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## Brines from the Mesozoic formations of northern and central Poland as a prospective source of chemical raw materials

### Introduction

The problem of limited and depleting mineral resources has been bothering many researchers. The rapid economic growth that took place in the twentieth century led to a several fold increase in industrial production and also significantly increased the extraction of raw materials. The amount of raw materials extracted after the Second World War significantly surpassed the production before 1939. Metals, non-metals, and fossil fuels are among the most important resources for the world economy. There are already shortages of metals such as indium. In the future this may also apply to gold, silver, tin, zinc, zirconium, cadmium, tungsten, copper, manganese, nickel, or molybdenum. The availability of some metals determines the development of advanced technologies, hence some of them are included in the group of so-called critical elements. These are elements of limited availability due to the lack of deposits (primary sources) and the inability to recover these elements from waste (secondary sources) (Brożyna and Kozioł 2014). Numerous steps are taken in order to ensure the availability of mineral resources necessary for the further economic development of the world. These include: savings in the consumption of raw materials, exploration of new deposits, exploitation of deposits with difficult geological and mining conditions, and maximization of recovery through recycling. Hence, an important role is played by alternative sources of these raw materials. These include, among others, groundwaters,

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especially those highly mineralized (brines), they may contain, in addition to main components such as magnesium and potassium, a number of other elements, such as iodine, bromine, boron, strontium, and lithium. These waters can be considered as a potential source of minerals.

The article analyzes the content of selected elements (metals and non-metals) in groundwater from the Mesozoic formations building geological units of northern and central Poland. The analysis focused on the content of iodine, lithium, magnesium, and strontium in water samples collected from deep boreholes in the research area. The areas of occurrence of groundwater most suitable for extraction of iodine, lithium, magnesium, and strontium were determined.

## 1. Sources and directions of use of bromine, iodine, lithium, magnesium and strontium

Highly mineralized groundwater may contain elevated contents of bromine, iodine, lithium, magnesium and strontium, elements with a wide spectrum of applications (Vainikka and Hupa 2012; Kamyk 2014; Lewicka 2014a, 2014b; Rebarý et al. 2014; Iodine 2018; Lithium 2018; Magnesium 2018; Strontium 2018).

Bromine is used, among others, in the pharmaceutical, chemical, food, electronic, agricultural, and drilling industries. Organic bromine compounds are used as pesticides and biocides in the agricultural and food industries. Bromine compounds are used as water disinfectants in swimming pools, steam baths, and industrial cooling systems. Bromine brines, which are concentrated solutions of calcium, sodium, and zinc bromides, are used for the preparation of drilling fluids. In the coal power sector, bromine compounds are used as a sorbent capturing mercury generated during coal combustion. Bromine compounds are also used in the pharmaceutical industry for the production of medicines, dyes and photographs. Bromine is used in the production of brominated flame retardants (BFRs). BFRs are components of the plastics used in the production of computers, television sets, mobile phones, furniture, cars, and foam insulation (Vainikka and Hupa 2012; Lewicka 2014a). According to the available data, the world production of bromine amounted to 670 thousand tons in 2006 and 350 thousand tons in 2017 (excluding US production). The largest producers of bromine are the United States, Israel, China, and Jordan. Bromine (in the form of bromide) is commonly found in seawater, salt lakes, and underground brines associated with oil deposits. The average concentration of bromide in seawater is approx. 65 mg/L and approx. 23 mg/L the Baltic Sea. A relatively high content of bromide is found in salt lakes with no outflow – up to 11000 mg/L in the Dead Sea (Kabata-Pendias and Pendias 1999; Tas et al. 2005).

Iodine and its preparations are used for the production of disinfectants (pharmaceutical industry), in medicine, for the production of dyes, and in photography. This element is also used in the electronics industry, in the production of organic semiconductors, and in computer techniques of creating digital images (Kaiho ed. 2014; Lewicka 2014a). Iodine is

commonly found, in small concentrations, in natural environment; it usually is accompanying chlorine and bromine. This element occurs mainly in the form of iodides and iodates (sodium and potassium iodide and sodium iodate). Iodine is present in seawater, groundwaters, and Chilean nitrate. The main producers are Chile (65% of world production) and Japan (32%). The annual production of iodine in 2017 was at the level of 31 thousand tons (excluding US production). The main sources of iodine are caliche sediments in Chile, waters accompanying shallow deposits of natural gas, and brines from deep aquifers. Global iodine resources amount to 6.4 million tons, of which 5 million tons are found in brines in Japan. In addition, seawater contains 0.06 ppm iodine; it is estimated that approximately 90 billion tons of iodine accumulate in the oceans (Rebary et al. 2014; Iodine 2018).

