

CHROMIUM CONTENT IN THE DRINKING WATER OF PLEVEN REGION – SOURCES AND HEALTH CONTROL

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Abstract. Ensuring access to high-quality drinking water in Bulgaria presents significant challenges due to an aging and deteriorating water distribution network, anthropogenic pollution of water sources, and the natural migration of chemical elements from geological substrates into groundwater. These factors contribute to the contamination of water resources with harmful substances such as heavy metals, pesticides, and fertilizers, posing serious risks to human health. Particular concern arises from chromium contamination, especially in regions with naturally elevated chromium levels. Hexavalent chromium (Cr⁶⁺) is toxic and carcinogenic, whereas trivalent chromium (Cr³⁺) is an essential trace element. This study analyses data on chromium concentrations in drinking water across the Pleven region over an eight-year period, based on monitoring conducted by the Regional Health Inspectorate – Pleven. Results show that approximately 26% of the 1,242 samples collected exceeded the maximum allowable chromium concentration of 50 µg/L, with the highest recorded value reaching 138.82 µg/L. According to both national and European legislation, the established limit applies to total chromium, without differentiating between its hexavalent and trivalent forms. These findings highlight the urgent need for increased monitoring and implementation of modern water treatment technologies to reduce chromium levels and ensure safe drinking water in the affected areas, with the primary goal of protecting public health and promoting sustainable management of Bulgaria's water resources.

Keywords: drinking water, hexavalent chromium, monitoring, public health, trivalent chromium

1. INTRODUCTION

One of the major challenges faced by water supply organizations in Bulgaria is ensuring the provision of high-quality drinking water to the population.

In most regions of the country, this process is hindered by several key factors:

- An obsolete and deteriorating water supply network, leading to substantial losses of potable water.
- Contamination of natural water sources used for domestic supply, caused by the intensive use of nitrogen fertilizers and pesticides in agriculture, as well as the discharge of untreated domestic and industrial wastewater.
- Migration of chemical elements such as chromium (Cr), iodine (I), strontium (Sr), molybdenum (Mo), and fluorine (F) from soils and bedrock into groundwater used for drinking purposes.

These factors pose significant challenges to the sustainable management of Bulgaria's water resources and underscore the need for urgent measures focused on infrastructure modernization, effective pollution control, and the adoption of best practices for water protection and conservation.

The deficiency or excess of certain microelements introduced into the human body through water or food may lead to so-called endemic (biogeochemical) diseases, including molybdenum-induced gout, strontium rickets, endemic goiter, fluorosis, etc. [1,2]. Furthermore, the presence of specific toxic elements in drinking water—such as beryllium, cadmium, chromium, and arsenic—has been linked to an increased risk of malignant diseases.

Toxic chemical substances in water may be of anthropogenic or natural origin. Contamination with heavy metals, radioactive elements, mineral fertilizers, pesticides, detergents, and other chemical compounds represents a serious issue, as conventional treatment and disinfection methods are not always effective in reducing their concentrations to safe levels.

Bulgarian researchers have identified several geopathogenic zones within the country, characterized by anomalous distributions of certain chemical elements that significantly affect the quality of life in the impacted areas [3]. These zones may span one or several administrative regions, such as those with elevated chromium concentrations in the drinking water of Northern Bulgaria—particularly in the Pleven, Vidin, and Montana districts.

Chromium is a naturally occurring metal found in ore deposits, rocks, and soils, as well as a pollutant introduced through human activities, including metallurgy, chemical manufacturing, hydrothermal

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power generation, and nuclear processes. In nature, chromium occurs primarily in two oxidation states:

- Hexavalent chromium (Cr^{6+}) – highly toxic and classified as a carcinogenic element.
- Trivalent chromium (Cr^{3+}) – an essential trace element involved in glucose metabolism.

Hexavalent chromium (Cr^{6+}) is more toxic than trivalent chromium (Cr^{3+}) because it is highly soluble, easily enters cells through sulfate transport channels, and is a strong oxidizing agent. Inside the cell, Cr^{6+} is reduced to reactive intermediates that generate oxidative stress and cause severe DNA damage, including mutations and DNA–protein cross-links, making it a known human carcinogen. In contrast, Cr^{3+} is poorly absorbed, less reactive, and does not readily reach intracellular targets, resulting in much lower toxicity.

Numerous studies conducted in Bulgaria and abroad have sought to identify the origin of chromium in groundwater [4,5]. Analytical data indicate that the chromium concentrations in the groundwater of Northern Bulgaria – particularly in the Pleven region – are predominantly of natural origin, resulting from the interaction between water and the rock and soil formations of the aquifers [6].

