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A First Insight into the Influence of Land Cover on the Hydrochemical Properties of Spring Waters Across a Lowland Landscape

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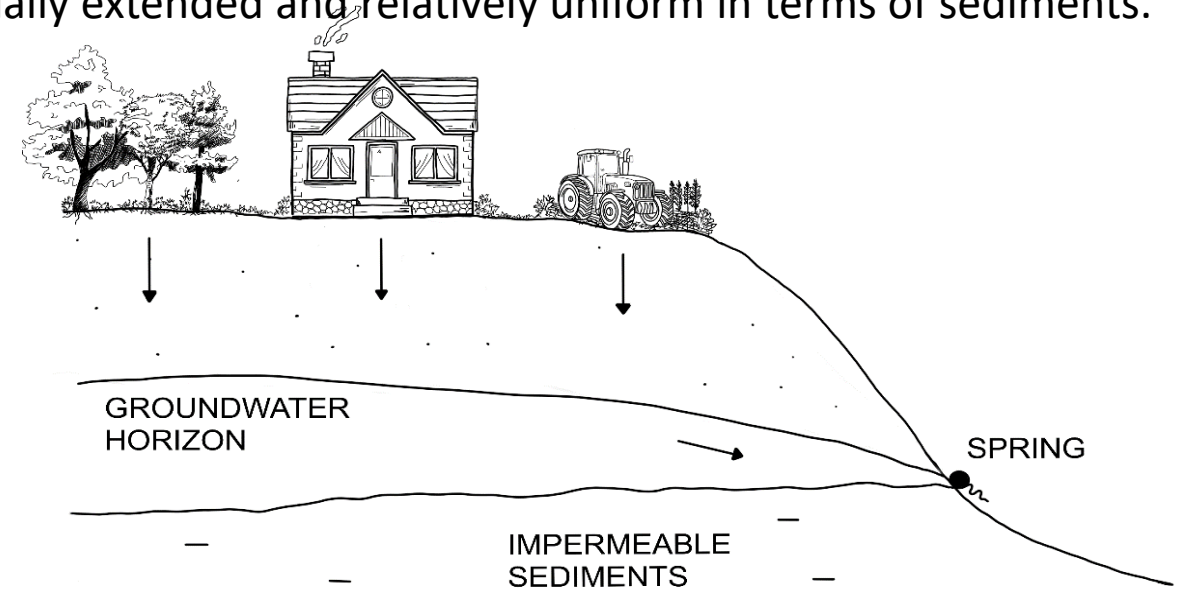
Introduction

- The relationships between chemical composition and land cover were investigated mainly in the river and lake catchments (Staponites et al., 2018, Kutyła et al., 2024).

- Such studies were not applied so far in the case of spring waters – the possibility of explaining their quality characteristics with the use of land cover properties is limited, as water chemical composition is driven mainly by geological factors.

- Quite favorable conditions for such investigations exist across lowland, post-glacial landscapes, where recharge areas of shallow aquifers are spatially extended and relatively uniform in terms of sediments.

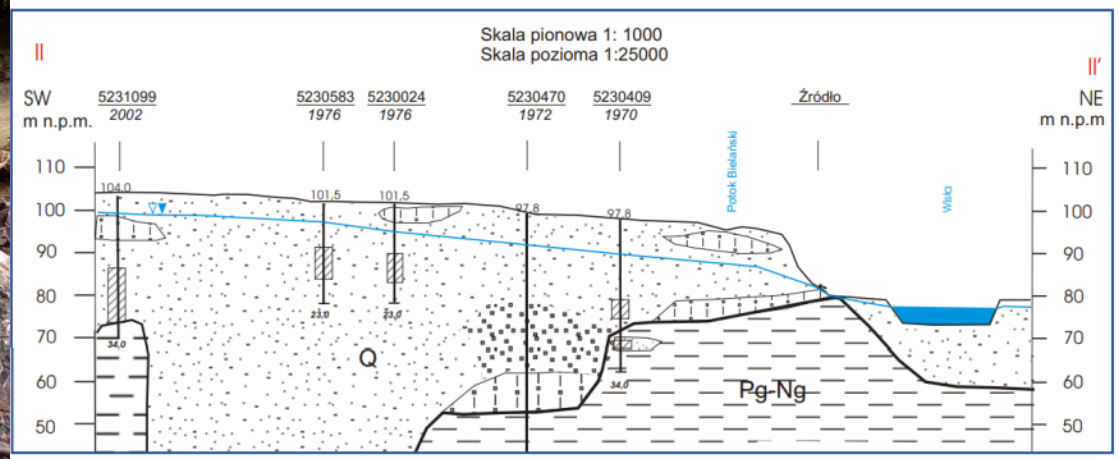
The study attempted to evaluate the relationships between the land cover and the hydrochemical properties of Quaternary spring waters across lowland landscape.



