Inorganic Chromium Speciation in Geothermal Water of the Podhale Trough (Southern Poland) Used for Recreational Purposes

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Abstract: The results of total chromium determination (by ICP-OES method) in samples collected from nine working wells named GW1–GW9, exploiting geothermal water from the Podhale Trough (southern part of Poland, near the Tatra Mountains), which is used for recreational purposes, were implemented for hydrogeochemical modeling to indicate dominating chromium speciation. The reliability of the results was determined by the application of a quality assurance/quality control program, both in the laboratory and during field work. Based on chromium speciation, the risk associated with the utilization of geothermal water was calculated. The outcome showed that the concentration of Cr(III) is almost equal to the total chromium concentration (1–2 µg·L⁻¹). Cr₉₀₀ concentrations were also used in a health risk assessment in the case of epidermal absorption (EDI_derm) during bathing in thermal pools and four assumed scenarios in relation to the handling of geothermal water. The effect of the very low Cr₉₀₀ concentration in the analyzed water on health risk calculation was estimated as low (hazard quotient value <10⁻⁷). In the case of risk matrix analysis, the environmental risks were estimated as moderate, major and very severe, dependent on the assumed scenario.

Keywords: geothermal system; chromium exposure; risk assessment; environmental sciences; hydrogeochemical modeling; renewable sources

1. Introduction

Chromium (electron configuration: [Ar] 3d⁵4s¹, sixth group, fourth period, block d) is the seventh most abundant element on Earth, residing mostly in the core and mantle; it is the 21st most abundant element in Earth’s crust, with an average concentration about 100 µg/g. The major sources of chromium in the crust are ultrabasic and basic rocks [1,2].

In ground and surface water chromium occurs primarily in two oxidation states: trivalent Cr(III) and hexavalent Cr(VI). Trivalent chromium is sparingly soluble in the aqueous environment and usually binds suspended particulate matter and accumulates in bed sediments, whereas hexavalent chromium is quite soluble and more mobile. Among the trace elements present in natural water, chromium belongs to the group of elements that migrate poorly in an aquatic environment. The mobilities and concentrations of these forms are various and dependent on several parameters, i.e., geological setting, pH, oxidation-reduction potential (E₉ₐ) and the presence of Fe and Al hydroxides. In natural water at neutral and alkaline pH, the mobility of Cr(III) is significantly limited by its adsorption on mineral surfaces. Under oxidation conditions, the major migrating forms of chromium in groundwater are anions like chromate (CrO₄²⁻) and dichromate (Cr₂O₇⁻²). In the acidic environment and reducing conditions, the predominant species of chromium are trivalent forms such as CrOH²⁺ and Cr³⁺.
Chromium also creates ion pairs and complexes. Ligands that may be bonded to the central atom of Cr can be neutral molecules (e.g., H$_2$O and NH$_3$) or anions (e.g., Cl$^-$, CN$^-$, F$^-$ and SO$_4^{2-}$) [2–7]. Chromium-bearing minerals such as chromite (FeCr$_2$O$_4$) are generally resistant to weathering. Chromium accumulation in groundwater, lake water and deposits is also associated with anthropogenic sources, mainly the industrial processes involved in the smelting of metalliferous ores, tanneries and automotive and aerospace industries [7–10].

From the biological point of view, Cr is a well-known element with confirmed properties that depend on its speciation. Chromium(III) was established as an essential dietary element in the 1950s. The trivalent form is also an essential nutrient, especially for mammals, and participates in the processes of lipid and protein metabolism. It is also important for maintaining the normal glucose tolerant factor, whilst Cr(VI) has been found to be carcinogenic for internal and external organs of living organisms [2,4,10–13].

Due to the toxic properties of chromium, the maximum permissible concentration of this element in water intended for human consumption, 50 µg·L$^{-1}$, was established by the European Union in the Council Directive 98/83/EC [14] as well as in the guides published by the World Health Organization [15]. In Polish regulations [16], a maximum permissible concentration (MPC) of total chromium in drinking water is defined as 50 µg·L$^{-1}$, which does not deviate from the global standards. Furthermore, taking into account the actual use of the geothermal water from Podhale for heating purposes and recreational swimming pools, the quality of water provided from the circulation system has to be controlled in accordance with the proper legal regulations [17,18]. Water from swimming pools has to be monitored in terms of certain biological parameters, including the presence of *Escherichia coli*, *Pseudomonas aeruginosa*, *Legionella* and coagulase-positive staphylococci, along with and the total number of microorganisms present at the temperature 36 ± 2 °C after 48 h in 1 mL of water. Furthermore, certain physicochemical parameters also have to be monitored, including $E_H$, pH, free chlorine, bound chlorine, turbidity, chloroform, $\sum$ THM/trichloromethanes (the sum of trichloromethane, bromodichloromethane, dibromochloromethane and tribromomethane), aluminum, iron, nitrates, ozone, isocyanuric acid and chemical oxygen demand [18,19]. In the case of total chromium, it is very important to notice that this element is not specified in Polish law regarding the physicochemical parameters of the recreational swimming pools using geothermal water. Its concentrations should be controlled because it could be released from the internal installation system if not properly flushed or from the geothermal water reservoir when the chromium-bearing minerals are present [5]. In the future, studied water could be used for drinking, among other purposes. In this scope, many tests have already been conducted in Poland, including recognition of scaling problems during geothermal water treatment processes [20–26]. The geothermal water could be also used in medicinal therapies due to the presence of specific components. Polish law specifies the threshold values for concentrations of specific components, beyond which the groundwater can be considered as potentially medicinal [27–30]. It also sets MPCs of undesirable components in excessive concentrations. The MPC for total chromium in the cases of drinking treatment or inhalation was set as 10 µg·L$^{-1}$. There is no regulation for the external use of water containing chromium [31]. There is a proposal to include Cr(VI) in the Third Watch List as a potential contamination risk for transitional and coastal water [32].