These findings highlight the necessity for comprehensive monitoring of the chemical composition of drinking water and the implementation of appropriate water resource management strategies in the affected regions.

2. OBJECTIVE

The objective of this study is to investigate the concentration and spatial distribution of chromium in groundwater sources used for drinking water supply in the Pleven region. Additionally, the study aims to evaluate potential methods and technologies for reducing chromium concentrations in potable water, thereby ensuring compliance with national and European water quality standards and safeguarding public health.

3. MATERIALS AND METHODS

A retrospective study was conducted to evaluate chromium concentrations in drinking water across the Pleven region over an eight-year period (2010–2017). Data were obtained from the Drinking Water Quality Monitoring Program implemented by the Regional Health Inspectorate (RHI) – Pleven.

The RHI – Pleven analyzed a total of 1,242 drinking water samples for chromium content by a photometric method, according to ISO 18724:2025. Water quality – Determination of dissolved chromium(VI) in water.

An assessment of the public water supply systems in the region was carried out to identify the groundwater bodies (GWBs) used for potable water abstraction. Chromium concentration data from the planned monitoring of groundwater bodies,

conducted by the Danube Basin Directorate (DBD), were analyzed for the same period. In addition, information from the River Basin Management Plans (RBMPs) for the periods 2010–2021, provided by the DBD, was reviewed to evaluate trends and potential sources of chromium contamination.

Furthermore, the study investigated methods for chromium removal from drinking water, emphasizing the applicability of modern water treatment technologies capable of reducing chromium concentrations to acceptable levels, in compliance with national and European Union water quality standards.

4. RESULTS AND DISCUSSION

The Pleven administrative region, situated in the Danubian Plain, covers an area of 4,653.3 km². It borders the following administrative regions – Lovech to the south, Vratsa to the west, and Veliko Tarnovo to the east, while the Danube River forms its northern boundary. The region comprises 123 settlements, including 14 towns and 109 villages, distributed across 11 municipalities: Belene, Gulyantsi, Dolna Mitropoliya, Dolni Dabnik, Iskar, Kneja, Levski, Nikopol, Pleven, Pordim, and Cherven Bryag. According to the 2021 census, the population is 226,120 inhabitants [7].

An analysis of the public water supply infrastructure in the Pleven region reveals that most systems were constructed in the mid-20th century. Despite their age, they continue to provide drinking water to all settlements in the region, including small villages with only a few dozen residents. Groundwater serves as the primary source of drinking water, with most settlements relying on individual water sources. Long-distance pipelines transporting water from remote sources and supplying multiple settlements are relatively uncommon.

Of the 105 water supply zones in the region, 90 operate as individual systems, each utilizing water sources located within the boundaries of the respective settlement. Only 15 are grouped systems, serving two or more settlements.

The quantity and quality of drinking water in the region are influenced not only by groundwater resources but also by the presence of the four main rivers flowing through the area: Iskar, Vit, Osam, and the Danube (Fig. 1). These rivers play an essential role in regional hydrology, contributing to the recharge of groundwater aquifers and affecting overall water availability and quality.

The groundwater resources in the Pleven region are drawn from distinct groundwater bodies (GWBs), which are classified and characterized in accordance with European and Bulgarian legislation [8,9]. The formation and properties of these GWBs are determined by the complex interaction of multiple factors, including physiogeographic elements (such as climate, relief, hydrology, and hydrography) and geological parameters (including geological structure, lithological composition of rocks, and

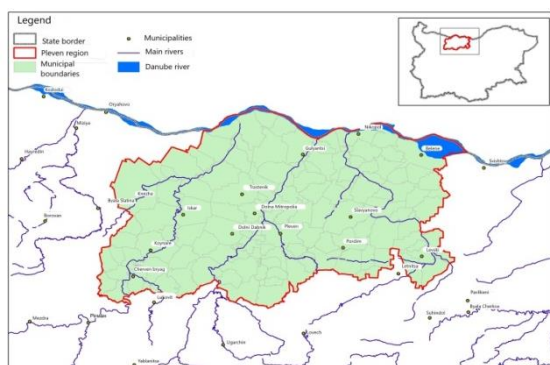


Figure 1 – Main rivers and territorial extent of the Pleven region

tectonic settings). Detailed descriptions of these characteristics can be found in specialized geological studies [10,11].

In the Pleven region, the drinking water supply for most settlements relies on 13 groundwater bodies, the majority of which consist of shallow aquifers (first aquifer horizon) [12]. These groundwater bodies represent the main sources of potable water and play a crucial role in maintaining regional water security.

According to European and national legislation, chromium (Cr) is a key chemical indicator of drinking water quality, with a current maximum allowable concentration (MAC) of 50 µg/L. Under Regulation No. 9 of 2001 on drinking water quality, a transitional period is in effect until January 12, 2036, after which the MAC must be reduced to 25 µg/L [8,13,14].