Methods and materials

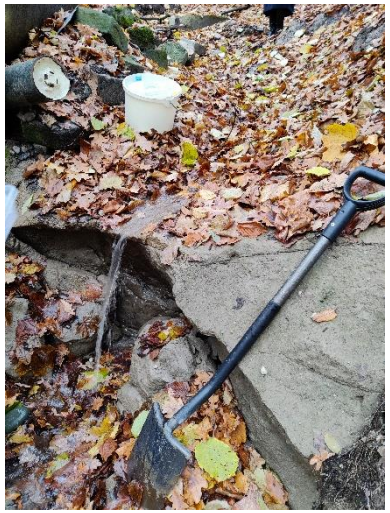
- The evaluation of land cover impact on groundwater quality was conducted on the basis **of 35 springs, located across Mazovian voivodeship,** mostly in the proximity of Warsaw. All selected **springs represent porous, descending and perrenial type of outflows**. Springs drain sandy aquifers laying over impermeable clays and loams (see below), mainly from Riss glaciation. **Springs were selected due to maximize variability of land cover** of their recharge areas.

- **Field investigations** were conducted **during November 2024**. In the field, water temperature, specific electrical conductivity (SEC) and pH were measured in situ with the use of Hanna HI98303 and HI98108 (with the accuracy of 0.4 °C, 2% of SEC scale and 0.1 pH). Spring discharge was measured with volumetric method.



Quaternary and Pliocene sediments in the cross-section of the Vistula Valley and Warsaw Escarpment

Discharge measurements



Impermeable loams

Methods and materials

- During field investigations, water samples were collected to the polyethylene bottles. They were immediately transported (on the same day) to the laboratory in 4°C, where the measurements of main cations and anions (macroelements), as well as trace elements (microelements) were conducted.

- Analysis of **macroelements** (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, SO_4^{2-}, Cl^{-}, F^{-}) and biogenic compounds (PO_4^{3-}, NO_3^{-}, NO_2^{-}, NH_4^{+}) was performed using a Metrohm ion chromatograph, while HCO_3^{-} was measured with the acidimetric titration method. The **concentrations of selected microelements** (B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Sb, Ba), being the indicators of anthropogenic pressure (de Almeida Ribeiro Carvalho et al. 2022), were determined using a Perkin-Elmer Elan DRC-e inductively coupled plasma mass spectrometer.