The objective of this study was to assess the risk related to the use of the analyzed water for recreational purposes. For this purpose, the total chromium determination in geothermal water in selected intakes from the Podhale Trough was conducted using the ICP-OES method. The next step was the geochemical modeling of chromium speciation in the geothermal water analyzed here.

2. Materials and Methods

Geothermal water in Podhale Trough, located in the southern part of Poland, near the Tatra Mountains (Figure 1), is captured with wells drilled at a depth from 2 to 5 km below surface level [33,34].
This geothermal water is mainly used for heating purposes, as well as in recreational centers, bathing areas and balneological therapies. On a small scale, geothermal water in Poland is used in fish farming (Atlantic salmon), food processing, wood drying, heating sports facilities, cosmetic production and recovery of iodine and bromine salts [17,35]. In Podhale, after recovery of heat and cooling in the heat exchanger, water is reinjected into the geological structure with the use of two receptive holes or discharged into surface water.

The Podhale geothermal reservoir comprises two major units of geological structure. The first one is composed of the Paleogene formation (Upper Eocene–Oligocene), which is the cover of the geothermal aquifer, and the Eocene carbonate series (Middle–Upper Eocene), which is the aquifer roof. The second unit is considered to be the water-bearing rocks of the Mesozoic formations (Lower Triassic–Jurassic–Middle Cretaceous). The thickness of the Paleogene series reaches 2.5–3.2 km, whereas that of the Mesozoic series exceeds 2.5 km. The depths of the boreholes actively exploiting geothermal water are in the range of 1 to 3.5 km [20,36–38].

In this study, geothermal water samples from nine working wells (named GW1–GW9) were analyzed.

The archival data were collected from long-term water monitoring conducted between 2010 and 2019 (N = 236 samples). The gathered data included values and concentrations of selected parameters, both physical (pH, electrical conductivity (EC) and temperature (T)) and chemical (major ions and specific components—where applicable). The unstable parameter measurements and chemical composition analyses were performed by different laboratories during the investigated period. The number of individual analyses for each intake is different due to the varying frequency of water monitoring research. These data were used to estimate variability in the physicochemical composition of analyzed water.

To avoid the influence of changes in sampling process and analysis methods on the risk assessment, the collection of samples from the nine working wells (GW1–GW9) for the risk assessment and modeling experiments was carried out on the same day (in October 2019), by one person, according to the requirements precisely described in ISO 5667-11:2009 [39]. The geothermal water wells were rinsed ca. 15 min before sampling and unstable parameter measurements to ensure the stability of the chemical composition of the water and avoid the contamination of water samples with substances that could be
present in an internal installation system. Stability was considered to be achieved if the consecutive measurements did not differ by 0.2 °C for temperature, 0.1 for pH and 5% for EC [7,40,41].

Furthermore, the laboratory and field QA/QC programs were implemented to ensure that samples were not contaminated during collection and transport. The QA/QC programs involved the collection of laboratory and field blank samples, duplicate samples and samples spiked with a known amount of total chromium. Application of the quality assurance and quality control programs allowed for calculation of statistical parameters to check if the sampling process and chemical analyses were done properly. All of the samples were collected in high-density polyethylene bottles and immediately transported to the laboratory.

During fieldwork, the following normal geothermal water samples and control samples were collected:

1. Nine normal unfiltered water samples were used for the determination of bicarbonates and chlorides by titration methods.
2. Nine normal water samples were filtered with a membrane filter of 0.45 μm pore diameter and acidified with concentrated nitric acid (1 mL HNO₃ per 100 mL of water sample) to allow for the control of the chemical analyses by ionic charge balance; these samples were used to analyze the concentrations of major ions, total chromium and other trace elements, considering detailed characteristics.
3. Two duplicate control samples were collected in the same way as the normal ones from randomly selected intakes; these samples were used to check the repeatability, expressed as relative percentage difference (RPD) between chemical analyses.
4. One blank (field) control sample was used to verify the influence of the transport process on the contamination of water samples and to compare with the laboratory blank.
5. Nine normal samples and one blank sample were spiked with a known amount (10 µg·L⁻¹) of total chromium to check the accuracy (recovery) of the chemical analyses.