The results of our study indicate that: 322 samples (25.9%) exceeded the limit of 50 µg/L, 275 samples (22.1%) were within the 25–50 µg/L range, 395 samples (31.8%) contained chromium concentrations between 0–25 µg/L, and 250 samples (20.1%) had chromium levels below the detection limit (Fig. 2).

These findings reveal that nearly one-quarter of all tested samples contained chromium concentrations exceeding the regulatory threshold, suggesting a persistent and regionally significant issue that warrants further investigation and remediation.

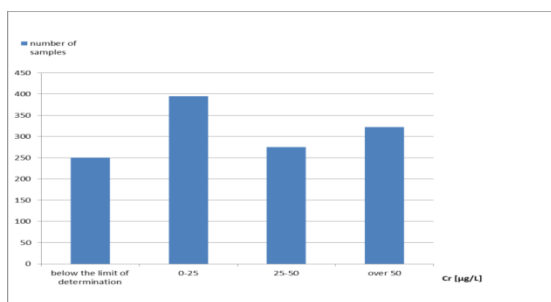


Figure 2 – Distribution of samples according to chromium content

Statistical analysis of data from 2010 to 2017 revealed that the average chromium concentrations in drinking water consistently exceeded the permissible limits in 12 settlements throughout the entire study period. In addition, six other settlements exhibited average concentrations ranging from 36.24 to 48.87 µg/L, indicating periodic exceedances during certain months or years (Table 1).

Table 1 – Settlements in the Pleven Region with Chromium Concentrations Exceeding the Limit for the Period 2010–2017

No.	Settlement	Municipality	N (no. of samples)	Avg. Cr [µg/L]
1	Slavovitsa	Dolna Mitropolia	36	124.00
2	Bozhuritsa	Dolna Mitropolia	42	102.00
3	Dolni Vit	Gulyantsi	24	96.58
4	Tatari	Belene	36	82.22
5	Brest	Gulyantsi	28	65.70
6	Dabovan	Gulyantsi	10	61.83
7	Muselievo	Nikopol	40	60.10
8	Petokladentsi	Belene	25	57.33
9	Cherkovitsa	Nikopol	12	51.10
10	Gigen	Gulyantsi	24	50.55
11	Evlogievo	Nikopol	8	50.44
12	Asenovovo	Nikopol	23	50.43
13	Zagrazhden	Gulyantsi	9	48.87
14	Novachene	Nikopol	65	48.80
15	Debovo	Nikopol	22	46.46
16	Stezherovo	Levski	29	43.77
17	Bozhurluk	Levski	25	41.75
18	Lenkovo	Gulyantsi	24	36.24

The highest average chromium concentrations during the study period were recorded in the villages of Slavovitsa and Bozhuritsa (Dolna Mitropolia Municipality) and Dolni Vit (Gulyantsi Municipality), exceeding the 50 µg/L limit by more than twofold—124 µg/L, 102 µg/L, and 96.58 µg/L, respectively. The maximum concentrations measured in these settlements were 138.82 µg/L

(Slavovitsa), 129.72 µg/L (Bozhuritsa), and 128.2 µg/L (Dolni Vit).

A parallel study for the same period found that some of the settlements listed in Table 1 also exhibited elevated nitrate concentrations in their public water supply systems. These included the villages of Gigen, Cherkovitsa, and Bozhuritsa, with average nitrate levels of 150.68 mg/L, 61.27 mg/L, and 42.92 mg/L, respectively [15]. No published studies were identified addressing the combined health effects of chromium and nitrate exposure in drinking water.

Chromium is a transition metal that can exist in oxidation states ranging from -2 to $+6$, though the most common forms are trivalent chromium (Cr^{3+}) and hexavalent chromium (Cr^{6+}). Divalent chromium (Cr^{2+}) is unstable and readily oxidizes to Cr^{3+} upon exposure to air, while zero-valent chromium (Cr^0) does not occur naturally and is physiologically inert, although it is present in iron alloys such as stainless steel [16].

The role of trivalent chromium (Cr^3) as an essential trace element is debatable. Some authors define it as an essential trace element that plays a role in the metabolism of carbohydrates, lipids and proteins. It is considered useful in preventing or mitigating metabolic disorders such as hyperglycemia and hyperlipidemia and may alleviate some symptoms of diabetes when administered orally [17]. Other studies have shown that beneficial effects in humans have not been unequivocally established [18]. However, Cr^{3+} can undergo oxidation in soil to form Cr^{6+} , a process influenced by manganese concentrations and soil pH. Elevated Mn content and alkaline conditions tend to accelerate this oxidation [19].