Spring in the Pilica River valley

Outflow from ascending spring in Osieck City

Artificial casing of the spring in the Świder River valley

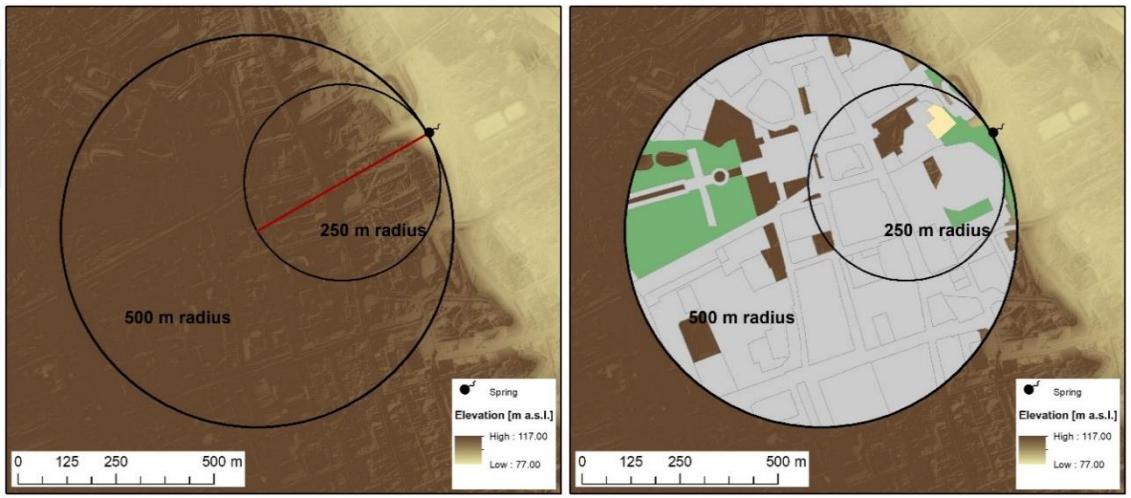
Methods and materials

- Land cover was calculated **in circular buffers of 500 and 250 m radius**, located in closest proximity to the recharge areas of spring. Such approach was adopted from surface water quality investigations (Gesley et al., 2022). **Two datasets** were used for land cover quantification – **Sentinel 2 Global Land Cover and Topographic Objects Database (BDOT10k).** Land cover classes were aggregated to three main types – **artificial, cultivated and forested areas**. Spatial analysis was performed in ESRI ArcMap 10.6.

- Contribution of land cover types in % and the concentrations of selected ions were linked **using the Spearman correlation analysis** (mainly due to the lack of the normal distribution of data and small sample size). Correlation analysis was performed in Statistica 12.0 software. A probability value of correlation of less than 0.05 was considered as statistically significant.

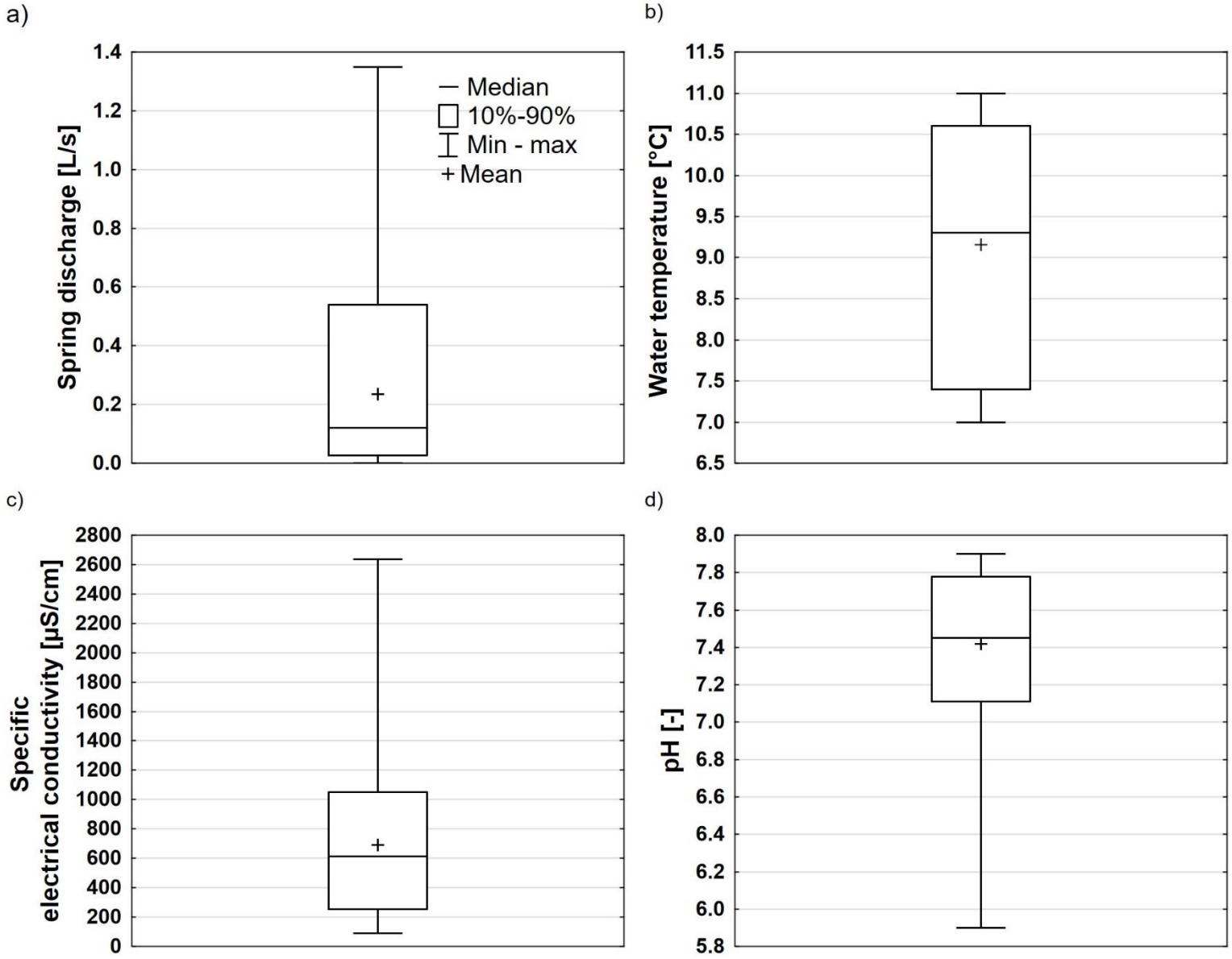
Classes used for land cover calculations