Lithium is a metal with a wide range of applications from the medicine, glass and ceramics, aluminum industry, to the production of television sets. Liquid lithium is used as a coolant in nuclear reactors. Metallic lithium is used as an admixture for special bearing alloys, increasing its hardness. This element is currently used for the production of lithium-ion and lithium batteries (Garrett 2004; Szlugaj and Smakowski 2014). Lithium is a very common but scattered element. It is suggested that significant amounts of lithium can be found in seawater; however, it cannot be obtained on an industrial scale as it usually occurs in trace amounts (0.2 ppm). The concentrated lithium is generally found in rocks (in the form of lithium silicate) and salt lakes (lithium carbonate and lithium chloride). Economically significant amounts of lithium can be found in granitic pegmatites, salty lakes, and sedimentary rocks (clays). In addition, some groundwaters, including geothermal waters and those accompanying hydrocarbon deposits, contain elevated lithium content. At the end of the 1990s, brines became the main source of lithium due to lower production costs compared to other methods of obtaining this element. In 2017, the global production of lithium (excluding US production) amounted to 43 thousand tons. The major producers are Australia (43.5% of world production), Chile (32.8%), and Argentina (12.8%). The global resources of this element are estimated at 16 million tons. Chile and China have the largest reserves of lithium (7.5 and 3.2 million tons, respectively) (Lithium 2018).

Magnesium is a metal used mainly for the production of aluminum alloys (more than 35% of the world production) and in die casting (about 30%). These alloys find application in structural elements of aircrafts and space crafts as well as cars and other vehicles. This element is also used for the production of beverage packaging, consumer electronics components (loudspeakers, LCDs, mobile phones, laptops, digital cameras, and cameras), power tools, sports and optical equipment (Lewicka 2014b). Magnesium is produced mainly from dolomite, magnesite, carnalite and water (marine water, bitter lakes, and brines). Large-scale production of magnesium uses secondary sources, mainly scrap of Mg-bearing alloys. The annual share in the production of magnesium from these sources is estimated at 810% (Lewicka 2014b). The largest producer of magnesium is China (84.5% of world production), followed by Russia (5.5%) and Israel (2.2%). In 2017, the world production of magnesium amounted to 1,100 thousand tons (excluding the US). The global magnesium resources are estimated at the level of 7,800 million tons (Kramer 2001; Magnesium 2018).

The largest producers of strontium are Spain (44.6% of world production), followed by Mexico (28%) and China (24.8%). The annual production of strontium is 202 thousand tons. Currently, the largest amounts of celestite concentrate are produced in Sichuan province (China), where strontium is also recovered from brines (Zigong area). Strontium resources amount to 6.8 million tons. Strontium is used as an additive to some types of glass; since the second half of the XX century until the end of the first decade of the XXI century it has been used for the production of cathode ray tubes. In addition, this element is used for the production of ceramic ferrite magnets, paints, pigments, medicines, in pyrotechnics, zinc electrolysis, and the ceramics industry (Kamyk 2014; Strontium 2018).

## 2. The occurrence of bromine, iodine, lithium, magnesium and strontium in brines of Mesozoic deposits

The Mesozoic formations building the geological units of northern and central parts of Poland (the Polish Permian-Mesozoic Basin of NE Poland, Marginal Trough, Mid-Polish Swell, Szczecin–Mogilno–Łódź–Miechów Trough, Fore-Sudetic Monocline, and the Silesian–Krakow Monocline) include a number of aquifers. The Lower Triassic, Lower Jurassic, and Lower Cretaceous deposits are well known as rich aquifers. In addition, groundwaters can be found in the Upper Triassic and Middle and Upper Jurassic deposits (Marek and Bojarski 1983; Bojarski and Sadurski 2000; Górecki ed. 2006; Hajto 2008). The Upper Triassic, Lower Triassic, Lower and Middle Jurassic, and Lower Cretaceous aquifers are represented by sandstones and sands; these are porous reservoirs. On the other hand, the Upper Jurassic aquifer, built predominantly of limestone, forms a fracture-flow karstic aquifer. The hydrogeological conditions in the Mesozoic deposits are mostly stable (Dowgiało 1971). Waters with the highest mineralization (up to 360 g/L) and anomalously high pressure zones occur in the Lower Triassic formations. Brines in the Jurassic and Cretaceous formations show gradually decreasing mineralization and lower values of pressure gradients. In the above mentioned aquifers, the zone of fresh groundwater is increasing (Paczyński and Płochniewski 1996).