Hexavalent chromium is known to have 100-fold more toxicity than trivalent chromium, for both acute and chronic exposures, due to its high solubility and mobility in water [20]. Cr^{6+} is highly toxic, mutagenic, and carcinogenic, and has been classified as a Group 1 human carcinogen by the International Agency for Research on Cancer (IARC). Its toxicity results from its strong oxidative potential and efficient cellular uptake via nonspecific anion transport proteins [21]. Once inside cells, Cr^{6+} is rapidly reduced to Cr^{3+} , producing reactive intermediates that disrupt normal cellular processes and trigger oxidative damage and apoptosis [22,23].

Chromium can enter the human body through multiple exposure pathways, including drinking water, food, air, smoking, and occupational exposure. The primary route of exposure in non-industrial populations is oral ingestion via contaminated drinking water. According to European and Bulgarian regulations, the maximum allowable concentration (MAC) for total chromium in drinking water is 50 µg/L, with no distinction made between Cr^{3+} and Cr^{6+} , despite evidence suggesting that approximately 90% of chromium in water occurs as Cr^{6+} [5].

A 2010 U.S. Environmental Protection Agency (EPA) statement justified the testing of total,

trivalent, and hexavalent chromium, emphasizing that both forms are interconvertible depending on environmental and physiological conditions; therefore, testing only one form would provide incomplete information [24]. In the human body, Cr^{6+} can be reduced to Cr^{3+} in the stomach and other organs [25].

Under the Regional Health Inspectorate (RHI) – Pleven monitoring program, only total chromium is measured. According to groundwater monitoring regulations, the MAC for total chromium remains 50 µg/L [26]. Data from the Danube Basin Directorate (DBD), however, indicate that testing is conducted for total chromium, as well as Cr^{3+} and Cr^{6+} separately. Between 2010 and 2017, 25 monitoring points across the Pleven region—covering all 13 groundwater bodies—were sampled for chromium in drinking water. The highest exceedances were recorded in the villages of Zagrazhden (73 µg/L) and Brest (80 µg/L), both drawing water from the same groundwater body. According to the River Basin Management Plans (RBMPs) 2010–2015 and 2016–2021, no anthropogenic sources of chromium contamination were identified. Chromium presence in groundwater in this region has been documented for decades, with geogenic origins—specifically, the interaction of water with chromium-bearing soils and rocks—considered the primary cause [6].

Conventional water treatment methods are generally ineffective at reducing chromium concentrations to safe levels. Specialized treatment technologies, such as ion exchange, are required to achieve compliance with drinking water standards. The main techniques for chromium removal from drinking water include:

- Biological treatment – employing specific bacteria capable of metabolizing or adsorbing heavy metals through membrane systems. This process is relatively slow, requiring the development of sufficient microbial biomass for effective purification.
- Flocculation – using chemical additives to form flocs that bind chromium ions for removal.
- Ion exchange – employing ion-exchange resins, though capacity limitations can restrict efficiency.

Although laboratory studies have described numerous methods for chromium removal from industrial wastewater, such as chemical precipitation, ion exchange, and solvent extraction, these technologies remain constrained by high operational costs and poor performance at low chromium concentrations [27]. Consequently, despite sustained efforts to commercialize remediation strategies for hexavalent chromium removal, their transition from laboratory-scale success to effective large-scale environmental application has been limited and slow [28].

Additionally, certain treatment methods were found to result in secondary contamination of the

treated water with other potentially harmful substances.

At present, chromium removal technologies have not been widely implemented in Bulgaria, although pilot methods were developed and tested for the Bozhuritsa water source in previous years [5,6].

5. CONCLUSIONS

The analysis and evaluation of the drinking water supply system and chromium concentrations in the Pleven region support the following conclusions:

1. The regional water supply infrastructure provides access to potable water for all settlements, including the smallest villages with only a few dozen inhabitants.
2. Despite regular regulatory monitoring of drinking water quality, several settlements continue to receive water with chromium concentrations exceeding the permissible limit of 50 µg/L. Moreover, three settlements exhibit combined contamination from both chromium and nitrates, posing additional health concerns.
3. Immediate, site-specific actions are required to ensure compliance with drinking water standards in affected areas. Possible measures include: identifying and developing alternative uncontaminated water sources, blending contaminated and clean water to achieve acceptable concentrations, and implementing modern water treatment technologies capable of effectively reducing chromium levels.

These conclusions highlight the urgent need for enhanced water treatment infrastructure, continuous monitoring, and the adoption of advanced purification technologies tailored to local hydrogeological conditions to protect public health and ensure safe drinking water in the Pleven region.

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