Dataset	Artificial areas	Cultivated areas	Forested areas
S2GLC	Class 62	Class 73	Sum of classes 82 and 83
TOD (BDOT10k)	PTZB, PTKM, PTPL	PTTR, PTUT	PTLZ



Results – spatial variability

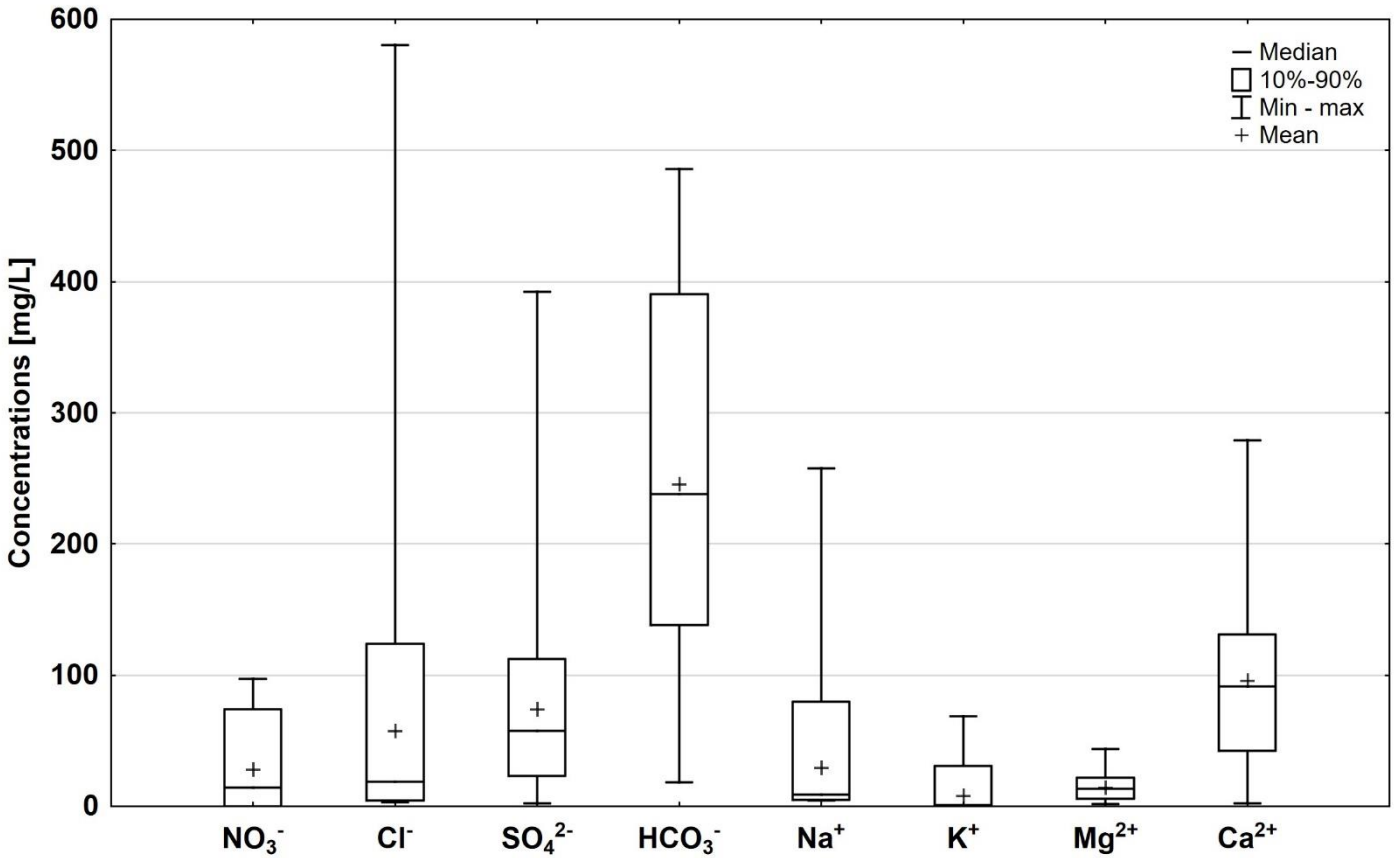
- Investigated springs exhibited **generally small discharge rates**, which usually do not exceed 1.0 L/s.
- Water temperature ranged from 7.0 to 11.0°C, which was dependent on the **degree of aquifer isolation.**
- SEC values **exhibited great variability**, ranging from 89 to even 2638 µS/cm, whereas their waters were usually **slightly alkaline**.



