The PCA was performed for groundwater taken from different types of land use- **forest** (both primary and secondary, marshy forests), **rural area with extensive agriculture** (grasslands, sporadically distributed small farms, undeveloped or abandoned lands), **intensive agriculture** (permanently arable lands, intensive pasturing). The results show that there are no significant difference in PC loadings. It can be explained by the difficulty to separate territories with different land use.

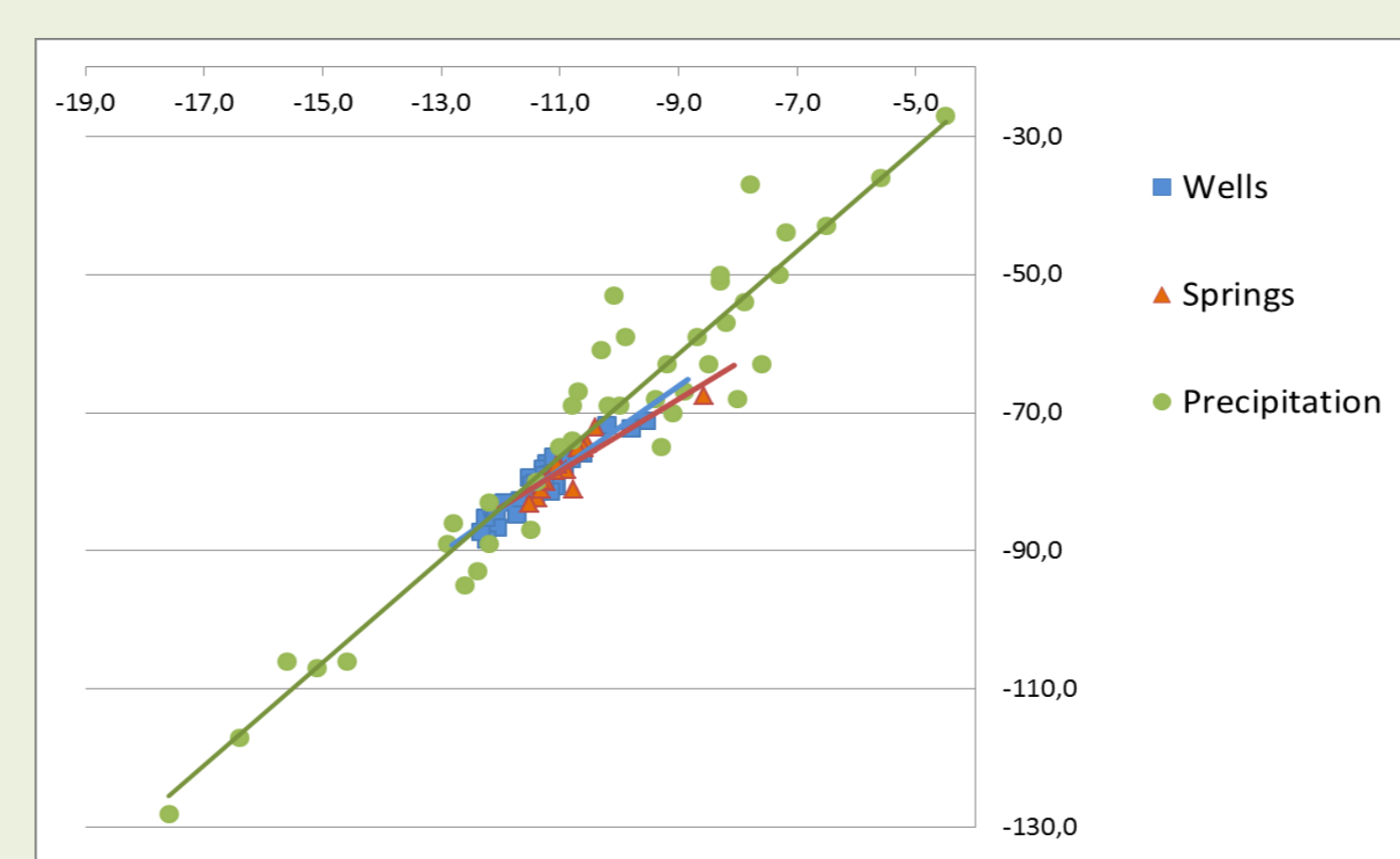


Figure 2. Oxygen-18 versus deuterium composition in Quaternary aquifer and precipitation. Precipitation from GNIP database (IAEA, 2006). Values are in δ ‰ VSMOW

Compared to groundwater results, precipitation has more variable results, depending on season and characteristics of precipitation, however relation between deuterium and oxygen-18 is more or less constant. Less depleted precipitation samples are in wider range, which can be explained by influence of individual rainfall. As it can be observed, most of groundwater and spring samples are close to meteoric water line which can indicate their meteoric origin, mismatch in trend line can be explained by influence of individual samples, which are shallower and likely contain not sufficiently mixed precipitation signal.