The analysis of occurrence of bromine, iodine, lithium, magnesium, and strontium in groundwater of the Mesozoic aquifers was carried out based on archival results of hydrochemical studies of groundwater from 155 deep boreholes located in northern and central Poland. Over the last 60 years, tens of thousands of deep exploratory boreholes were drilled in Poland. They were used for the purpose of prospecting of mineral resources or for exploration of the geological structure of the country. Polish Geological Institute conducts works focused on the exploration of deep geological structure of Poland, basing, among others, on measurements and research carried out in deep exploratory boreholes. The results of the research, analysis and synthetic studies have been published since the 1970s in the “Profile Głębokich Otworów Wiertniczych” (Profiles of Deep Drilling Holes) series of the Polish Geological Institute (1972–2015). The data on the content of the mentioned chemical com-

ponents contained in the “Profiles of Deep Drilling Holes” and the “Catalogue of boreholes and deep wells” (Górecki ed. 1990) were used. In the majority of boreholes, several aquifers were tested and the content of main ions and selected micronutrients, as well as mineralization, were determined.

The chemical composition of approximately 203 water samples from the Triassic, Jurassic and Cretaceous formations was analyzed. Groundwaters from the Lower Jurassic deposits were subjected to the most thorough examination (100 determinations). Among the examined components, only magnesium was determined as the main component in all of the tested samples. Bromine concentrations were tested in the majority of waters. The other analyzed components (iodine, lithium, and strontium) were determined using smaller amount of samples.

The occurrence of bromine, iodine, lithium, magnesium, strontium and total dissolved solids (TDS) in brines in the Mesozoic formations was analyzed on the basis of descriptive statistics (mean, median, standard deviation, skewness, and kurtosis) of concentrations of these chemical components. The statistics were calculated for Triassic, Jurassic, and Cretaceous aquifers (Table 1–3). Due to the smaller data set of concentrations of strontium

Table 1. Descriptive statistics of selected chemical components and TDS of waters from Triassic aquifers

Tabela 1. Statystyki opisowe wybranych składników chemicznych oraz sumy rozpuszczonych składników stałych wód z utworów triasu

Parameter	Number of water samples	Mean value	Median value	Minimum value	Maximum value	Standard deviation	Skewness	Kurtosis
TDS (mg/L)	78	106 149.10	92 800.00	172.80	360 000.00	87 588.81	0.99	0.39
Mg <sup>2+</sup> (mg/L)	70	1 317.66	1 027.22	3.20	9 233.30	1 392.98	2.85	13.97
Br <sup>-</sup> (mg/L)	78	342.92	165.45	0.20	3 012.82	524.17	3.14	11.67
I <sup>-</sup> (mg/L)	40	6.27	4.49	0.00	40.00	7.78	3.04	10.13

Table 2. Descriptive statistics of selected chemical components and TDS of waters from Jurassic aquifers

Tabela 2. Statystyki opisowe wybranych składników chemicznych oraz sumy rozpuszczonych składników stałych wód z utworów jury

Parameter	Number of water samples	Mean value	Median value	Minimum value	Maximum value	Standard deviation	Skewness	Kurtosis
TDS (mg/L)	171	60 609.78	55 776.00	25.10	345 900.00	53 150.41	1.22	3.75
Mg <sup>2+</sup> (mg/L)	164	654.13	416.65	0.02	2 1157.00	1 794.96	9.79	107.67
Br <sup>-</sup> (mg/L)	171	93.49	63.16	0.50	879.00	139.11	3.43	13.77
I <sup>-</sup> (mg/L)	95	6.58	4.00	0.11	101.00	11.72	6.08	45.51

Table 3. Descriptive statistics of selected chemical components and TDS of waters from Cretaceous aquifers

Tabela 3. Statystyki opisowe wybranych składników chemicznych oraz sumy rozpuszczonych składników stałych wód z utworów kredy

Parameter	Number of water samples	Mean value	Median value	Minimum value	Maximum value	Standard deviation	Skewness	Kurtosis
TDS (mg/L)	55	24 671.22	12 300.00	350.0	125 720.0	29 113.59	1.53	2.04
Mg <sup>2+</sup> (mg/L)	53	191.62	60.00	0.8	660.0	217.56	0.88	-0.68
Br <sup>-</sup> (mg/L)	54	31.30	15.45	0.2	325.0	50.32	50.32	4.11
I <sup>-</sup> (mg/L)	28	3.25	1.75	0.1	13.0	3.52	3.53	1.27

Table 4. Descriptive statistics of lithium and strontium contents from waters in Mesozoic aquifers

Tabela 4. Statystyki opisowe zawartości litu i strontu w wodach z utworów mezozoicznych

Element	Number of water samples	Mean value	Median value	Minimum value	Maximum value	Standard deviation	Skewness	Kurtosis
Li <sup>+</sup>	37	2.12	1.31	0.0	14.6	2.88	3.03	10.49
Sr <sup>2+</sup>	34	80.28	40.15	0.0	411.0	100.85	2.09	4.34

and lithium, the parameters of descriptive statistics were calculated for the entire Mesozoic (Table 4).