Distribution of discharge a), water temperature b), specific electrical conductivity (c) and pH (d) of the investigated springs in November 2024

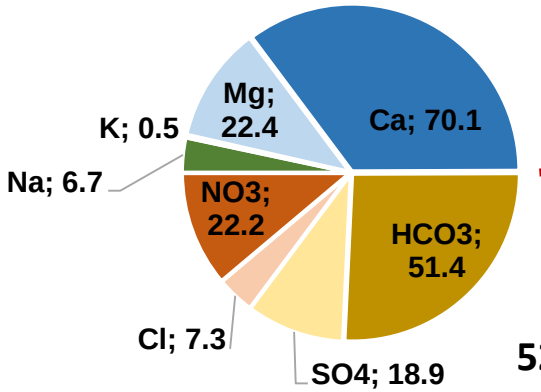
Results – spatial variability

- **Distribution of concentrations values of main cations and anions suggests their different origin**; Ca^{2+}, Mg^{2+} and HCO_3^- exhibited distribution similar to normal (their variability is related mainly with sediment lithology), whereas distribution of NO_3^- , Cl^-, Na^+ and K^+ is asymmetrical and documents their anthropogenic origin.
- Most of the spring waters represent **two-ionic, simple HCO_3-Ca type** (according to the Szczukariew-Prikłoński method).

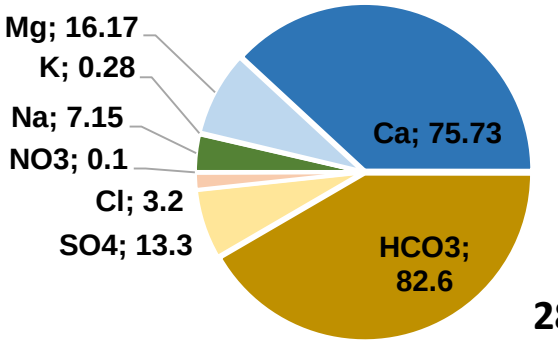


Distribution of main cations and anions concentrations in the investigated springs in November 2024

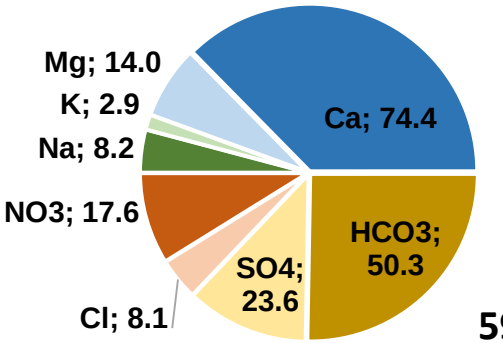
Spatial variability of chemical composition



