minerals

Article

High Content of Boron in Curative Water: From the Spa to Industrial Recovery of Borates? (Poland as a Case Study)

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Abstract: Boron minerals are a sought-after raw material. The European Union's total dependence on imported borates means that this has been a critical material since 2014. Due to the increased use of borates in modern economies, data on the predicted boron demand in the coming years indicate that it may become a critical element on a global scale. Formerly, the high boron content in groundwater was the basis for qualifying it as medicinal water (boric water). Nevertheless, the current information on the potential toxicity of boron and the narrow margin between deficiency and toxicity of boron in the human body has caused a tightening of the limits of this element in water intended for human consumption. For this reason, metaboric acid has lost its position as a specific component of curative waters. However, despite the fact that boron is not currently a specific component of curative waters, it is found in measureable concentrations in Polish medicinal water considered therapeutic based on other valuable specific components. High boron content in curative water may be the cause of the problems in some spas when obtaining certificates confirming the therapeutic properties of waters. Literature data indicate that waters with high boron content (above 25 mg/L) should not be freely available for drinking in pump rooms and other places in health resorts. To identify the situation with Polish health resorts, the content of boron in 248 curative water samples was analyzed. In 154 of these samples, the boron concentration was relatively low and did not exceed 5 mg/L. However, in the remaining 94 samples, the boron content exceeded 5 mg/L, and 38 samples had boron content exceeding 30 mg/L. Ten of the 248 samples of curative water had a boron concentration above 100 mg/L, which may be a potential source of boron for industrial recovery. The highest concentration of boron was noticed in a water sample from the Wysowa health resort and was 187.6 mg/L. Unfortunately, most of water intakes with a high concentration of boron (above 100 mg/L) are low-yielding wells. Based on the data collected, Rabka appears to be the best candidate for small-scale boron production in terms of boron content and water resources values.

Keywords: borate; high content of boron in water; curative water in Poland

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1. Introduction

The boron content in the lithosphere is relatively high. The value of the boron concentration in the continental crust is on average 10 mg/kg. Boron does not exist in nature as a pure element. It is found in bonded form [1,2]. There are over 200 different boron minerals in nature. Commercially, the most important boron minerals are compounds containing boron oxide in varying proportions, i.e., tincal (borax) ($Na_2B_4O_7.10H_2O$), kernite ($Na_2B_4O_7.4H_2O$), colemanite ($Ca_2B_6O_{11}.5H_2O$), ulexite ($NaCaB_5O_9.8H_2O$), hydroboracite ($CaMgB_6O_{11}.6H_2O$), boracite ($Mg_3B_7O_{13}Cl$), pandermite ($Ca_4B_{10}O_{19}.7H_2O$) and szaibelyite (ascharite) ($Mg_2B_2O_5.H_2O$) [3,4]. However, today, borax is the most important mineral for the borate industry. Borax occurs in the largest exogenous boron deposits in the world (Boron, California; Kyrka, Turkey; and Tincalayu, Argentina) [5]. Most commercial borate deposits in the world are exploited by opencast mining. Boron is also obtained from the brine from Searles Lake (USA) and Chinese sources via controlled evaporation or carbonation [6,7].

In the hydrosphere, the main reservoir of boron is seawater, which has an average content of 4.5 mg/L [2,8]. This is because marine clays are richer in boron than other types of rock [9]. In most groundwater, typical boron concentrations are below 1.0 mg/L [2]. A natural source of boron in groundwater is leaching from rocks and soils containing borates and borosilicates [10]. Boron enrichment also occurs as a result of human activity (industry, agriculture, detergents that contain sodium perborate); therefore, water and sewage may contain boron of anthropogenic origin from several to several dozen milligrams per liter [11].

Due to the wide use and demand for boron, sources other than borate deposits are sought. It is well known that there are numerous boron-rich brines in the world, such as salt lake brines, oil field waters, and various types of underground brines [12]. To date, many methods have been developed to separate boron from aqueous solutions, i.e., fresh water and different types of brines and sewage [12,13]. The topic of boron recovery from thermal waters has already been discussed in Poland [14,15]. Various methods of obtaining boron from aqueous solutions are found not only in the literature but also in patents [16–20]. These methods have been tested on a laboratory scale, but some have also been field tested [21]. Methods based on ion exchange and adsorption processes are usually suitable for waters with low boron concentration [22,23]. Reverse osmosis has been extensively tested in desalination [23,24]. The precipitation methods are instead used in aqueous solutions with higher boron content [24].

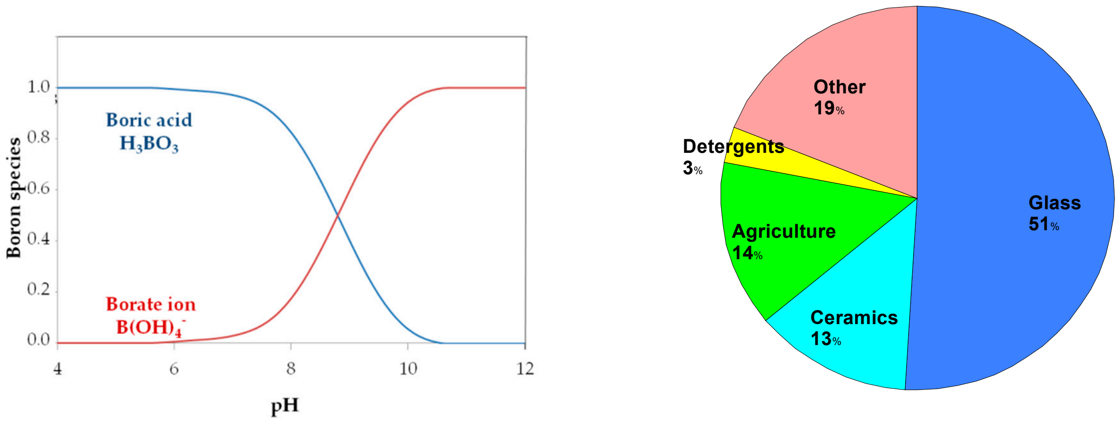
However, so far, there are no widely used methods for recovering boron from aqueous solution. The main problem is the complex chemistry of boron and the fact that known boron extraction methods are relatively expensive [21]. From an economic point of view, a valuable boron concentration in brine is above 100 ppm [14].

