Dissertation supervisor: prof. dr hab. Andrzej Sadurski

SUMMARY OF THE DOCTORAL DISSERTATION

Analysis of field methods of hydrogeological prospection (groundwater sampling methods) used to assess water quality of the first aquifer at selected groundwater monitoring points of the national Groundwater Observation and Research Network of PGI-NRI

Michał Wyszomierski, M.Sc.

Groundwater sampling for quality assesment is an inseparable part of groundwater monitoring research. Obtained results are very often referred as a "hydrogeological image".

Field research are the core of every groundwater monitoring focused at assessing the groundwater quality and chemical status. Improper groundwater sampling and errors in adapting the sampling method to a specific purpose of ten lead to erroneous results and generate significant errors. Regardless of using high-class measuring equipment, high accuracy and precision of laboratory tests, mistkes in a sampling process have a significant impact on the representativeness and reliability of the tests results.

With the implementation new editions of the European Standards: ISO 5667-11:2009 „Water quality – Sampling – Part 11: Guidance on sampling of groundwaters „Water quality - Sampling - Part 11: Guidelines for sampling of groundwater" and EN ISO/IEC 17025:2017 „General requirements for the competence of testing and calibration laboratories", for the first time the attention was focused to the importance of sampling process: „in defined laboratory processes (laboratory analytics) (...) one of the most important aspects is sampling and collecting representative material".

There are few comparative studies available on the discussed scope. Published materials are often incomplete, which prevents their practical application to a wider range of issues. Available characteristcs are usually focused on comparing two methods with each other.

The main purpose and goal of the research is the analysis, quality and quantity evaluation of groundwater sampling methods used for groundwater chemical status and quality assessment. The key task is to determine the impact of the applied groundwater sampling methods on the results variability and to assess the reliability and representativeness of groundwater field tests.

The analysis is based on the author results of field experimental tests, during simultaneous sampling of research points (wells and piezometers of the National Groundwater Observation and Research Network of PGI-NRI) using five different methods.

The analysis of field methods of hydrogeological prospecting included classic (conservative) methods, requiring purge pumping before sampling (submersible impeller pump and suction pump), as well as modern methods as “low-flow” sampling (peristaltic pump) and discrete “no purge” and “past purging” sampling techniques (Hydrasleeve® discrete passive bailer).

In this dissertation, the author presented sampling methodological guidelines for each of the analyzed methods. Due to the different method of groundwater sampling in the indicated methods, different physical and hydrodynamic conditions during sampling, it can be expected that the results of the simultaneous sampling may differ. All the sampling methods that were used in the experimental tests are methods recommended by the ISO 5667-11:2009 and are considered equivalent methods, so the reached results should be the same.

During the test points selection for testing discussed methods, the author recognized 1234 wells and piezometers used for assessing Groundwater Bodies (GWB’s) chemical status during diagnostic monitoring in 2019.

To achieve necessary representativeness, comparability and homogeneity of the test points in hydrogeological conditions, the author selected boreholes located in the area of a single river basin (the Vistula River basin), in the first aquifer, occured in pore or pore-groove layers, without or with a thin isolation from the surface, free or slightly tensioned water level. The depth of shallow aquifers, typically ranges from a few to several metres and the depth of boreholes rarely exceeds 30m. The dominant type of recharge is infiltration. The chemical composition of the grundwater at the test points depends on the kind of the water-bearing formations, soil layers above the aquifer, variable local flow- and atmospheric- conditions. The predominant chemical type of groundwater is: HCO_3-Ca, HCO_3-SO_4-Ca-Mg, HCO_3-Cl-Na-Ca.

In addition to the following conditions, the technical and construction of the tested wells/piezometers enabling simultaneous sampling of groundwater using five methods was taken into account. The technical condition of the tested monitoring points did not affected the sampling conditions and did not disturb the chemical composition of the groundwater samples. All the boreholes used in experiment have homogeneous construction, allowing for installation of the sampler/bailer in the filter zone. The minimum diameter was larger or equal to 100 mm, the depth of the static water level did not exceed 7 m. The wells had to be capable of pumping efficiency at a capacity of 2,4m^3.

The number of test points and control samples was in accordance with the guidelines of EN ISO 5667-14:2016 Water quality – Sampling – Part 14: „Guidance on quality assurance and quality control of environmental water sampling and handling". The hydrogeological characteristics are presented including the GWB's.