2.1. Reagents, Solutions and Reference Materials

Deionized water (18.2 MΩ·cm) for blank samples was obtained using the Milli-Q system (Millipore, Bedford, MA, USA). Working solutions were prepared by dilution with acidified (Nitric Acid, 69.0–70.0%, BAKER INSTRA-ANALYZED Reagent) deionized water as necessary. The standard solutions (ICP multielement standard IV and VI Certipur and V TraceCERT, Merck) with certified values were used for the spectrometer calibration. Certified reference material (TMDA 64.3 ECCC) and an environmental water sample (treated as an additional control sample) with a known matrix were used for quality control during instrumentation. For titration methods, the duplicate samples and certified reference material were analyzed (ION 96.4 ECCC). While the samples underwent the measurements of the physical parameters, the quality program included calibration and control of pH and EC probes with appropriate buffers (Hamilton, VWR), and temperature measurements were conducted with a calibrated thermometer with a specific calibration certificate.

2.2. Instrumentation

Field measurements of pH value, oxidation-reduction potential (Eₚₚ) and electrical conductivity (EC) were conducted with the use of a WTW Multimeter (ProfiLine pH/Cond 3320). The temperature was measured with a calibrated liquid thermometer whose scale covered the temperature range of geothermal water. The measurements were conducted according to the ISO standards [39,42,43].

The samples were analyzed for total chromium concentration using an Optima 7300 DV inductively coupled plasma optical emission spectrometer (ICP-OES) from PerkinElmer [44] in the Hydrogeochemical Laboratory of the Department of Hydrogeology and Engineering Geology at AGH University of Science and Technology.
Moreover, during instrumental analysis performed in the laboratory the inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS; Elan 6100, PerkinElmer) and titration methods were used for determination of particular elements used for control of ionic charge balance of each chemical analysis, the denomination of hydrochemical type of the geothermal water and for speciation modeling.

The ICP-OES method was used not only for the chromium analyses but also for the determination of Ca, Fe, K, Li, Mg, Mn, Na, S (recalculated on SO$_4^{2-}$), Si, Sr and Zn; ICP-MS was used for determination of trace elements (Ag, Al, As, B, Ba, Be, Br, Cd, Co, Cu, Hg, I, Mo, Ni, P (recalculated on PO$_4^{3-}$), Pb, Sb, Se, Ti, Tl, V, W and Zn); and titration methods were used determination of bicarbonates and chlorides, according to the standards given in [44–47]. The characteristic parameters (like precision, accuracy and uncertainty) for the determination of selected compounds with the use of each method are presented in Table S1. Estimations include the sampling process.

The laboratory has implemented an internal quality control system and participates regularly in proficiency tests and interlaboratory comparisons with satisfactory results (Z score absolute value lower than 2).

The precision of the analytical methods used, expressed as a relative standard deviation (%RSD) was determined by the laboratory during a standard process of method validation and was lower than 20%. The precision of chromium determination by the ICP-OES method that was obtained by the laboratory was 2.09%. The recovery values for all parameters were in range of 94–105%; the recovery value for Cr was established at 100.3%. Both parameters met the requirements contained in worldwide guidelines [48]. Expanded measurement uncertainty took into account all of the characteristic method parameters, and its values for all chemical compounds were in the range of 10–19%; for chromium, it was equal to 13.38%.

2.3. Speciation Modeling

Concentrations of chromium speciation in the analyzed geothermal water samples were calculated using a program created by the United States Geological Survey (USGS)—PHREEQC. Hydrogeochemical modeling is based on initial conditions of the solution entered into the program, i.e., pH, temperature, oxidation-reduction potential and concentrations of individual elements. The calculations were conducted with the use of the MINTEQ database because only this one allows for the determination of chromium speciation [49].

Redox potential was indirectly used in modeling of chromium speciation in the particular geothermal water collected. For the needs of speciation modeling, E_H was presented as a theoretical activity of electrons in a solution (pe) [50,51]. Then, the temperature of each geothermal water sample was applied, and other parameters were applied as needed.

2.4. Risk Assessment

The geothermal water analyzed here is used for recreational purposes, so the main hazard due to the presence of chromium this water results from the possibility of its direct contact with the skin during bathing in thermal pools. For this reason, the potential health risk associated with chromium occurrence was assessed. The calculations were conducted separately for adults, teenagers and children [52]. The hazard quotient (HQ) and daily intake through dermal absorption (EDI$_{derm}$) were estimated [53]. The risk assessment was conducted in two ways. The first scenario included the deterministic approach where the results obtained from chemical analyses were directly used in calculations. In the second approach, the measurement uncertainty estimated during laboratory investigations was included in the decision process. Both calculations were based on results whose reliability was verified during the examination of the instrumental methods.