Boric acid and borate ion are two dominant forms of inorganic boron in natural aqueous systems. The pK value (pK = −logK) of boric acid varies depending on pH, ionic strength, and temperature of the solution, where K is equilibrium constant of the reaction:

$$H_3BO_3 + H_2O \leftrightarrow B(OH)_4^- + H^+ \quad (1)$$

For example, the value of pK is 9.24 at 25 °C in fresh waters [25]. On the other hand, for seawater with a salinity of 35%, the value of pK at 10 °C is 8.76, and at 35 °C it is 8.47 [26,27]. Nevertheless, the pH of the aqueous solution is the most significant parameter which determines the ratio of undissociated boric acid to borate ions in water. Depending on the boron concentration in water, various boron-containing species may be found. Low and medium concentrations of boron occur in the aqueous environment as boric acid H_3BO_3 ($B(OH)_3$) or borate ion $B(OH)_4^-$ [28]. The distribution of two dominant forms of inorganic boron in natural aqueous systems versus pH is presented in Figure 1a. Water-soluble polyborate ions, i.e., $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^-$, $B_3O_3(OH)_5^-$ and $B_5O_6(OH)_4^-$ are formed at higher concentrations of boron in water in the pH range of 6–12 [25]. However, the formation of polyborate ions is negligible when the boron concentration in the aqueous solution is below 290 mg/L [29].

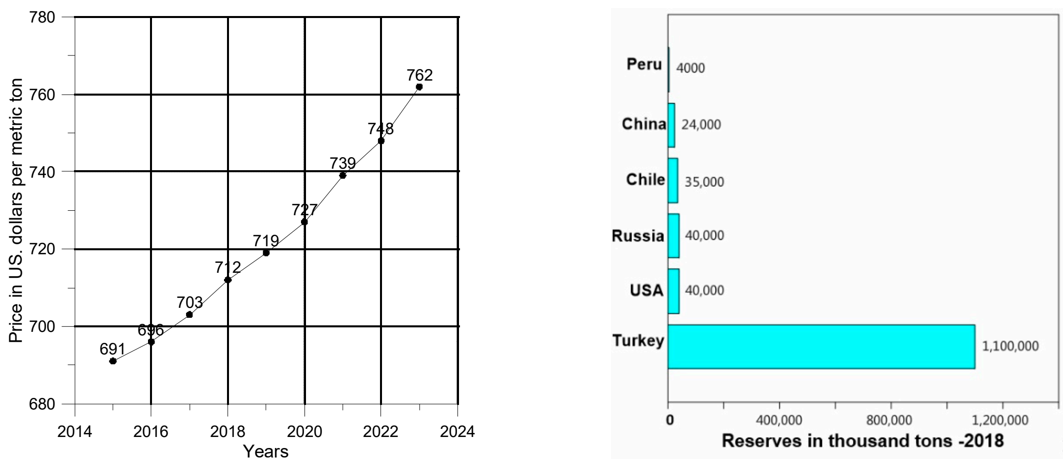
Boron is a valued raw material in industry, primarily for glass, ceramics, agriculture and household chemicals (Figure 1b, [30]). Currently, the industrial demand for this element is growing due to the development of modern architecture (fiberglass insulation materials, flame retardants). A significant demand for raw boron materials also results from the development of electronics, telecommunications (LCD screens), and the automotive, aviation and energy industries [4]. The price of raw boron materials increases with the increase in market demand. The chart shows a predicted continuous increase in the price of raw boron materials in the coming years (Figure 2a, [31]).



(**a**) (**b**)

Figure 1. (**a**) The distribution of two dominant forms of inorganic boron in natural aqueous systems versus pH [26], (**b**) global boron end-use share by application [30].

Since 2014, borates have been classified by the European Union as critical raw materials. In 2008, the European Commission initiated activities aimed at creating a collective raw materials policy [32]. As part of these activities, a list of critical raw materials has been published every three years since 2011. The list contains raw materials of very high economic importance, the supplies of which are at risk of shortage. The EU is 100% dependent on imported borates. Turkey, which has the largest boron deposits in the world, supplies 98% of this element to the EU market (Figure 2b, [33]).



(**a**) (**b**)

Figure 2. (**a**) Medium-term forecast for boric acid prices worldwide from 2015 to 2023 [31], (**b**) world boron reserves as of 2019, by major countries [33].

Statistics from 2019 indicate that Turkey is the largest producer of boron minerals in the world (2500 thousand metric tons). Chile, China and Bolivia are next, with productions of 400, 250 and 210 thousand metric tons, respectively [34,35]. The list of the world's 10 largest producers of boron minerals also includes Argentina, Peru, Russia, Kazakhstan, and, since 2018, Germany. The United States is certainly also one of the top ten producers of boron minerals. However, the US data is currently withheld and not included in the total world mining production. For example, US boron mineral production in 2005 and 2010 was 1230 and 1150 thousand metric tons, respectively, while the production of boron minerals in Turkey in 2005 and 2010 was 1700 and 1850 thousand metric tons, respectively [36,37].

Globally, borates are not considered a critical raw material or are referred to as a moderate resource scarcity mineral [38–41]. However, projections based on increasing market demand for borates indicate that "non-critical boron minerals" could become "highly critical" within 70 years [38].

The therapeutic properties of various waters used in numerous spas have been proven by long-standing medical observations and by clinical research. In 1911, the first European classification of medicinal waters was introduced. This classification resulted from the recognized pharmaco-dynamic factors of individual specific water components. The minimum concentration values of these specific components in therapeutic groundwater are presented in Table 1. However, including water with an appropriate physico-chemical composition in the category of therapeutic waters depends on obtaining a certificate and administrative decisions. In Poland, the quality of therapeutic waters is controlled by the Polish Institute of Hygiene.

In the first balneological classification, which was adopted at the First International Balneological Congress in Nauheim in 1911 and then supplemented in 1934 in Salzuflen, an HBO_2 concentration of 5 mg/L was defined as the limit above which water was classified as therapeutic. The antiseptic effect of water with HBO_2 concentrations above 5 g/L was observed [42,43]. In Poland, boron has had the status of a specific component of curative water since the first classification was proposed by Maria Szmytówna and adopted at the Congress of the Polish Balneological Society in Inowrocław in 1956. Currently (since 2006 [44]), the Polish Geological and Mining Law [45] does not define boron water, because recent reports show that high doses of boron may be harmful to human health. According to Nielsen [46], the lethal dose of boron is 3 g for infants and 15–29 g for adults. The European Union recommends 1.0 mg/L as a safe concentration of boron in water intended for human consumption [47,48]. The fact that the concentration of boron exceeds the allowed values in some curative waters of Poland has already been discussed [49–51]. However, while currently metaboric acid is not a specific component of the healing waters, it is present at detectable concentrations in many waters considered therapeutic based on the other specific components listed in Table 1. However, despite the fact that metaboric acid is not currently a specific component of curative waters, it is present in detectable concentrations in many waters with increased mineralization, including those considered therapeutic on the basis of other specific components.

Table 1. Criteria for classification of medicinal waters.

