Occurrence and Health Impact of Naturally Occurring Elements in Hungarian Drinking Water Resources

Theses of the PhD Dissertation

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Budapest
2024

Introduction

Drinking water can have a significant impact on human health, therefore its quality has been well-regulated both in the European Union and in Hungary for a long time. The national legislation is based on the EU Directive 2020/2184 on the quality of water intended for human consumption (hereinafter: DWD), which came into force on January 12, 2021. This directive places even greater emphasis on the risk-based approach to drinking water safety, which was also featured in its predecessor, Directive 98/83/EC.

The DWD requires monitoring of over one hundred chemical components in drinking water, most of which are primarily anthropogenic in origin. Geological metals, metalloids, and non-metals receive less attention, although sodium, iron, manganese, arsenic, boron, and selenium have been parameters under monitoring previously. The DWD – and the Hungarian Government Decree 5/2023 (I. 12.) transposing it (hereinafter: Government Decree) – introduced the monitoring of additional, primarily natural elements (starting from January 12, 2026), such as uranium, calcium, magnesium, and potassium.

The changes in regulation and the risk-based approach justified the need for a national, comprehensive survey, encompassing all public drinking water supplies of Hungary. This survey focuses on the investigation of naturally occurring elements, including risk assessment and analysis of potential health impacts.

Objectives

Following objectives were addressed:

1) Survey of the natural element concentration in drinking water and water sources.
2) Characterisation if the quality of Hungarian drinking water sources and public drinking water at the settlement level based on natural element content.
3) Evaluation of the temporal and spatial stability of natural element concentrations.
4) Investigation of the association between the total alpha activity and uranium content of supplied drinking water.
5) Assessment of the impact of water treatment technologies on non-target components.
6) Assessment of the health impact associated with the tested natural elements:
    - Quantitative risk assessment of elements with known or potential adverse health impact in drinking water

- Assessment of the contribution of drinking water to selenium intake.
- Investigation of the health impact of calcium and magnesium in drinking water.
- Assessment of the correlation between lithium concentration in public drinking water and suicide mortality rates.

Materials and methods

In the survey, barium (Ba), beryllium (Be), boron (B), zinc (Zn), calcium (Ca), potassium (K), cobalt (Co), lithium (Li), magnesium (Mg), molybdenum (Mo), sodium (Na), strontium (Sr), selenium (Se), titanium (Ti), uranium (U), vanadium (V), and zinc (Zn) concentration of the drinking water supplied by public water supply systems in Hungary was investigated.

The survey was conducted in two phases. The first phase involved a preliminary survey between 2016 and 2018 (elements examined: B, Ca, Co, K, Li, Mg, Na, Se, U, V, Zn), in which one representative sample was taken per water supply system from the distribution network. This was followed by a detailed survey between 2018 and 2022 (elements examined: B, Ba, Be, Ca, Co, K, Li, Mg, Mo, Na, Se, Sr, Ti, U, V, Zn), where samples were taken both before and after the water treatment, where applicable.

The sampling was carried out in accordance with ISO 5667-5:2006 standard, and the analytical tests were carried out at the National Center for Public Health and Pharmacy using inductively coupled plasma mass spectrometer (hereinafter: ICP-MS) according to the MSZ EN ISO 17294 standard.

The comparison of the two surveys' outcomes – assessing the temporal and spatial stability of element concentrations – was carried out at the settlement level using paired t-tests and Pearson correlation analysis. For settlement-level characterization of drinking water quality, the results of each water supply system were assigned to all settlements they supply.

The characterization of drinking water sources was based on B, Ba, Be, Ca, Co, K, Li, Mg, Mo, Na, Se, Sr, Ti, U, and V concentrations in the pre-treatment or untreated samples for from the detailed survey. Principal component analysis (PCA) and hierarchical cluster analysis (HCA) were used for the analyses.

The impact of drinking water treatment technologies on B, Ba, Ca, Co, K, Li, Mg, Mo, Na, Se, Sr, Ti, U, and V was evaluated using paired t-tests of the pre- and post-treatment samples from the detailed survey, Kruskal-Wallis H-tests and Mann-Whitney U-tests.