Extensive use of this geothermal water can also be hazardous for the environment, with the main source of this hazard being water discharge to surface watercourses after heat is recovered heat from it. Therefore, the environmental risk was also assessed using a 5 × 5 risk matrix [54,55].
3. Results and Discussion

The authors have gathered archival data regarding the chemical composition of geothermal water in studied wells. The archival experiments were usually conducted for the major ions and/or the specific components that can give a medicinal character to the water, especially when it is used in balneology and thermal spas. The mean values of the basic field parameters (pH, EC and temperature) and concentrations of major ions determining the hydrochemical type are presented in Table S2.

The analysis confirmed the studies conducted by many scientists which revealed that the chemical composition of geothermal water of the Podhale Trough is stable over time [33,37,56–60]. The results of our study were compared to archival data and are in the range of natural changes in the chemical composition of investigated geothermal water (Figure S1). Therefore the further analyses are based on the results of the latest sampling series.

Results of analyses of selected physicochemical parameters (such as pH, redox potential (E\(_\text{H}\)), electrical conductivity (EC), temperature (T), total dissolved solids (TDS), fluoride ion concentration, metasilicic acid content and hence hydrochemical type) in collected samples are presented in Table 1. The results were used in geochemical modeling.

| Geothermal Water Well | pH  | E\(_\text{H}\) (mV) | EC (mS/cm) | T (°C) | TDS (mg L\(^{-1}\)) | F\(^-\) (mg L\(^{-1}\)) | H\(_2\text{SiO}_3\) (mg L\(^{-1}\)) | Hydrochemical Type |
|-----------------------|-----|-------------------|------------|--------|---------------------|-----------------|----------------------|------------------|
| GW\(_1\)              | 6.64| −5.9              | 3.41       | 84.9   | 2192.9              | 2.62            | 69.25                | SO\(_4\)-Cl-Na-Ca, F |
| GW\(_2\)              | 6.67| 103.8             | 3.38       | 83.8   | 2215.8              | 2.62            | 69.00                | SO\(_4\)-Cl-Na-Ca, F |
| GW\(_3\)              | 6.63| −118.1            | 3.42       | 67.4   | 2245.6              | 2.66            | 70.79                | SO\(_4\)-Cl-Na-Ca, H\(_2\text{SiO}_3\), F |
| GW\(_4\)              | 6.91| −117.6            | 2.53       | 74.5   | 1648.8              | 2.47            | 63.73                | SO\(_4\)-Cl-Na-Ca, F |
| GW\(_5\)              | 6.91| −182.5            | 2.04       | 60.5   | 1446.5              | 2.64            | 48.79                | SO\(_4\)-Na-Ca, F |
| GW\(_6\)              | 7.56| −135.9            | 0.42       | 34.7   | 233.5               | 0.346           | 19.89                | HCO\(_3\)-Ca-Mg |
| GW\(_7\)              | 7.56| −72.2             | 0.40       | 23.3   | 222.0               | 0.223           | 7.98                 | HCO\(_3\)-Ca-Mg |
| GW\(_8\)              | 7.53| −126.7            | 0.330      | 25.4   | 186.6               | 0.179           | 5.73                 | HCO\(_3\)-Ca-Mg |
| GW\(_9\)              | 6.65| −153.7            | 1.39       | 76.9   | 1077.8              | 1.48            | 64.66                | SO\(_4\)-Ca |

In light of the Polish regulations described in Geological and Mining Law [61], groundwater with a temperature above 20 °C can be treated not only as geothermal water but also potentially as curative water. These laws also mention criteria regarding the minimum concentrations of the chemical parameters, i.e., fluoride (2 mg L\(^{-1}\)) and silica expressed as a concentration of the metasilicic acid (70 mg L\(^{-1}\)), above which the water can have medicinal properties. According to the data collected during fieldwork, it can be seen that the water from all wells can be treated as geothermal. It could be used in balneotherapy due to the occurrence of specific components such as fluorides and metasilicic acid at the levels exceeding the threshold values recommended (GW\(_1\)–GW\(_5\)).

According to the purpose of the presented article and the fact that authors have focused on chromium in investigated geothermal water, the shortened verification of the ICP-OES method was applied. The verification included calculation of the laboratory limit of quantification, estimation of the variability during analysis and, as the last step, calculation of the expanded measurement uncertainty. A low chromium concentration was expected based on previously observed values during long-term water monitoring in the GW\(_1\) well. The measured total chromium concentrations were in the range of 1–3 µg L\(^{-1}\) (Figure 2).