Name of Waters (Specific Component)	The Minimum Concentration Value of the Specific Component for Groundwater with Content of Dissolved Solid Minerals of at Least 1 g/L		
	1911 (Europe)	1956 (Poland)	2006 (Poland)
Ferruginous waters (Fe^{2+})	10 mg/L	10 mg/L	10 mg/L
Fluoride waters (F^-)	2 mg/L	1 mg/L	2 mg/L
Iodide waters (J^-)	1 mg/L	1 mg/L	1 mg/L
Bromide waters (Br^-)	5 mg/L	5 mg/L	*
Sulfide waters (S^{II})	1 mg/L	1 mg/L	1 mg/L
Silica waters (H_2SiO_3)	50 mg/L	100 mg/L	70 mg/L
Radon or radioactive waters (Rn)	1 pCi (37 Bq/m^3)	2 pCi (37 Bq/m^3)	2 pCi (74 Bq/m^3)
Arsenic waters (arsenic, As^{III}/As^{V})	0.2 mg/L	0.7 mg/L	*
Boric waters (HBO_2)	5 mg/L	5 mg/L	*
Carbonated waters (CO_2)	not established	250 mg/L	250 mg/L
CO_2 reach waters (CO_2)(Carbonated water)	not established	1000 mg/L	1000 mg/L

^{II} and $^{III, V}$—oxidation states of sulfur and arsenic atom, * not defined by the Polish Geological and Mining Law.

In summary, high boron content in water can be both an advantage and a disadvantage. Medicinal water with high boron content that is used for therapy can be a problem for spas, but high boron content in water provides great opportunities for obtaining borate, which is classified by the EU as a critical raw mineral. The main aim of this study is to highlight the high content of boron in curative water and potentially consider it as a source of boron for industrial applications. For this purpose, the set of data on physico-chemical parameters of curative waters from various available sources (scientific articles, certificates confirming the healing properties of water and research conducted for health resorts by the Faculty of Petroleum Engineering of the AGH University of Science and Technology) was collected. This made it possible to systematize the data on the content of boron in Polish curative waters. This is the first comprehensive report of this type. The result is information about the location of medicinal waters with high boron content in Poland. These data can be used to discuss the possible harmfulness of high boron content in curative waters. The collected dataset can also be useful when considering the prospects of boron recovery from these waters, especially since no boron minerals are mined or produced in Poland.

2. Materials and Methods

2.1. Geological Setting

In terms of geological structure and hydrogeological conditions, Poland is divided into four areas: Precambrian Platform, Palaeozoic Platform, Sudetes and Carpathians [52,53]. These units are then divided into smaller regions. Precambrian platform and Paleozoic platform cover the area of the Polish Lowlands. In the platform areas, mineral waters mainly occur in Cretaceous, Jurassic and Triassic formations. The Sudetes area is a complex of structural mosaics that were shaped, predominantly, during the Variscan orogeny. There are various types of geological units built of different rocks: magmatic, metamorphic and sedimentary series. The Carpathians province includes the Outer Carpathians, the Inner Carpathians, Pieniny Klippen Belt and the Carpathian Foredeep. The Outer Carpathians are composed of Cretaceous and Paleogene flysch formations (shales and sandstones). These rocks were overthrust from the south and folded in several orogenic cycles in the Paleogene and Neogene through to the late Miocene. The Carpathian Foredeep is a part of the large sedimentary basin linked with Alpine Molasse basin filled with predominantly clastic sediments of the Miocene age. The characteristic feature of the area is evaporates (gypsum, anhydrite and salt). These chemical sediments have an impact on the chemistry of the groundwater. More details about the geological structure of Poland linked with therapeutic waters can be found in [53]. The majority of water used for balneotherapy is found in the Sudetes and the Carpathians.

2.2. Physico-Chemical Parameters of Curative Waters

There are underground waters almost all over Poland that are characterized by mineralization of at least 1.0 g/L or the content of specific components in concentrations adopted for medicinal waters. These waters are used for treatment by drinking, bathing, and as a medicinal aerosol in graduation towers. These curative waters are exploited in Polish spas and towns without the status of health resorts. The names of 248 analyzed water intakes and their physico-chemical data are presented in Table S1 (Supplementary Materials). Of the data on the physico-chemical parameters of these waters come from published data (scientific articles), collected certificates confirming the therapeutic properties of these waters, and research carried out by Lewkiewicz-Małysa et al. for health resorts by the Faculty of Petroleum Engineering of AGH University of Science and Technology (unpublished data) [54–77].

2.3. Statistical Analysis

The relationship between boron concentration and other water parameters was investigated for the whole dataset. It should be noted that the set of available chemical parameters for the tested waters was different. Analyses were carried out in spas in order to obtain certificates confirming the healing properties of water contain detailed information about the composition of the waters. On the other hand, the analyses found in scientific publications typically contain information on the concentration of main ions and specific components. Therefore, the correlation analysis was limited to those components for which sufficient data was collected (for major ions: Na^{+}, Ca^{2+}, Mg^{2+}, Cl^{-}, SO_4^{2-}, CO_3^{2-} and HCO_3^{-}).

Data analysis was performed using the Statistica 13.1 program. First, the graphical point distributions were analyzed, and then the linear correlation coefficients were calculated. The values of Pearson's correlation coefficient that were statistically significant and indicated a strong correlation ($r > 0.7$) are discussed in the text. The figures include graphs that show the strong correlation between the water parameters. The graphs are presented on a logarithmic scale in order to better visualize a large amount of data with high variability of values.

3. Results

The intakes of the curative waters are presented against the background of geological units in Poland [52] in Figure 3. The research collection included 248 curative waters from both natural sources (springs) and boreholes in various geological regions of Poland. The map (Figure 3) shows 51 locations (30 of which are health resorts), and the colors of the points indicate different boron levels in the investigated waters. Red points indicate boron concentrations up to 5 mg/L; blue indicates concentrations between 5 and 25 mg/L; green denotes concentrations above 25 mg/L. Moreover, the data for curative waters with boron concentrations above 25 mg/L (location, name of water intake, and selected physicochemical parameters) are presented in Table 2.