For the investigation of the relationship between uranium content and total alpha activity in drinking water, uranium results from the preliminary survey and total alpha activity data available from the national water quality database (2016-2019) were compared. Pearson correlation analysis was used for this analysis.

For the quantitative risk assessment, tolerable daily intake (TDI) or reference dose (RfD) values – and recommended daily intake (ADI) values in the case of Se – were compared to the highest measured and 95th percentile concentrations in drinking water at the settlement level. Health risk quotient (HRQ) was calculated based on a body weight of 70 kg and a daily consumption of 1.1 liters of drinking water. Risk assessment was conducted for B, Be, Ba, Co, Mo, Se, V, U, and V.

The health impact studies for Ca and Mg were based on the Ca and Mg results at the settlement level, mortality data from the Hungarian Central Statistical Office (HCSO), the 2009 and 2019 National Nutrition and Nutritional Status Surveys (OTÁP), and the 2022 census data. Spearman rank correlation and multivariable linear regression were applied in the studies.

For the Li health impact study, Li results from the preliminary survey were used. Additional data were provided by the HCSO demographic database (suicide cases, mortality rates due to alcoholic liver disease) and the National Territorial Development and Spatial Planning Information System (TEIR) database (religiosity, income). Multivariable linear regression was applied in the analysis.

Results and discussion

A total of 3,972 samples were collected and analyzed during the preliminary survey (1,424 samples) and the detailed survey (2,548 samples). Comparing the results of the two surveys, concentrations of B, Mg, K, Co, and U were not significantly different. Although differences for Li, Na, Ca, V, and Se were statistically significant, the actual discrepancy of the concentrations were not considered relevant from a water hygiene perspective. A notable exception was Zn, where no correlation was found between the surveys' results, and therefore it was excluded from further analyses.

For the characterization of drinking water sources, results of 1,256 samples, originating from 82% of the drinking water sources (1,155 samples), were used. The majority (84%) of the samples were from deep groundwater, 8.8% from karst water, 2.5% from bank-filtered water, 2.3% from shallow groundwater, 1.4% from surface water, and less than 1% from mixed water sources. Water sources did not segregate based on water type, except for karst water, which showed a distinct (primarily Ca and Mg-dominated) profile. Based on HCA and PCA, six

clusters were identified based on elemental profiles, mostly showing characteristic geographical distributions.

The water treatment technologies used in drinking water supply in Hungary do not have a significant impact on the analysed elements. Even statistically significant differences were found irrelevant from a water safety or technological perspective. Technologies using breakpoint chlorination with significant amounts of sodium hypochlorite only resulted in an increase of 1.9-7.2 mg/l Na, a 10-15% increase.

To investigate the correlation between uranium content and total alpha activity in drinking water, 4,365 total alpha activity results and uranium results corresponding to 3,150 settlements were included. A statistically significant, moderately strong, positive correlation was found between the two variables (r: 0.6772, p-value: <0.05).

Based on the quantitative risk assessment – with the exception of V – the tested elements pose negligible or low risk on national level. Moderate risk levels were only observed for B, Co, Mo, and U when considering the highest measured concentrations. This affected 4 settlements for Co, 5-5 for B and U and 12 for Mo. The assessment of V is inconsistent, with conflicting RfD values (0.07-7 µg/kg bw) found in the literature. Considering this, and the 140 µg/l drinking water limit applied in some EU Member States (e.g., Italy), it can be concluded that the risk for V is also negligible.

The newly introduced 30 µg/l limit for U was exceeded only at one drinking water source (41 µg/l). Even the third of the limit (10 µg/l) was only exceeded in 15 drinking water sources, with the 99th percentile concentration being 11.5 µg/l.

Only the intake calculated from the highest Se concentration (29 µg), measured in one settlement, is sufficent to cover the recommended intake for various age groups (26-35 µg), while the 99th percentile Se concentrations in drinking water of the settlements is an order of magnitude lower than the maximum value (2.6 µg/l).

The Ca and Mg concentrations in drinking water are generally favorably high, showing characteristic geographical differences and varying over a wide concentration range. The median concentration of Ca is 68 mg/l (minimum 2.7 mg/l, maximum 189 mg/l) and of Mg 22 mg/l (minimum <0.5 mg/l, maximum 81 mg/l). Drinking water in Hungary could contribute 8-9% of the recommended daily Ca intake in half of the settlements, and even 10-12% in a quarter of them, while for Mg, this could be 7-8% or 11-13%, respectively.