The laboratory limit of quantification (LOQ) of chromium was calculated based on the results of repeated measurements of consecutive laboratory blank samples in relation to the formula presented by Fleming et al. [62] on the level of 1 µg L\(^{-1}\).

Obtained relative percentage differences (%RPD) were calculated based on the duplicate control samples and reached 5.7 and 12.2% for current studies. The obtained RPD values are lower than 20%, which is a maximum permissible value in environmental research [48,63].
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Recovery was assessed by the analysis of the spiked samples where the added known concentration of chromium standard solution was 10 µg·L⁻¹. The results of recovery were obtained by comparison of spiked and unspiked samples for all geothermal water intakes. Calculated values of recovery were in the range 93–114% with an average of 100.9% and met requirements of international standards [48].

Calculated relative standard uncertainty for chromium determination at the level of 1 µg·L⁻¹ in the current study is 18.7%, and relative expanded uncertainty (U) is 37.4% (expansion coefficient k = 2, confidence level of 95%). The Cr concentrations determined during the last sampling campaign together with estimated measurement uncertainty are presented in Table 2.

### Table 2. Results of Cr determination and measurement uncertainty (U).

| Geothermal Water Well | Cr<sub>tot</sub> ± U (µg·L⁻¹) |
|-----------------------|--------------------------------|
| GW<sub>1</sub>        | 1.20 ± 0.45                    |
| GW<sub>2</sub>        | 1.06 ± 0.40                    |
| GW<sub>3</sub>        | 1.10 ± 0.41                    |
| GW<sub>4</sub>        | 1.40 ± 0.52                    |
| GW<sub>5</sub>        | 2.03 ± 0.76                    |
| GW<sub>6</sub>        | 1.19 ± 0.45                    |
| GW<sub>7</sub>        | 1.89 ± 0.71                    |
| GW<sub>8</sub>        | 1.05 ± 0.39                    |
| GW<sub>9</sub>        | 2.18 ± 0.82                    |

Most of geothermal water exhibits reducing properties [2,64,65]. In light of a previously conducted study, all of the analyzed geothermal water samples represent reducing conditions, with E<sub>H</sub> varying from −5.9 to −182.5 mV and temperature ranging from 25.4 to 76.9 °C.

### 3.1. Speciation Modeling Results

The results of chromium speciation modeling are presented in Table 3. They show that the predominant form of chromium occurrence in the geothermal water basin of Podhale is probably Cr(III). Almost 100% of all chromium concentration in geothermal water is represented by the more stable form of chromium—trivalent—occurring in geothermal water due to reducing conditions of the aquatic environment tested [2,64,65].
Table 3. Results of chromium speciation modeling.

| Geothermal Water Well | Cr\text{tot} (\mu g L\textsuperscript{−1}) | Cr(III) (\mu g L\textsuperscript{−1}) | Cr(VI) (\mu g L\textsuperscript{−1}) |
|-----------------------|----------------------------------------|------------------------------------|----------------------------------|
| GW\textsubscript{1}    | 1.20                                   | 1.20                               | 1.30 × 10\textsuperscript{−19}    |
| GW\textsubscript{2}    | 1.06                                   | 1.06                               | 7.56 × 10\textsuperscript{−22}    |
| GW\textsubscript{3}    | 1.10                                   | 1.10                               | 5.44 × 10\textsuperscript{−24}    |
| GW\textsubscript{4}    | 1.40                                   | 1.40                               | 3.91 × 10\textsuperscript{−22}    |
| GW\textsubscript{5}    | 2.03                                   | 2.03                               | 2.62 × 10\textsuperscript{−29}    |
| GW\textsubscript{6}    | 1.19                                   | 1.19                               | 1.72 × 10\textsuperscript{−27}    |
| GW\textsubscript{7}    | 1.89                                   | 1.89                               | 3.66 × 10\textsuperscript{−27}    |
| GW\textsubscript{8}    | 1.05                                   | 1.05                               | 4.88 × 10\textsuperscript{−31}    |
| GW\textsubscript{9}    | 2.18                                   | 2.18                               | 3.51 × 10\textsuperscript{−23}    |

The modeled concentration of the hexavalent form is negligible (\(<10\textsuperscript{−19} \mu g L\textsuperscript{−1}\)) and does not influence the total concentration of Cr; Cr\text{tot} = Cr(III) (Table 3). The concentrations of total chromium and hence Cr(III) in particular geothermal water wells vary from 1.0 to 2.2 \mu g L\textsuperscript{−1}. The concentrations of Cr\text{tot} were always below the threshold values of 50 \mu g L\textsuperscript{−1} recommended for drinking water under international and Polish law [14–16]. Furthermore, the results obtained, enlarged by measurement uncertainty estimation, do not influence the use of this water in balneotherapeutic drinking purposes, inhalation and external use, where the maximum Cr concentration was established at the level 10 \mu g L\textsuperscript{−1} [31]. Many tests were done regarding the reuse of geothermal water from the Podhale Trough. Research studies were conducted which proved that after reverse osmosis processes water (permeate) could be successfully used as drinking water after secondary enrichment in minerals. It is also possible to recover balneological resources from the retentate, where the concentrations of substances are increased [21,66,67].