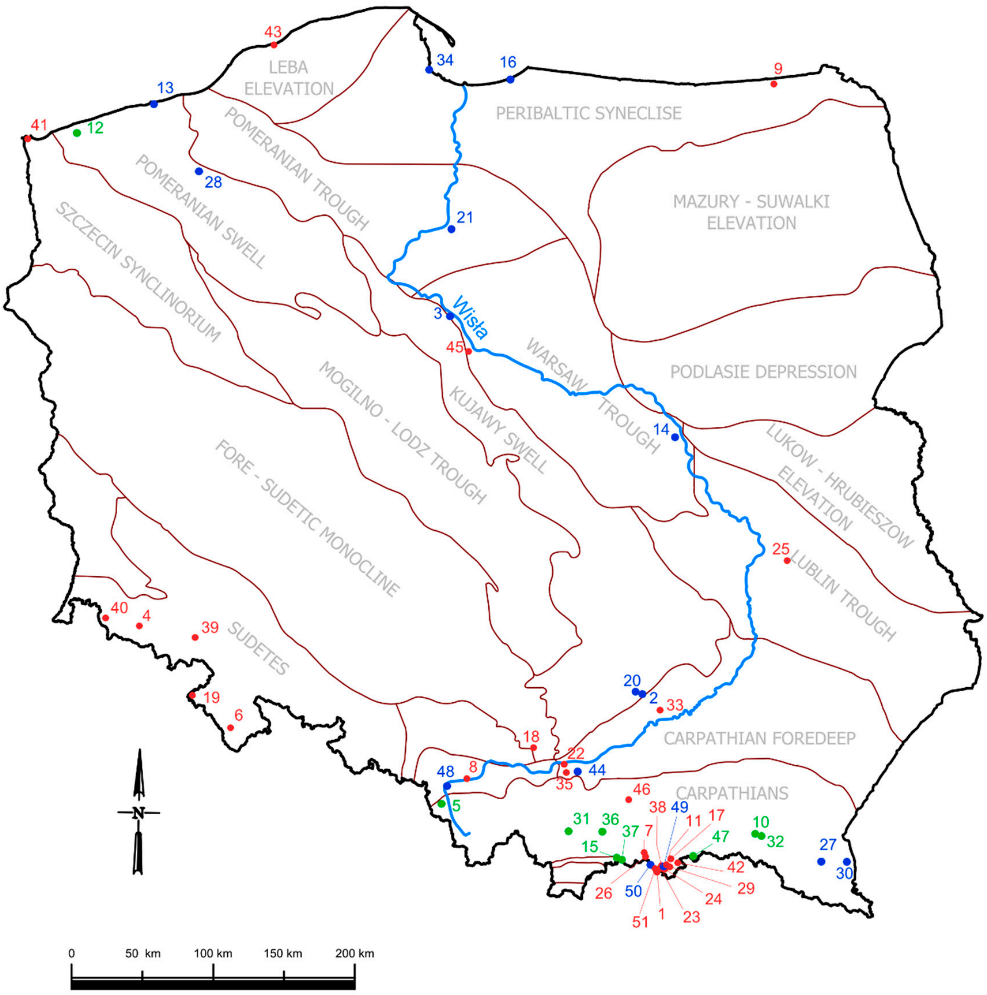


Figure 3. Locations of the investigated curative water on the background of main tectonic structures (• red ≤ 5 mg/L; • blue >5 and ≤25 mg/L; • green color >25 mg/L of boron). 1—Andrzejówka, 2—Busko-Zdrój, 3—Ciechocinek, 4—Jelenia Góra (Cieplice Śląskie-Zdrój), 5—Dębowiec 6—Długopole-Zdrój, 7—Głębokie, 8—Goczałkowice-Zdrój, 9—Gołdap, 10—Iwonicz-Zdrój, 11—Jastrzębik, 12—Kamień Pomorski, 13—Kołobrzeg, 14—Konstancin-Jeziorna, 15—Krościenko nad Dunajcem, 16—Krynica Morska, 17—Krynica-Zdrój, 18—Krzeszowice, 19—Kudowa-Zdrój, 20—Las Winiarski, 21—Marusza, 22—

Kraków (Mateczny), 23—Milik, 24—Muszyna, 25—Nałęczów, 26—Piwniczna-Zdrój, 27—Polańczyk, 28—Połczyn-Zdrój, 29—Powroźnik, 30—Rabe, 31- Rabka-Zdrój, 32—Rymanów-Zdrój, 33—Solec-Zdrój, 34—Sopot, 35—Kraków (Swoszowice), 36—Szczawa, 37—Szczawnica, 38—Szczawnik, 39—Szczawno-Zdrój, 40-Świeradów-Zdrój, 41—Świnoujście, 42—Tylicz, 43—Ustka, 44—Wieliczka, 45—Wieniec-Zdrój, 46—Wojkowa, 47—Wysowa-Zdrój, 48—Zabłocie, 49—Złockie, 50—Zubrzyk, 51-Żegiestów-Zdrój.

Table 2. Curative waters with boron concentrations above 25 mg/L.

Location	Name of Water Intake	TDS	pH	Type of Water	HBO_2 (mg/L)	B (mg/L)	Ref.
Dębowiec	D-2	32,398.37	6.72	Cl-Na	110.24	27.22	[61]
Iwonicz	Zofia 6	11,066.00	7.26	Cl-HCO_3-Na	168.00	41.48	[58]
Iwonicz	Lubatówka 12	19,676.00	7.32	Cl-HCO_3-Na	157.50	38.89	[58]
Iwonicz	Lubatówka 15	15,717.97	7.62	Cl-HCO_3-Na	255.34	63.05	[58]
Iwonicz	Zofia 3	12,263.53	7.60	Cl-HCO_3-Na	226.97	56.04	[58]
Kamień Pomorski	Edward II	35,016.54	6.35	Cl-Na	110.24	27.22	[61]
Krościenko	Stefan	7317.40	9.70	HCO3-Cl-Na	162.80	40.20	[54]
Krościenko	Michalina	8558.50	6.50	HCO3-Cl-Na	233.30	57.60	[54]
Rabka	Krakus	24,806.64	7.53	Cl-Na	418.07	103.23	[72]
Rabka	Rafaela	24,138.00	6.60	Cl-Na	522.80	129.09	[72]
Rabka	Warzelnia	9101.54	7.81	Cl-Na	195.90	48.37	[58]
Rabka	Bolesław	23,219.00	6.50	Cl-Na	483.90	119.48	[72]
Rabka	Helena	17,924.17	8.46	Cl-Na	133.17	32.88	[58]
Rabka	Rabka 18	25,504.95	7.40	Cl-Na	440.78	108.83	[58]
Rabka	Rabka 19	19765.74	7.85	Cl-Na	210.37	51.94	[58]
Rabka	Rabka IG-1	21,993.20	6.50	Cl-Na	339.20	83.75	[72]
Rabka	Rabka IG-II	25,596.12	7.50	Cl-Na	547.43	135.17	[58]
Rymanów	RZ-1	22,643.00	7.11	Cl-Na	208.10	51.38	[58]
Rymanów	RZ-2	9279.00	7.52	HCO3-Cl-Na	128.10	31.63	[58]
Rymanów	Ignacy	4312.00	6.95	Cl-HCO_3-Na	101.82	25.14	[58]
Rymanów	RZ-4 (IG-1)	6466.00	7.14	Cl-HCO_3-Na	126.60	31.26	[58]
Rymanów	RZ-6	6126.00	6.95	Cl-HCO_3-Na	102.71	25.36	[58]
Rymanów	Celestyna	8207.00	6.67	Cl-HCO_3-Na	162.67	40.17	[58]
Rymanów	Klaudia	7724.00	6.44	Cl-HCO_3-Na	157.42	38.87	[58]
Rymanów	Tytus	7981.00	6.42	Cl-HCO_3-Na	146.43	36.16	[58]
Rymanów	Basenowe	7446.00	6.38	Cl-HCO_3-Na	140.38	34.66	[58]
Szczawa	Szczawa I	17,287.00	6.63	HCO_3-Cl-Na	494.00	121.98	[58]
Szczawa	Szczawa II	22,227.00	6.73	HCO_3-Cl-Na	459.00	113.33	[58]
Szczawa	Dziedzilla	5135.70	6.30	HCO_3-Cl-Na	145.00	35.80	[54]
Szczawa	Hanna	5460.00	6.00	HCO_3-Cl-Na	190.90	47.14	[54]
Szczawa	Krystyna	12,691.00	6.70	HCO_3-Cl-Na	227.00	56.05	[54]
Szczawnica	Magdalena	25,849.00	6.79	HCO_3-Cl-Na	599.30	147.98	[58]
Szczawnica	Wanda	6707.00	6.49	HCO_3-Cl-Na	144.00	35.56	[58]
Szczawnica	Stefan II (Dzikie)	6913.00	6.09	HCO_3-Cl-Na	192.00	47.41	[61]
Szczawnica	Józef (B-4)	11,722.00	6.30	HCO_3-Cl-Na	268.20	66.22	[58]
Wysowa	Aleksandra	23,751.00	6.89	HCO_3-Cl-Na	760.00	187.65	[58]
Wysowa	Józef II	4991.00	6.23	HCO_3-Cl-Na	150.60	37.19	[58]
Wysowa	W-11 (Henryk)	5225.00	6.46	HCO_3-Cl-Na	177.70	43.88	[58]
Wysowa	W-15	6166.00	6.34	HCO_3-Cl-Na	197.00	48.64	[58]
Wysowa	W-13 (Anna)	11,715.00	6.53	HCO_3-Cl-Na	367.00	90.62	[58]
Wysowa	W14(Franciszek)	14,448.00	6.72	HCO_3-Cl-Na	448.50	110.74	[58]
Wysowa	W-16	6523.00	7.20	HCO_3-Cl-Na	170.10	42.00	[58]