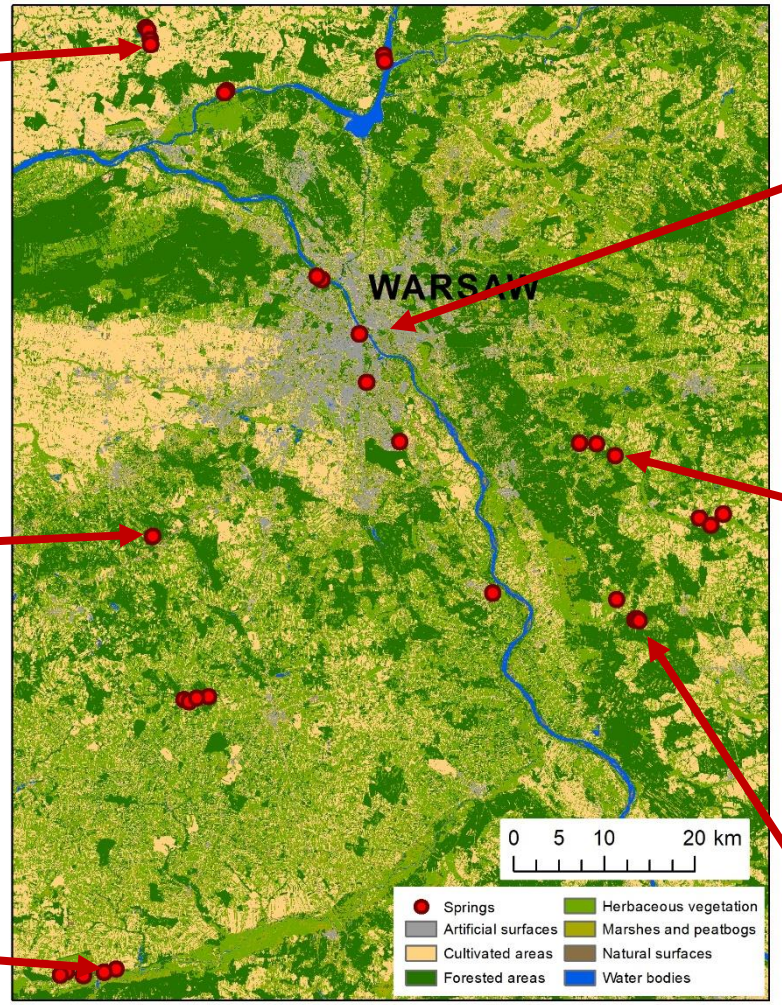
523 mg/L



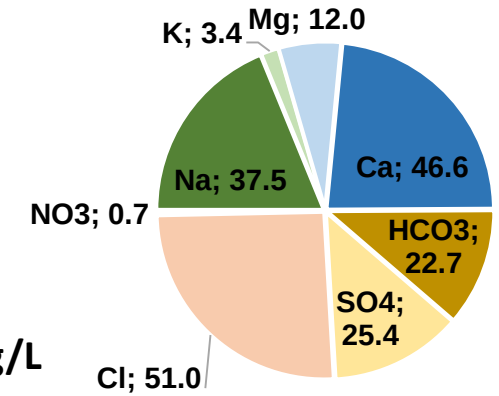
285 mg/L



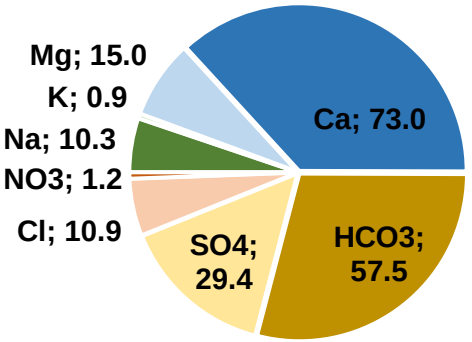
597 mg/L



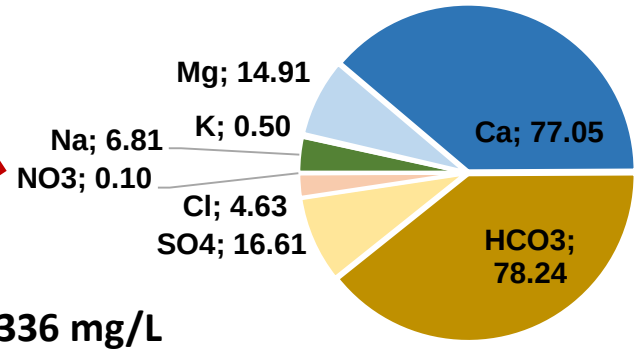
The area of the circles does not correspond to the TDS values. Contribution of main cations and anions is given in % mval/L