Taking into account the results obtained in this study, it can be seen that the concentrations of total chromium in geothermal water in the Podhale Trough are in the range of the natural hydrogeochemical background for this element (0.1–10 \mu g L\textsuperscript{−1}). In clean groundwater, its concentrations do not exceed 20 \mu g L\textsuperscript{−1} [7]. In studies conducted considering the natural geothermal fluids in the world, the concentration of Cr\text{tot} was found to be in the range of <0.01–660 \mu g L\textsuperscript{−1} in Iceland and reached 330 \mu g L\textsuperscript{−1} in Turkey [2,68]. The concentration of total chromium is strongly dependent on the pH of the geothermal water and presence of ions such as SO\textsubscript{4}\textsuperscript{2−}, HCO\textsubscript{3}−, Cl\textsuperscript{−}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and Na\textsuperscript{+} [2,68]. In natural geothermal water, Cr(III) exists mostly in the form of metal hydroxy speciation, where the hydroxides play the role of ligands [69]. In natural water, it is desirable to have Cr(III) as the prevailing speciation (as opposed to Cr(VI)) due to its nontoxic properties. The presence of hexavalent chromium in nature is rare [70]. Its environmental presence is related to industrial activities (e.g., tanneries, chromium ore processing plants, slag–soil systems or deposition of steel production waste on landfills) [7,71–74]. In particular, Cr(VI) in natural water may occur in surface water near which chromite-bearing formations are observed [5] The differences in chromium speciation ratio (Cr(III)/Cr(VI)) may be a result of seasonal changes [75].

3.2. Analysis of the Risk of Exposure to Chromium

The geothermal water analyzed here is used for recreational purposes. The main hazard due to the presence of chromium in this water results from the possibility of its direct contact with the skin during bathing in thermal pools. For this reason, the potential health risk associated with chromium occurrence was assessed. The chromium concentration in the risk model was set as 2 \mu g L\textsuperscript{−1} (deterministic approach), as this was the highest value that was found in the geothermal water analyzed here. Calculations were conducted separately for adults, teenagers and children (Fallahzadeh et al.
The hazard quotient \( (HQ_{\text{derm}}) \) and daily intake through dermal absorption \( (EDI_{\text{derm}}) \) were calculated as follows (USEPA 2016):

\[
HQ_{\text{derm}} = \frac{EDI}{RFD}
\]

(1)

\[
EDI_{\text{derm}} = \frac{C_w \cdot SA \cdot K_p \cdot F \cdot ETs \cdot EF \cdot ED \cdot 10^{-3}}{BW \cdot AT}
\]

(2)

where RFD is a reference dose of chromium in a specific exposure pathway (mg·kg\(^{-1}\)·day\(^{-1}\)), set as 1.5 \( \times \) 10\(^{-5}\) mg·kg\(^{-1}\)·day\(^{-1}\) after Smith (1994) and Fallahzadeh et al. [52]; \( C_w \) is a concentration of chromium in geothermal water; SA is surface area and was set as 18,182 cm\(^2\) for adults, 14,321 cm\(^2\) for teens and 7422 cm\(^2\) for children (after Wu et al. [76]); \( K_p \) is a dermal permeability constant (set as 10\(^{-3}\) cm·h\(^{-1}\) after Williams et al. [77]); F is a fraction of surface skin contact with water and was set as 0.9 (after Williams et al. [77]); ETs represents exposure time and was estimated at 0.004 h (3 h a month) in the swimming pool; EF is exposure frequency and was set as 12 days·year\(^{-1}\); ED is exposure duration, set as 30 years for adults, 15 years for teens and 6 years for children [78]; BW is body weight and was set as 79 kg for adults, 61.5 kg for teens and 23.6 kg for children (on-line access (04.04.2019): https://bit.ly/2TSUoHZ); and AT is averaging time and was set as 18,250 days for adults, 5475 days for teens and 2190 days for children [78].

Calculated daily intake of chromium through epidermal absorption \( EDI_{\text{derm}} \) is 5.45 \( \times \) 10\(^{-11}\) mg·kg\(^{-1}\)·day\(^{-1}\) for adults, 5.51 \( \times \) 10\(^{-11}\) mg·kg\(^{-1}\)·day\(^{-1}\) for teens and 7.44 \( \times \) 10\(^{-11}\) mg·kg\(^{-1}\)·day\(^{-1}\) for children. The estimated \( HQ_{\text{derm}} \) values are lower than 1 in all age groups (Table 4). The risk of being exposed to chromium poisoning is low, which is confirmed by the \( HQ_{\text{derm}} \) values obtained: 3.6 \( \times \) 10\(^{-6}\), 3.7 \( \times \) 10\(^{-6}\) and 5.0 \( \times \) 10\(^{-6}\) for adults, teens and children respectively. It can be stated that for three to five people out of one million are exposed to chromium poisoning by epidermal absorption. In general, where the \( HQ_{\text{derm}} \) values are lower than 1, the noncarcinogenic health effects from different trace elements in the human population are unlikely [53,79,80].