The tested waters were either two-ionic or multi-ionic. They were divided into groups according to the Szczukariew–Prikłoński classification that is used for medicinal waters. The type of water was determined on the basis of the content of ions above 20% milivals. The datasets for each water type were different (from 1 to 50). Therefore, some waters classified as having similar ionic compositions (although they were not in the same group according to the Szczukariew–Prikłoński classification) were grouped together. Groups with only one type of water according to the Szczukariew–Prikłoński classification (i.e., Cl-Na, Cl-HCO_3-Na and HCO_3-Cl-Na) and groups with similar water types were created. The group of waters designated by us as SO_4 comprised waters in which the SO_4 ion was present in an amount greater than 20% milivals. This is, in fact, the group of waters categorized by the Szczukariew–Prikłoński classification as types Cl-SO_4-Na, SO_4-Cl-Ca-Na, SO_4-Cl-HCO_3-Mg, SO_4-HCO_3-Na, SO_4-HCO_3-Ca-Mg, SO_4-HCO_3-Cl-Na, SO_4-Ca and SO_4-Ca-Mg. On the other hand, in the group we called HCO_3-Ca (Mg-Na), there were also waters of the types HCO_3-Ca-Mg and HCO_3-Mg-Na (according to the Szczukariew–Prikłoński classification).

The analyzed waters belonging to the Cl-Na type occurred in the sedimentary covers of the Precambrian and Palaeozoic platforms (Triassic, Jurassic and Cretaceous sandstones). The mineralization increases with the depth of the aquifers and ranges from 3 to 79 g/L. The waters of the Cl-Na type form a small group among the Carpathian mineral waters; their mineralization ranges from 9 to 146 g/L, and in the Carpathian Foredeep (their mineralization ranges from 6.8 to 79 g/L). The complicated geological structure results in the mineralization of the waters not b3ing correlated with the depth of the deposits in which these waters occur.

Healing waters of the HCO_3-Ca (Mg, Na) type, including carbonated waters, are found in the Sudetes and Carpathians. In the Sudetes, they occur in Precambrian rocks (mica shales, granite gneisses), and in Szczawno they flow from fissure springs from Lower Cambrian sandstones. Mineralization of these waters ranges from 0.6 to 3.8 g/L. In the Carpathians, waters of the HCO_3-Ca (Mg, Na) type occur in Cenozoic (Palaeogene–Neogene) formations, and their mineralization ranges from 0.6 to 25 g/L. Waters of HCO_3-Cl-Na type occur in the Carpathians. Their mineralization ranges from 1 to 15 g/L. In the area of Rymanów and Iwonicz there are Cl-HCO_3-Ca type waters with mineralization from 6 to 20 g/L. Waters of the "SO_4" type occur in the area of the Carpathian Foredeep. These are waters of types SO_4-Cl-Na (Mg, Ca) and Cl-SO_4-Na with mineralization from 2.3 to 17 g/L. In the Busko–Zdrój region, they occur in cenonomann sands and sandstones and kimerite marls, and in the area of Krakow in the sandstones and marls of Palaeogene–Neogene formations (Krzeszowice) and Miocene gypsum (Krakow–Mateczny). Outside the Carpathians, the list also includes waters of the SO_4-HCO_3 (Cl) type (thermal waters occurring in the dislocated Lower Carboniferous granites in Jelenia Góra–Cieplice (Sudetes). Mineralization of these waters ranges from 0.6 to 3.8 g/L.

When interpreting the relationship between the chemical parameters of waters, it should be remembered that the analyzed data set is a heterogeneous set. Cl-Na type waters come from a large area of Poland (all hydrogeological provinces), and deposits lying from a few meters to over 1000 m. Waters of other groups (divided according to the Szczukariew–Prikłoński classification) come from shallower aquifers, as well as from a limited area.

The basic statistical data of the tested waters indicate that the highest concentrations of boron are found in Cl-HCO_3-Na and HCO_3-Cl-Na waters (Table 3, Figure 4).

Table 3. Descriptive statistics of the curative water dataset.

Type of Water	N	Mean	Median	Min.	Max.	Standard Deviation	Coefficient of Variation	B = f(TDS) PCC *
Cl-HCO3-Na	16	32.81	32.96	8.73	63.05	14.05	42.83	0.67
HCO3-Cl-Na	47	35.93	22.20	0.07	187.65	41.12	114.45	0.93
Cl-Na	50	23.94	7.01	1.00	135.17	35.94	150.11	
SO4	17	1.12	0.50	0.15	4.28	1.35	120.60	
HCO3-Ca (Na-Mg)	118	1.05	0.47	0.05	14.00	2.04	193.64	

* PCC—Pearson correlation coefficient.

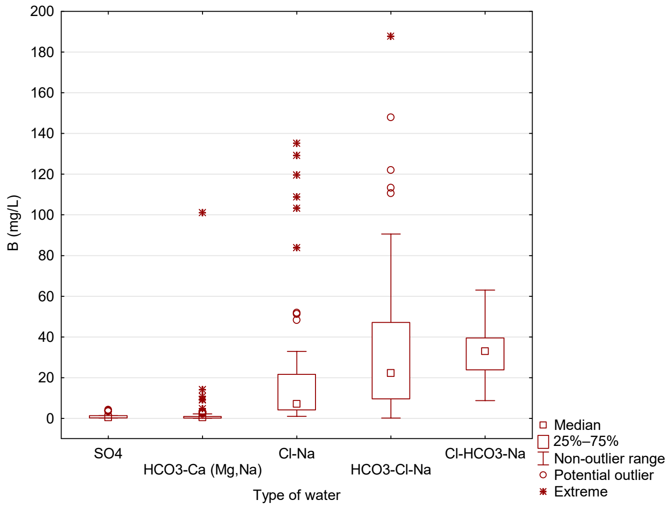


Figure 4. Boxplot of boron concentration in curative water in Poland.