2055 mg/L



155 mg/L



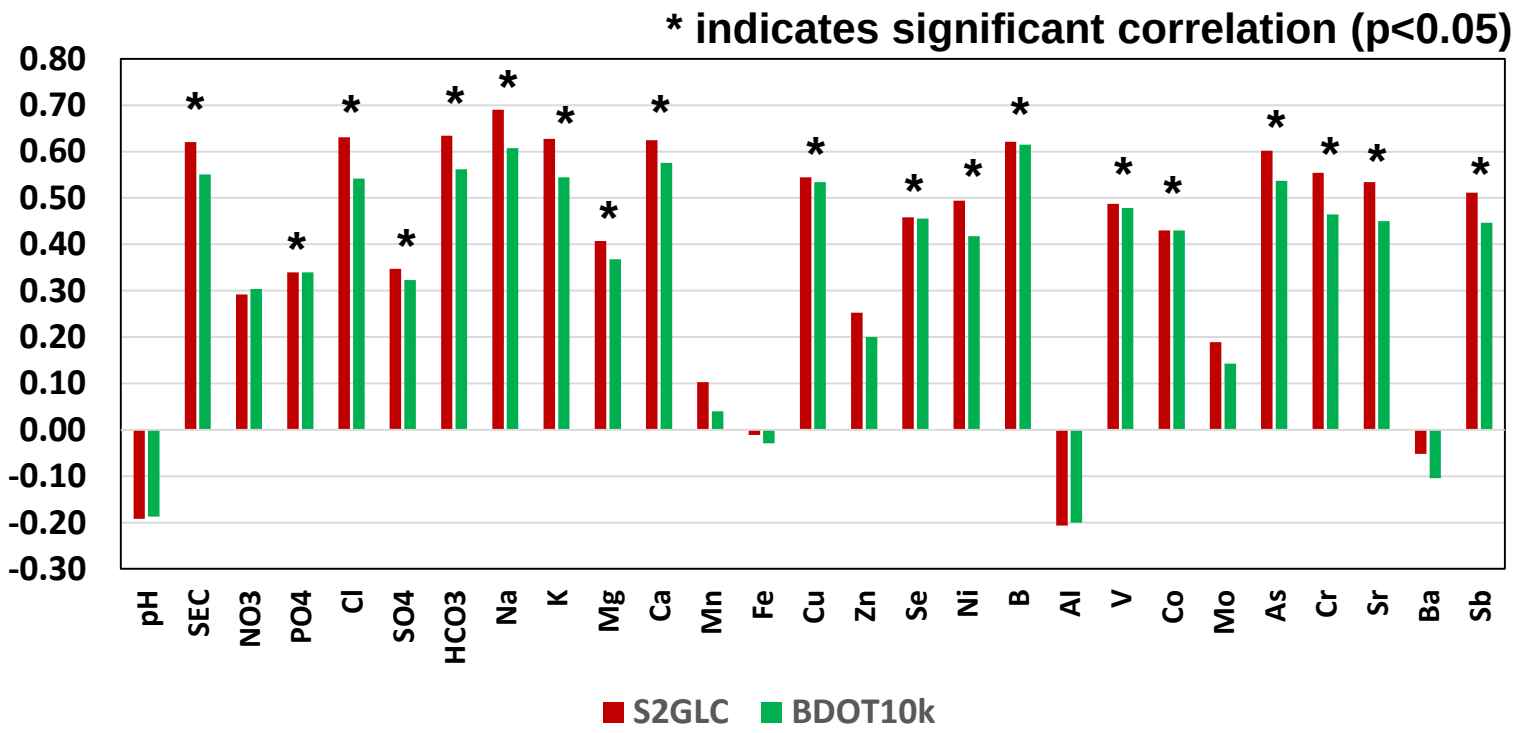
336 mg/L

Results – correlation analysis

- Both datasets, **S2GLC and BDOT10k** (Topographic Objects Database) **represented similar correlation performance**, however, slightly higher correlation performance was obtained for S2GLC dataset for artificial areas.