| Parameter | Adults | Teenagers | Children |
|-----------|--------|-----------|---------|
| \( EDI_{\text{derm}} \) (mg·kg\(^{-1}\)·day\(^{-1}\)) | 5.45 \( \times \) 10\(^{-11}\) | 5.51 \( \times \) 10\(^{-11}\) | 7.44 \( \times \) 10\(^{-11}\) |
| \( HQ_{\text{derm}} \) | 3.6 \( \times \) 10\(^{-6}\) | 3.7 \( \times \) 10\(^{-6}\) | 5.0 \( \times \) 10\(^{-6}\) |

The second approach, which took into account the estimated relative expanded uncertainty, was also applied (Table 4). Here, the only parameter that changed was chromium concentration, which rose from 2 to 2.74 μg·L\(^{-1}\) (upper limit of uncertainty interval). In consequence, \( EDI_{\text{derm}} \) rose to 7.49 \( \times \) 10\(^{-11}\) mg·kg\(^{-1}\)·day\(^{-1}\) in the adults, 7.57 \( \times \) 10\(^{-11}\) mg·kg\(^{-1}\)·day\(^{-1}\) in teens and 1.02 \( \times \) 10\(^{-10}\) mg·kg\(^{-1}\)·day\(^{-1}\) in children. The \( HQ_{\text{derm}} \) is still lower than 1, even though the values grew to 5.0 \( \times \) 10\(^{-6}\), 5.0 \( \times \) 10\(^{-6}\) and 6.8 \( \times \) 10\(^{-6}\) for adults, teens and children, respectively.

For health risk assessment, not only the concentration of heavy metal but also the degree of metal intake by an organism is important in influencing the final result. HQ calculations are generally based on total concentrations of heavy metals. The correlation between adsorption of heavy metals by an organism and total concentrations of metals is neglected. The intake dose of toxic forms, i.e., Cr(VI) and especially its aqueous morphologies present in water, should be taken into account because the speciation of heavy metals, rather than their total concentrations, plays a significant role in assessing health risk [81]. In the worldwide research, a noncarcinogenic hazard quotient for groundwater
with a low epidermal adsorption effect was calculated to be on the level of 0.155 mg·kg\(^{-1}\)·day\(^{-1}\) [82]. Furthermore, for groundwater used for irrigation purposes, Cr was found to pose a significant noncancer risk (1.20–2.99/1000 people) [80]. In the publication of Tseng et al. [83], a dynamic model for exploring the interrelationship between the Wu River watershed and contamination with Cr(VI) in the period 2018–2048 was prepared. It was found that the accumulation of Cr(VI) will be still increasing. The estimated health risk for Taiwanese people living in this agricultural region and using surface water for irrigation was in the range 10\(^{-4}\)–10\(^{-6}\) and led to gastric cancer. Wen et al. [84] report contamination of coastal water by the intrusion of saline water that caused the growth of heavy metals concentrations in groundwater. This growth did not increase the ecological risk, which was assessed as low, but it caused a high risk of cancer in the population of children and adults. The calculated risk was at an unacceptable level according to the intervals proposed by Fryer [85]. In turn, the work of Yin et al. (2019) showed that hexavalent chromium accumulates in edible tissues of fish, namely the head, ventral muscles and dorsal muscles. Fish farms operating in the vicinity of urbanized and industrial areas are at risk of the accumulation of heavy metals in fish; thus, people consuming these fish can be exposed to harmful factors. When considering drinking water delivered with a drinking water supply system (DWSS), attention should be paid to the possibility of pipe scaling and residual fraction occurrence from which heavy metals (including chromium) can be released. The health risks in relation to the leaching of chromium from pipe scales and the residual fraction were estimated as low and moderate, respectively. This is mainly due to the mineralogical origin of Cr, which is bound by Fe–Mn oxides in the case of the scaling phenomenon [86]. Another example of a health risk associated with chromium occurrence is that of the groundwater contaminated with this element near a chromite mine in Iran; the risk occurs due to the water being used for drinking and also through direct skin contact [52]. Other trace metals including chromium were examined within drinking water indigestion [87], but the HQ value for chromium did not indicate a potential toxic effect.