Correlation analyses were performed for the concentrations of TDS and major ions (Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, CO_3^{2-} and HCO_3^-) in relation to boron concentration, covering two aspects simultaneously, i.e., analysis of the graphical point distributions, and calculation the linear correlation coefficients. Boron concentration versus the sum of dissolved solids (mineralization of water) is shown in Figure 5. This relationship is presented both on a linear and logarithmic scale. The linear correlation coefficient for Cl-HCO_3-Na type waters is 0.67 (less than 0.7), and the graphical distribution of points may indicate the linear relationship between boron content and mineralization (Figure 5). However, the dataset contains a small amount of data (N = 16) and it is difficult to draw general conclusions. In the case of waters of the HCO_3-Cl-Na type, almost a full correlation between boron concentration and mineralization of water is observed (Table 3, Figure 5). This correlation ($r > 0.7$) is not seen in the case of other types of water.

In HCO_3-Cl-Na type waters, there is also a linear correlation between the boron concentration and the concentration of HCO_3^- and Na^+ ions, and the linear correlation coefficients are 0.95 and 0.91, respectively (Figure 5). The value of the Pearson's correlation coefficient in the case of other correlations was below 0.7 ($r < 0.7$).

The chemical composition of the analyzed water is presented in Figure 6 (Piper diagram). Boron in concentrations above 25 mg/L occurs only in sodium chloride and sodium bicarbonate waters. In this type of water, boron is present in various concentrations. Nevertheless, most waters of this type are characterized by concentrations above 5 mg/L. It should also be noted that in waters with a high boron concentration, sodium dominates among the cations (present in an amount above 80% milivals—left triangle in the diagram), while among the anions, chlorides occur in various concentrations (from over 20% milivals to over 99%—right triangle of the diagram). Boron in concentrations above 5 mg/L is not present in waters of magnesium chloride and calcium bicarbonate types.

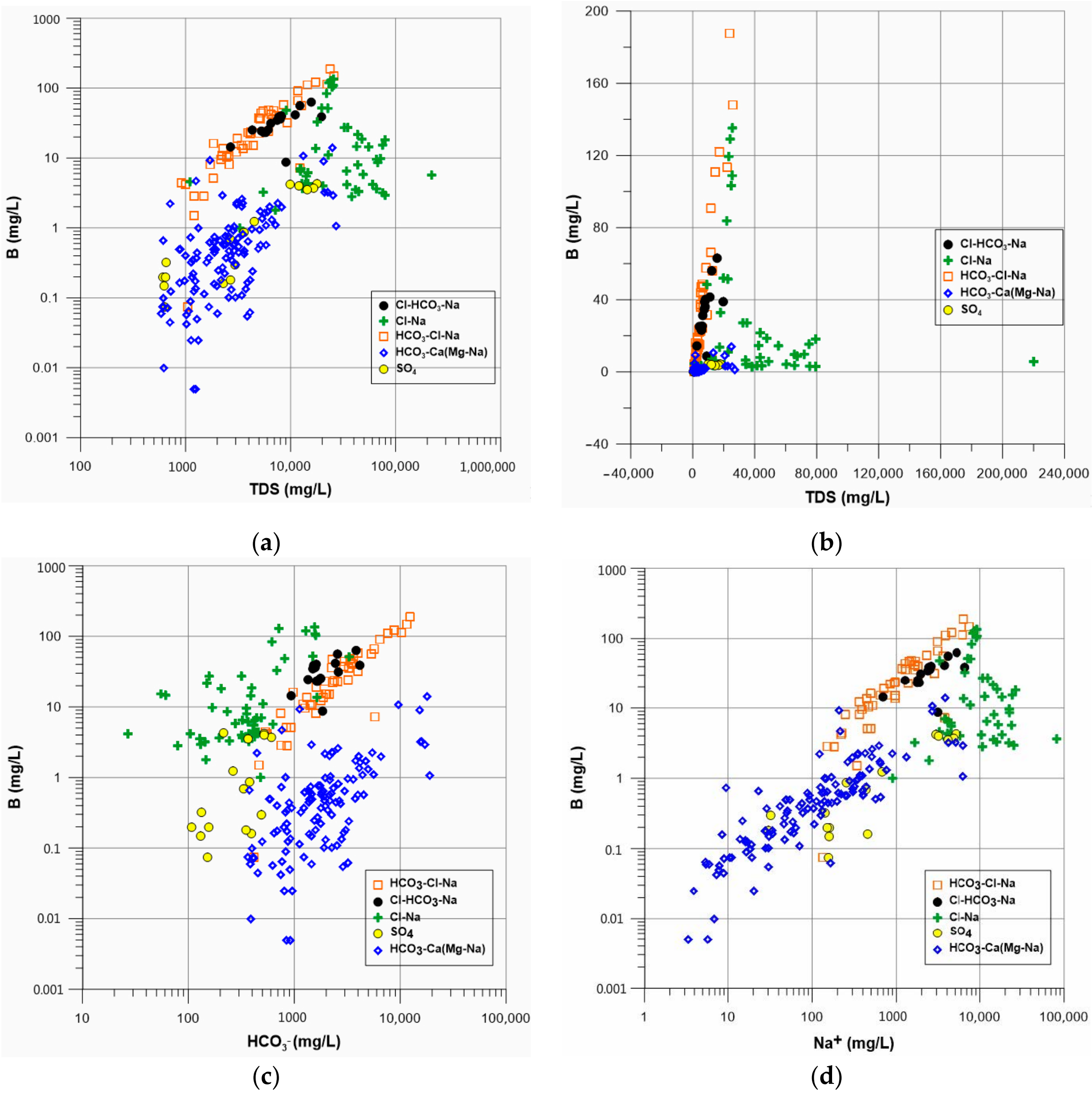


Figure 5. Boron concentration versus: (**a**) the sum of dissolved solids (mineralization of water)—double-logarithmic graph; (**b**) the sum of dissolved solids (mineralization of water)—linear graph; (**c**) HCO_3^- concentration—double-logarithmic graph (**d**) Na^+ concentration in curative waters—double-logarithmic graph.