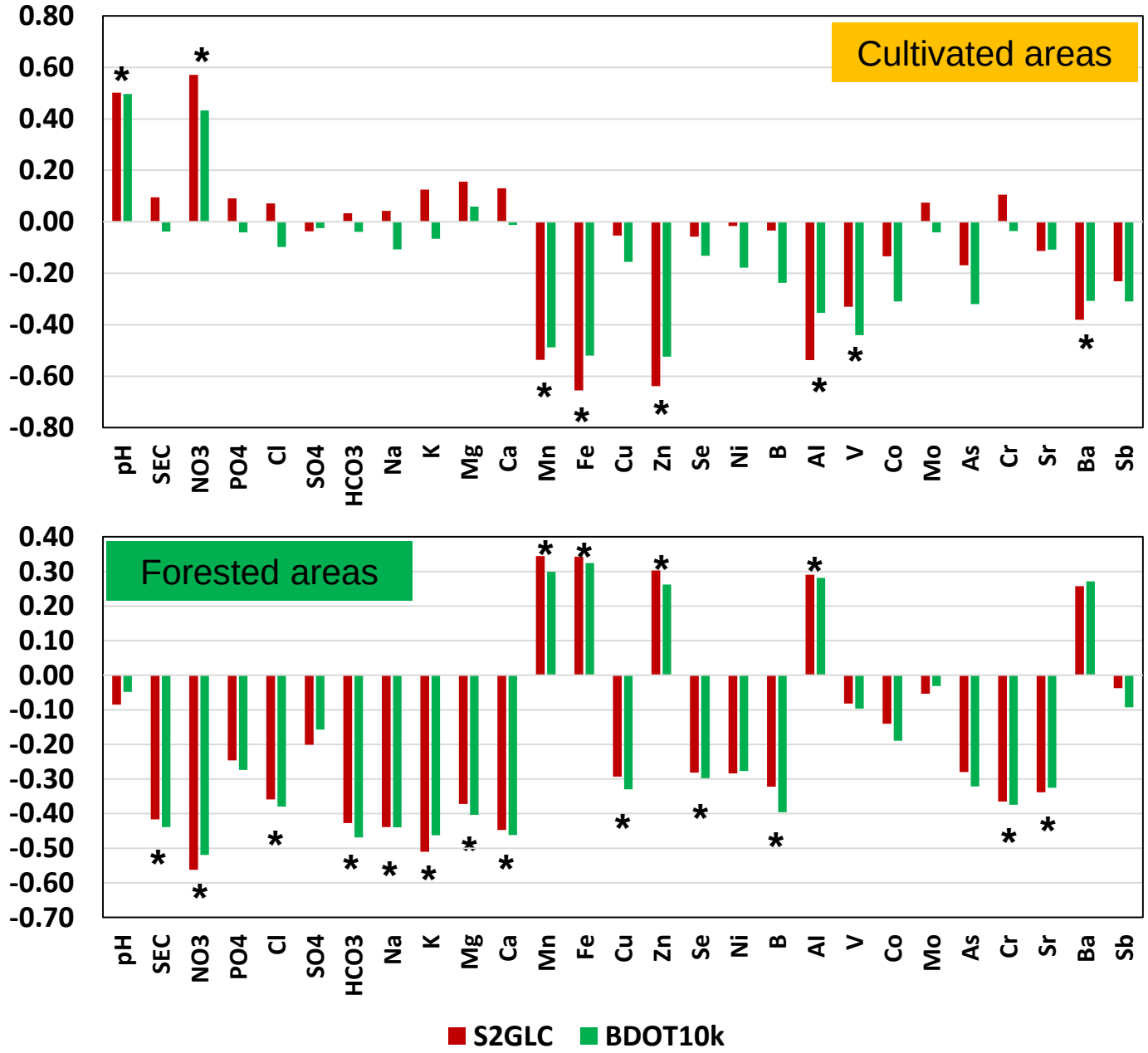
- **Buffer with 250 m radius was not used in correlation analysis** due to many zeros in the dataset (some land cover types were not represented in buffer zones).

- Increased **SEC values** and **major cations and anions** concentrations, such as Cl^-, K^+, Na^+, PO_4^{3}, and SO_4^{2-} were **positively related with artificial areas**. **Significant positive relationships** were also documented for most of the **trace elements**, such as B, Cr, Ni, Cu, Se, and As.



Results – correlation analysis

- **Concentrations of NO_3^- were positively linked with the contribution of cultivated areas.** Opposite relationships were noted in case of some metals, such as Mn, Fe, Zn and V.
- **Forested areas have a purifying effect on ion composition**; the concentrations of the most of the macroelements and some microelements were negatively correlated with the percentage of forested areas.



*** indicates significant correlation (p<0.05)**

Conclusions

- Significant variability of physico-chemical properties of spring waters were documented across lowland landscape.

- The results suggest that the land cover of spring recharge areas could partially explain variability of springs hydrochemistry. The **presence of artificial surfaces**, being an indicator of anthropogenic activity, **lead to increase the concentrations of the most of the macro and microelements**, particularly Cl^-, K^+, Na^+, B, As, and Cr. **The pollution of groundwater with NO_3^- ions was related with cultivated areas** (fertilizers and cattle). **Forests presence in the spring recharge areas** was responsible for **the decrease of the concentrations of ions**.

- The results could be applicable in terms of identification of groundwater vulnerability. However, further studies are needed using more complex metrics and regarding seasonality of the relationships.

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