The risk of chromium presence in geothermal water is not only connected with human exposure risk. Extensive use of geothermal water can be hazardous for the environment, mainly during water discharge to surface watercourses after heat recovery. Therefore, the risk was assessed with the use of a 5 × 5 risk matrix [54,55]. Risk (\(R_e\)) was calculated by multiplying probability (likelihood/frequency (L/F)) by impact (severity of consequence (SC)) for all of the following hazards:

1. Geothermal water injection into formation (L/F = 5, SC = 1).
2. Discharge of geothermal water to surface watercourses in the case of fish farming (L/F = 3, SC = 4).
3. Discharge of geothermal water to surface watercourses in the case of surface water chemical status changes (L/F = 3, SC = 2).
4. Oxidation of Cr(III) to toxic Cr(VI) due to changes in redox conditions (L/F = 5, SC = 5).

For the first scenario, the L/F factor was defined as 5 because the geothermal water is reinjected into the formation after heat recovery. For the second and third scenarios, the L/F was set as 3 because the water used for recreational purposes is discharged to the surface watercourses or/and the sewage system. The severity of consequence for the first assumption is the lowest due to the fact the reinjected water is only chilled; in this regard, there is no potential ecological risk. In the case of fish farming, SC was established at the level of four due to the possibility of accumulation of chromium in tissues [88,89]. The chemical status changes of surface water are not very possible due to the low concentration of Cr in geothermal water, and hence the S/C factor equals 2. The greatest potential impact on the environment is due to the oxidation of Cr(III) to the cancerogenic, mutagenic and genotoxic [53] hexavalent form; therefore, in this case, the L/F and SC have been given the highest values (5).

The risk levels were divided into minor (risk score below 5), moderate (risk score between 5 and 9) major (risk score between 10 and 19) and very severe (risk above 20) (Figure 3).
While considering discharge to surface water where potential fish farming can be set up, the risk is major, which are related to the diagenetic processes of the aquatic system. The geochemical water can be reused as a potential source for different uses of groundwater are still expanding. Many examples in reference to other scientific areas can be found elsewhere [90–103]. Studies concerning probabilistic risk assessment in groundwater, i.e., undergoing bioremediation and quality assessment, have been conducted [104,105].

In summary, when it is possible or when there are suspicions that chromium can be an important environmental contaminant, or there is a possibility of Cr(VI) occurrence, the data collected from fieldwork should include identification of the valency of the chromium. It is actually estimated that the ratio of Cr(III) speciation to Cr(VI) is 1:6. The recognition of chromium speciation in environmental research is an issue of key importance due to the carcinogenic, mutagenic and genotoxic properties of the hexavalent form [53].

4. Conclusions

The main purpose of the research presented here was to evaluate the health and ecological risks of chromium in relation to geothermal water utilization. Chromium as a toxic element is quite poorly recognized in geothermal water sources around the world, as evidenced by the small number of publications on this topic. Its occurrence in trivalent or hexavalent form is dependent on various environmental conditions, i.e., geological setting, pH and E_H2O, and the presence of Fe, Al and Mn hydroxides. Knowledge about chromium occurrence in water that can be used for drinking purposes is important for choosing the proper geothermal water treatment.

In this work, the recognition of chromium occurrence in the geothermal water from nine wells located in the Podhale Trough in Poland was presented. During field and laboratory work, the QA/QC program was implemented. The limit of quantification for chromium calculated with the ICP-OES method was 1 µg·L\(^{-1}\), and the accuracy ranged from 93–114%. The estimated relative expanded uncertainty was 37.4%. Along with the uncertainty declared by the laboratory (13.38%), it has to be mentioned that the LOQ was lowered from 2.5 to 1 µg·L\(^{-1}\) in this study. Growth in total uncertainty is a natural factor caused by deterioration in precision and accuracy.

The results showed that the total concentration of this element in analyzed samples varied from 1.0 to 2.2 µg·L\(^{-1}\). The dominant form of chromium occurrence is Cr(III), which is associated with reducing conditions of the aquatic system. The geothermal water can be reused as a potential source...
of drinking water, whereas the trivalent chromium can oxidize to more toxic hexavalent speciation; therefore, it is important to control the concentrations of chromium speciation in light of geothermal water being used for purposes other than heating.

Our research also introduces a novelty in the form of risk assessment for geothermal water, which is nowadays mainly used in balneotherapy. The risk assessment was conducted by using two methods: the risk model, which was used to evaluate the human exposure to chromium compounds during bathing in thermal pools, and the semiquantitative risk matrix, which was used to consider overuse and actual handling of the geothermal water of the Podhale Trough.

This research revealed that the risk of being exposed to chromium poisoning in Podhale thermal pools is low, which is confirmed by low hazard quotient (HQ_{derm}) values. The presence of Cr in studied water and its impact on the environment is dependent on the assumed scenario. When considering geothermal water injection into the formation, the calculated risk (R_e) is moderate; however, the calculated risk is moderate when the geothermal water is discharged to surface watercourses and major when the discharge occurs near fish farms. Changing the oxidation state of Cr(III) to Cr(VI) presents a very severe environmental risk if the concentration of Cr is significant.

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