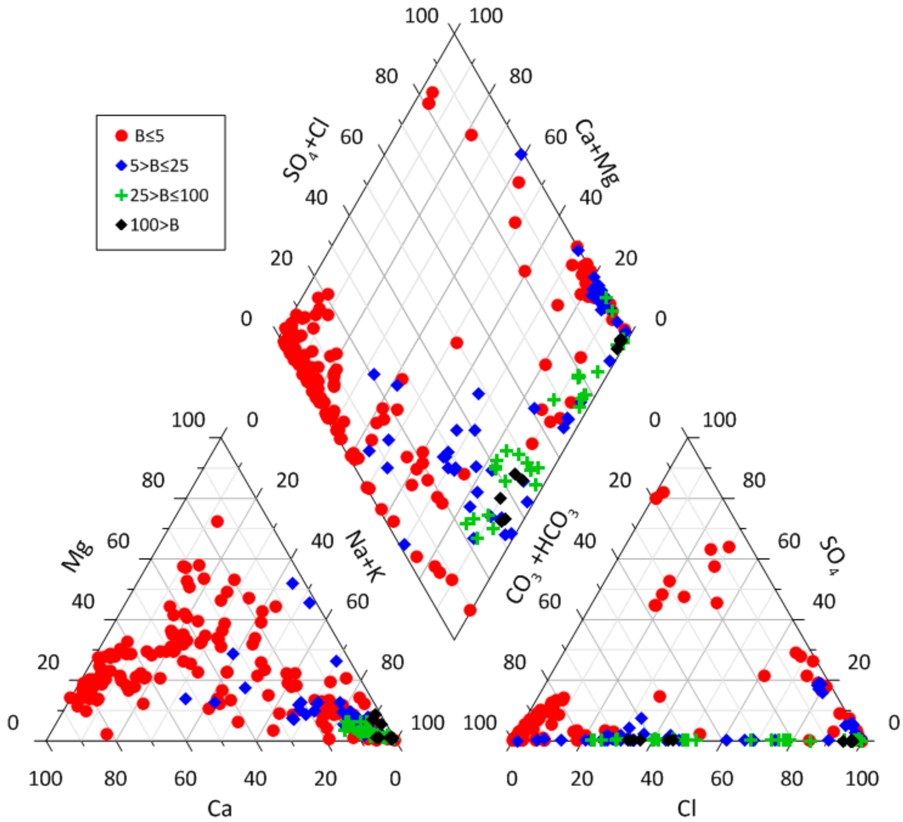


Figure 6. Piper diagram of curative water.

4. Discussion

4.1. Boron and the Chemical Composition of Water

The analyses conducted in this paper show a strong correlation between boron concentration and Na^+, HCO_3^- ions and the sum of dissolved solids (mineralization of water) in the HCO_3-Cl-Na water type. The relationship between boron concentration and mineralization indicates that the origin of boron is determined by the same processes that influence the increase in mineralization. The factor determining the differentiation of the concentrations of individual ions is the time of water circulation. A large part of the water in which HCO_3^- ions are present in concentrations above 20% milivals comes from shallower depths (it either flows out from springs or is accessed through wells, which are exceptionally deep—up to 500 m). In highly mineralized waters coming from deep circulation zones (usually Cl-Na type), the processes determining their chemistry are more complex. The lack of relationship between boron and other components may be the reason for this. In the literature, an evaluation of the processes controlling the geochemical constituents with the relationship of boron and other ions in waters has been conducted [78–80]. In these studies, the concentration of boron in waters was analyzed in the context of other chemical parameters (ion ratios). In the Polish waters analyzed by us, the Cl/B molar ratio ranges from less than 1 to 11,090. The analyzed waters come from geologically diverse areas of Poland, and the obtained values of the Cl/B molar ratio have a very wide range. Therefore, at the present stage of research, it is difficult to link the values of the Cl/B molar ratio with the processes determining the chemistry of these waters.

The strong correlation between boron concentration and mineralization of water is not seen in investigated water types other than HCO_3-Cl-Na. This is partly consistent with literature data from other regions of the world. The boron concentrations in selected Polish natural mineral and spring waters did not show any relationship between this component and mineralization [50]. Research on the chemistry of groundwater with different levels of mineralization from several regions of the world generally does not indicate a relationship between boron concentration and mineralization [81–83]. Nevertheless, an increase in boron concentration with mineralization is observed in the case of waters accompanying salt deposits. An example would be the waters of the Gorleben salt dome [84] or salt salars [85].

4.2. The Influence of Boron on the Human Body and Legal Acts Regarding the Content of Boron in Water

Boron is found in small amounts in the human body and is an important element for its proper functioning. The best sources of boron (1.0–4.5 mg/100 g) are dried fruits, nuts, avocados and legumes [3,86]. Boron is supplied to the human body by food, respiration and through the skin (especially damaged skin). The role of boron has not yet been fully defined. Beneficial effects of boron on calcium–phosphorus metabolism, i.e., the human skeletal system, have been found. Boron supports the absorption of calcium and its retention in the body, thereby preventing bone demineralization and osteoporosis [87,88]. Other benefits of boron supplementation are improvement of brain function and psychomotor response, and the treatment or prevention of arthritis [87–89].

The fact is that an excessive dose of boron is dangerous to humans. Numerous cases of poisoning with this component have been recorded. The tolerable upper intake levels (UL) of boron are 3, 6, 11 and 17 mg/day for children ages 1–3, 4–8, 9–13 and 14–18 years, respectively. For adults, the UL is 20 mg/day [90]. The upper level of boron intake is the highest daily intake of this nutrient that presents no risk of adversely affecting human health in the general population. The acute lethal dose of boron for humans is in the range of 0.4–0.9 g/kg body weight [90].

The first WHO (World Health Organization) publication concerning water quality parameters was published in 1958 as 'International standards for drinking-water' [91]. In 1963 [92] and 1971 [93], the second and third editions of this book were published under the same title. Neither 'International standards for drinking-water' [91–93] nor 'European standards for drinking-water' [94,95] contained information about the content of boron in water. It was not until 1984 that boron was first mentioned in 'Guidelines for drinking-water quality' (1st ed.) [96] and was listed among 37 inorganic constituents of potential health significance. At that time, however, a guideline value of boron was not suggested for drinking water. The second edition of 'Guidelines for drinking-water quality' in 1993 recommended that a safe concentration of boron was 0.3 mg/L [97]; in 1998 (in Addendum to Volume 1 on selected chemical substances), this was changed to 0.5 mg/L [98]. Recently, boron standards for safe drinking water have been relaxed, and the WHO has suggested changing the former adopted limit to 2.4 mg/L [99,100].

The European Union continues to recommend 1.0 mg/L as a safe concentration of boron in water intended for human consumption [47,101]. Despite changes in WHO guidelines, EU recommendations have retained the original more stringent boron concentration limits [47]. Polish law is in line with EU standards and the guide value for boron in water intended for human consumption is 1.0 mg/L [48,102]. For natural mineral waters, the limit of boron concentration is 5.0 mg/L [103]. For medicinal water products, limits of 5.0 and 30.0 g/L were set for drinking and inhalation lasting more than 1 month, respectively. No limits have been set for medicinal baths [104].