Determined range of analysed physicochemical parameters, was focused on the possibility of the widest possible application of the experimenta lresults in the analysis and quality assessment of groundwater and corresponds to the analytical range of water chemical status monitoring in accordance with the guidelines of the Regulation of the Minister of Maritime Economy and Inland Navigation of 11 october 2019 on the Criteria and method of assessing the status of groundwater bodies (Journal of Laws 2019, item 2148).

For the purposes of field evaluation and statistical analysis, a total of 960 "in situ" analyses and for 12,240 individual laboratory analyses were performed for 51 physicochemical parameters of inorganic indicators.

In the analyses and statistical evaluation of the results, author was using the statistical software SAS/Stat v 15.2. This allowed for multivariate mathematical (statistical) analysis. A multi-parametric GLM (Generalized Linear Models) statistical model was used, including a number of different statistical models analysed with each other: ANOVA, ANCOVA, MANOVA, MANCOVA. The analysis carried out enabled a quantitative and qualitative assessment of the groundwater sampling methods

Used in the statistical analysis Post-Hoc HSD Tukey'sTest (Honest Significant Difference test) was carried out to detect significant differences between the analysed groundwater sampling methods. This made it possible to identify the influence of the groundwater samplin gmethod on the variability of the chemical test results.

Another statistical analysis used in the dissertation was the Passing-Bablok robust regression model, which is a symmetric linear model that is robust to the presence of outliers. This model uses a non-parametric approach, so it does not require assumptions about probability distributions. The presented method can be used for comparative studies of measurement methods.

The results of the experimental work, the statistical analysis carried out and the mathematical modeling allowed a reliable quanty and quality evaluation of the field methods of hydrogeological reconnaissance used in the assessment of groundwater chemical status.

The results of the study allow us to draw the following conclusions:

- the reliability of the tested sampling methods is very similar, and there are no grounds for rejecting or preferring particular methods,

- in the discussed groundwater sampling methods, statistical “significant differences” between methods were identified on the basis of the analysis,

- differences in the average concentrations of analyzed indicators in individual methods, can be considered as “BIAS” - systematic error of the method, interpreted at the same time as technical load/technical variability of the method.

„BIAS” - systematic error, can be corrected with an appropriate rule based on the Passing-Bablok robust regression model. This made it possible to define calibration procedures for individual methods and reconcile results from different sampling methods at the level of a single method used to obtain a consistent comparable result, eliminate inconsistencies and lead to a uniformly consistent version of the data.

The experimental tests carried out, moreover, made it possible to identify “significant differences” between the groundwater sampling methods. This made it possible to define universal factors and analytical loadings that can affect the variability of the chemical analysis, resulting from the use of a particular method.

Identified factors are:

- the pumping regime determines the catchment area of the test point considered as “the area from which the groundwater sample comes”,

- for conventional methods, the „mechanical treatment” of groundwater samples and changes in pressure and temperaturę, as well as cavitation effect, have a significant impact on the chemical variability of the sample,

- for conventional methods, a reduced concentration of dissolved gases is observed - degassing of samples associated with the process of mechanical treatment of the sample, high flow rate and the co-occurring effect of cavitation,

- no-purge or low-flow sampling methods - are sensitve to variability of atmospheric conditions, in particular, changes in ambient temperature during water sampling - the risk of rapid heating of the sample.

The results presented in this dissertation, allow to define additional guidelines for groundwater monitoring field research. Obtained results in the quantitative analysis of the sampling methods used, allow to select optimal method and can be used in the so-called targeted sampling, focused on detecting extreme values of concentrations of specific physicochemical indicators.

For cyclic groundwater monitoring researches, a very important aspect that determines the reliability and validity of the results is the implementation of monitoring by conducting sampling at a given point, in a constant unchanging method. The variability and technical variance of the various methods of hydrogeological prospecting, when different sampling methods are used, can significantly disturb and mask the natural variability of the chemical composition of groundwater samples. It can by affecting the reliability of the results and their interpretation. The canon of groundwater sampling during cyclic monitoring, should require the need to use the same type of sampling equipment. Every changes should be noted in sampling protocol.

In the situation when at a given point, for a variety of reasons, there is a risk of not to ensure comparabe results. Author has developed and proposes for practical use the application of a new tool in assessing the groundwater chemical status. This tool is the calibration procedures defined by the Author in this dissertation - empirical conversion formulas (transformations) allowing for the reconciliation of results.