CONCLUSIONS

- **PCA show that Quaternary groundwater composition mainly depends on site lithology and agriculture intensity. Sediment composition also influence feeding conditions and hydrogeochemical processes.**
- **Quaternary composition are mainly affected by carbonate and gypsum dissolution, by diffuse contamination from agricultural areas (dolomites, potassium fertilizers) and by mixing with upcoming chlorine sodium saline groundwater or less frequent seawater intrusion.**
- **There are no significant difference in groundwater composition from areas with different types of land use. This can be explained by difficulty to separate territories with various land use.**

Table 1. Principal component loadings

	PC 1	PC 2	PC 3	PC 4	PC 5
SO ₄	0,893	0,029	0,034	0,082	0,051
Li	0,886	0,042	0,023	-0,048	0,050
F	0,793	0,097	0,039	0,003	0,099
Sr	0,774	0,096	0,038	0,037	-0,049
Ca	0,676	0,636	-0,012	0,100	0,047
Alkalinity	0,103	0,833	0,125	0,076	0,085
Mg	0,452	0,728	0,085	0,189	0,018
EC	0,532	0,650	0,452	0,167	0,047
U	-0,058	0,536	-0,067	0,044	-0,089
Ba	0,000	0,293	0,151	-0,149	0,225
Na	0,028	0,118	0,931	0,035	-0,041
Cl	0,054	0,215	0,915	0,003	-0,066
Al	-0,108	-0,241	0,533	0,063	0,242
Br	0,161	0,154	0,514	-0,064	-0,069
NH ₄	0,167	-0,132	0,386	0,346	0,296
P _{tot}	-0,052	-0,101	0,326	0,214	0,042
N _{tot}	-0,032	0,437	-0,078	0,755	-0,171
K	0,097	0,046	0,180	0,724	0,181
NO ₃	-0,052	0,459	-0,126	0,710	-0,208
Rb	0,042	-0,15	0,156	0,644	0,353
As	-0,154	0,099	0,017	-0,096	0,666
Co	-0,155	0,202	-0,052	-0,028	0,640
pH	-0,031	0,153	-0,045	-0,077	-0,544
Fe	0,277	-0,074	0,084	0,118	0,538
Si	0,431	-0,004	0,023	-0,064	0,435
Mn	0,087	-0,055	-0,004	0,116	0,314
Zn	0,112	0,215	-0,033	0,030	0,289

Table 2. Principal component loadings for groundwater samples taken from sand deposits

	PC 1	PC 2	PC 3	PC 4	PC 5
Li	0,921	-0,041	0,058	-0,126	0,081
SO ₄	0,868	0,126	0,310	0,022	0,124
Sr	0,833	0,160	0,075	-0,081	-0,029
F	0,825	-0,096	-0,071	0,128	0,097
Ca	0,771	0,060	0,144	0,524	0,055
K	0,083	0,872	0,117	0,083	0,058
N _{tot}	0,035	0,865	-0,014	0,268	-0,113
NH ₄	0,046	0,775	0,230	-0,014	0,142
Rb	0,049	0,712	0,037	0,013	0,228
NO ₃	0,017	0,660	-0,143	0,337	-0,239
P _{tot}	-0,054	0,515	0,140	-0,129	0,130
Cl	0,019	0,075	0,965	0,092	0,016
Na	-0,003	0,055	0,959	0,075	0,030
EC	0,292	0,234	0,839	0,332	0,059
Br	0,139	0,093	0,724	0,069	-0,039
Alkalinity	0,121	0,201	0,240	0,786	0,030
Mg	0,487	0,089	0,327	0,664	0,011
Ba	-0,077	-0,108	0,099	0,491	0,239
U	-0,073	0,123	0,008	0,484	-0,088
pH	-0,028	-0,028	0,010	-0,022	-0,631
Si	0,409	-0,099	-0,068	0,010	0,608
Co	-0,129	0,123	-0,066	-0,053	0,546
Fe	0,315	-0,113	0,261	0,112	0,540
As	-0,106	0,306	0,066	0,003	0,517
Al	-0,164	0,121	0,236	-0,297	0,449
Mn	0,057	0,010	0,000	0,141	0,284
Zn	0,125	0,008	-0,024	-0,025	0,235