The Li content of drinking water also shows characteristic geographical differences and varies over a wide concentration range. The median concentration for Li is 9.3 µg/l (minimum <1.0 µg/l, maximum 263 µg/l).

A statistically significant negative correlation (a slight protective effect) was found between Mg concentration in drinking water and mortality related to cardiovascular diseases in the entire population, as well as between Li content of drinking water and suicides in men.

Theses

1) In my research, I created a water quality profile for 15 geogenic elements (B, Ba, Be, Ca, Co, K, Li, Mg, Mo, Na, Se, Sr, Ti, U, and V) for 82% (1,155) of the operating drinking water sources based on 1,256 samples and for drinking water of all Hungarian settlements (3,155) based on 3,972 samples.

2) I found that the quality of drinking water in terms of B, Ca, Co, K, Li, Mg, Na, Se, U, and V can be considered stable from a public health perspective both over time (comparing the two periods) and spatially (based on samples taken from different points of the water supply system). For these parameters, the network entry point of the waterworks can be accepted as a designated sampling point for water quality monitoring.

3) Regarding the operating drinking water sources, I make the following observations:

- **a.** Natural elements exhibit characteristic geographical distributions, some of them reaching elevated concentrations in confined areas. The observed spatial distributions confirm that the quality of groundwater is determined not only by the geological composition of the aquifer but also the characteristics of groundwater flow systems (e.g., pH, temperature, redox potential, dissolved gas content). These influence the dissolution of elements into the water, resulting in differences in groundwater composition even within the same aquifer.
- **b.** It can be stated that karst water sources differ from deep groundwater sources, based on the analysed natural elements, primarily due to the presence of Ca and Mg. However, no such differentiation was observed among other types of water sources (surface water, shallow groundwater, bank-filtered water) based on these elements, confirming the close hydrogeological connection between surface water, bank-filtered water, and groundwater.

4) I found that the drinking water treatment technologies used in Hungary do not significantly alter the natural element composion. Even in waterworks using

breakpoint chlorination with significant amounts of sodium hypochlorite, sodium content of drinking water is not increased to a hazardous level. Accordingly, the strategy for reducing the number of monitoring samples for Na in water quality monitoring should be reviewed.

5) Based on the quantitative risk assessments, I make the following statements:

- **a.** It can be stated that the newly introduced U parameter in drinking water is generally present in low concentrations in Hungarian drinking water sources and poses a low risk nationwide in municipal drinking water.
- **b.** I found that other elements with potential adverse health effects, such as B, Be, Ba, Co, Mo, Se, and V, pose negligible or low risk nationwide in Hungarian drinking water sources and municipal drinking water.
- **c.** The drinking water sources and warer supply systems that require increased attention for any potentially harmful natural elements have been identified. The locally occurring, at most moderate risk, can be managed locally. Compliance with the DWD and the Government Decree regarding U does not pose significant challenges or require interventions at the national level.

6) It can be stated that the uranium content and total alpha activity of the supplied drinking water are closely associated, implying that most of the total alpha activity originates from uranium. This is advantageous from a public health perspective since the dose coefficients of radionuclides ^{238}U and ^{234}U are an order of magnitude smaller than those of other alpha-emitting radionuclides (^{226}Ra, ^{210}Po).

7) Based on the epidemiological studies related to municipal drinking water, I make the following statements:

- **a.** It can be stated that municipal drinking water consumption does not significantly contribute to the necessary Se intake nationally.
- **b.** It can be stated that municipal drinking water can be a significant source of Ca and Mg intake. This is especially important for Ca, as the majority of the Hungarian population does not consume the recommended amount.
- **c.** Based on the results of the first national epidemiological study in Hungary, it is likely that the Mg content in municipal drinking water has a protective effect against cardiovascular disease-related mortality,

although the impact of unfavorable socioeconomic conditions is more significant.

d. Based on the results of the first national epidemiological study in Hungary, it can be stated that the Li content of municipal drinking water has a protective effect against suicide-related mortality in male population, although the protective effect of other factors, such as religiosity and income is more significant.

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