The presence of boron in the therapeutic waters of Poland has already been the subject of research [49–51,105,106]. The authors of previous studies indicated that HBO_2 in a concentration above 5 mg/L (above 1.25 mg/L of boron) is present in 57 intake waters located in 16 health resorts. The larger set of data collected in our study confirms its frequent presence in medicinal waters.

In a large number of curative waters, the boron concentration is low (in 140 cases, it did not exceed 1 mg/L). In the case of 46 waters (15 Cl-HCO_3-Na type, 19 HCO_3-Cl-Na type and 12 Cl-Na type), the boron concentration exceeded 25 mg/L (125 mg/L of HBO_2). These waters were found in nine locations (eight in the Carpathians and one on the Baltic coast—Kamień Pomorski). In the Carpathians, waters with boron concentration above

25 mg/L were found in five health resorts (Iwonicz, Rabka, Rymanów, Szczawnica and Wysowa), and the remaining three were found in Krościenko, Szczawa and Dębowiec.

However, the problem of high boron concentration in medicinal water is not without significance. In the case of 94 waters, the maximum permissible concentration value for water cure therapy (5 mg/L of B) was exceeded. In 38 waters, the maximum permissible boron concentration for inhalation therapy was exceeded (30 mg/L of B). Curative waters are, in most cases, administered in pump rooms and are therefore are not widely available. However, it is important for consumers of these waters (including patients) to be aware that waters with a boron content above 5 mg/L should not be consumed for more than a month, and waters containing more than 25 mg/L boron should be consumed very carefully [49].

4.3. The Prospect of Boron Recovery from Water with High Boron Content

There is no doubt that modern economies will have to develop effective methods for removing boron from waters (sewage) in the near future due to the demand for this raw material and health and environmental issues. High concentrations of boron compounds in drinking water can be harmful for humans. Due to the standards regarding the maximum permissible boron content in drinking water, it is necessary to remove excess boron during water treatment. This would have a positive impact on the environment and create a new source of boron, which is especially valuable as the demand for this raw material is constantly growing.

An important aspect of effective boron recovery from water is the economic viability of the process. The boron concentration in an aqueous solution for which boron production would certainly be profitable depends on many factors (total water composition, market price of boron minerals, prices of materials and chemicals needed to run the process, etc.). Although simple, economical methods of boron production from water (sewage) on an industrial scale have not yet been developed, there is great interest in this topic, and we are convinced that these methods will soon be widely used. According to the Duyvestern et al. [16], a valuable concentration of boron in brine is 100 ppm, and in Russia boron content above 200 mg/L is considered to be industrially valuable [107].

Unfortunately, most water intakes with a high concentration of boron (above 100 mg/L) are low-yielding wells [54,108–110] (Table S2). For example, in the Wysowa–Zdrój health resort, the designated exploitation resources range from 0.016 m^3/day (water intake—Aleksandra) to 24 m^3/day (W-14 water intake) [54]. Therefore, it is unlikely that cost-effective boron recovery, even on a small scale, could be achieved from a single water intake (potential production of H_3BO_3 in kg/day from this water is listed in Table S2). The analysis of the obtained data shows that the best candidate is the IG-II geothermal water intake in Rabka, with exploitation resources of 108 m^3/day [108] and potential production of ca. 80 kg of boric acid per day. However, in our opinion, simultaneous extraction of boron from several intakes in one place would bring the best expected economic effects. The analysis of the collected data shows that the best location for small-scale boron extraction would be Rabka, where five medicinal waters have boron content above 100 mg/L and their exploitation resources would add up.

5. Conclusions

The main aim of our work was to point out the problem of high content of boron in medicinal waters. For this purpose, the boron concentration in 248 water samples waters with medicinal certification was analyzed. The collected data set allowed for an examination of chemistry of these waters and also the possible relationships between boron concentration and other parameters of the curative waters. The tested waters were two-, three- and multi-ionic. According to the Szczukariew–Prikłoński classification, they belonged to a variety of groups: Cl-Na, Cl-HCO_3-Na, HCO_3-Cl-Na, Cl-SO_4-Na, SO_4-Cl-Ca-Na, SO_4-Cl-HCO_3-Mg, SO_4- HCO_3-Na, SO_4- HCO_3-Ca-Mg, SO_4- HCO_3- Cl-Na, SO_4-Ca, SO_4-Ca-Mg, HCO_3-Ca-Mg and HCO_3-Mg-Na. It is interesting that in the case of the HCO_3-Cl-Na water type, a very good correlation (Pearson correlation coefficient of 0.93) between boron concentration and the sum of dissolved solids (mineralization of water) was found. This strong correlation was not seen in other types of investigated water, which is consistent with literature data from other regions of the world. Moreover, in the HCO_3-Cl-Na water type, Na^+ and HCO_3^- ions were also correlated with the boron content (r > 0.7).

The collected data indicate that boron is a relatively common component of the investigated waters. In a large number of water samples, its content was rather low, and in 140 cases it did not exceed 1 mg/L. However, the problem of high boron concentration in medicinal water is not without significance. In the case of 42 waters (15 Cl-HCO_3-Na type, 19 HCO_3-Cl-Na type and 12 Cl-Na type) from nine locations (Dębowiec, Iwonicz, Kamień Pomorski, Krościenko, Rabka, Rymanów, Szczawnica, Szczawa, Wysowa), the boron concentration exceeded 25 mg/L, and 10 intakes of curative water had a boron concentration above 100 mg/L. The highest boron content of 187.6 mg/L occurred in the Aleksandra intake at the Wysowa–Zdrój health resort. The current information regarding the narrow margin between deficiency and toxicity of boron in the human body may result in future in the loss of the medicinal certification for some waters. Of course, it should be remembered that the pharmacodynamic effect of boric acid alone in solution may differ from that of mineral water, in which boron is just one of many components.

The data we collected on boron concentration in therapeutic waters will also be useful when considering the prospects of boron recovery from these waters, especially since boron minerals are a sought-after raw material. Based on the collected data, taking into account not only the boron content, but also the value of water resources that can be exploited, the most promising would be the simultaneous production of boron from several water intakes in Rabka. The analysis of the obtained data shows that the best candidate is in Rabka the IG-II geothermal water, with exploitation resources of 108 m^3/day and potential production of ca. 80 kg of boric acid per day.

The increasing consumption of boron minerals works in two ways: on the one hand, we are looking for sources of borates; on the other hand, high consumption causes water and soil contamination with boron compounds. In both cases, there is a need to recover boron from aqueous solutions. Although simple, economical methods of boron production from water (sewage) on an industrial scale have not yet been developed; however, there is great interest in this topic, and we are convinced that these methods will soon be widely used.

Supplementary Materials: The following are available online at https://www.mdpi.com/2075-163X/11/1/8/s1, Table S1: Curative water and potentially curative water with concentration of boron above determination limit. Table S2. Characteristic of water intakes with a boron concentration above 100 mg/L.

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