### 2.1. The presence of bromine, iodine and magnesium in brines in the Triassic deposits

The Triassic deposits in northern and central Poland show different facies development. The lower part of the Lower Triassic is developed as sandstone-mudstone-clay series, while the upper part is in the form of carbonate rocks. The Middle Triassic is represented by carbonate rocks. The Upper Triassic is represented by a mudstone-clay series with inserts of limestones, anhydrites and rock salts (Kuyavia and Pomerania). In the Lower Triassic profile, aquifers are made of irregularly occurring sandstones and conglomerate packages of small thickness (Buntsandstein). However, it should be noted that sandstone packages with poor petrophysical parameters and small thickness, irregularly occurring in the Upper Triassic deposits (Upper Keuper), have water-bearing properties (Bojarski and Sadurski 2000).

The mineralization of waters in the Lower Triassic formations varies within very wide limits: from ordinary waters (from 0.4 g/L) occurring in the marginal parts of the

reservoir to saturated brines (415 g/L) in the axial parts of the Swell and Mogilno–Łódź and Szczecin Troughs. In the marginal basin and in the northern part of the Fore-Sudetic Monocline, the mineralization of water exceeds 150–200 g/L. In the remaining areas it amounts to 50 g/L. The Lower Triassic sediments contain saturated brines of the Cl-Ca-Na type with a high degree of chemical composition transformation (Bojarski and Sadurski 2000; Hajto 2008). In the Upper Triassic formations, water with the highest mineralization (200–300 g/L) is found in the area of the Kuyavian Swell and Łódź, Szczecin, and Warsaw Troughs. In other areas the mineralization of water ranges from a few (marginal zones) to 100 and 100–200 g/L (Górecki ed. 2006).

The examined samples were dominated by waters of Cl-Na type (according to the classification by Shchukaryev and Priklnsky) (49 water samples), and Cl-Na-Ca type (23 samples). The concentrations of magnesium, bromine, and iodine are highly variable (Table 1). The distribution of the analyzed elements in the waters of the Triassic formations indicates that their values are concentrated around the mean (kurtosis value greater than zero – leptokurtic distribution), while most of the results are above the mean (right-sided asymmetry).

## 2.2. The presence of bromine, iodine, and magnesium in brines in the Jurassic deposits

The Lower Jurassic sandstone and mudstone-clay series are interbedded. Aquifers are composed of sandstones with a variable grain size interbedded with poorly permeable claystones, sandy clays, mudstones, and sandy mudstones. Sandstone, sandstone-conglomerate-sandstone, and sandstone-dolomitic deposits of the Middle Jurassic profile, separated by poorly permeable sediments (claystones and siltstones), have water-bearing properties. Water in the Upper Jurassic formations occur in limestone and sandstone complexes (Bojarski and Sadurski 2000; Hajto 2008).

The mineralization of water in the Lower Jurassic deposits depends on the depth. On outcrops and in peripheral parts of individual units the mineralization does not exceed 2 g/L. The highest mineralization was found in the axial parts of the Łódź, Szczecin, and Warsaw Troughs – up to around 100–200 g/L. In the remaining areas, the mineralization of waters changes from approx. 10 to 100 g/L. Brines in the Lower Jurassic deposits are waters of Cl-Na type, which generally are characterized by a low level of chemical transformations and the  $r_{Na/rCl}$  indicator of 0.80–0.95. In the case of water in the Middle Jurassic formations, the mineralization ranges from below 1 g/L (outcrops and groundwater recharge areas) to over 150 g/L (Konin region). As in the case of water in the Lower Jurassic formations, groundwater in the region of the troughs, especially their axial zones, is usually characterized by higher mineralization. The mineralization of groundwater in the Upper Jurassic formations varies within very wide limits: from below 2 g/L (outcrop zone) to over 120 g/L (NW part of the Łódź Trough, the central part of the Szczecin Trough). Lower mineralization (50–70 g/L) is recorded in the case of the Upper Jurassic deposits of the Warsaw Trough

and NE part of the Lublin Trough. However, the Upper Jurassic deposits are dominated by water with a mineralization in the range from 2 to 20 g/L. The waters in the Upper Jurassic formations are of the Cl-Na type and show a low degree of chemical transformation. In the marginal zones, they transform into waters of the sulfate-sodium and bicarbonate-sodium type (Bojarski and Sadurski 2000; Hajto 2008).

The analyzed samples were dominated by waters of the Cl-Na (141) and Cl-Na-Ca type (8), while waters of the Cl-HCO<sub>3</sub>-Na type were determined in 12 cases. The concentrations of magnesium, bromine, and iodine are highly variable (Table 2). The distribution of the concentration of the analyzed elements in the groundwaters of the Jurassic formations indicates that their values are centered around the mean, while most of the results are above the mean.

### 2.3. The presence of bromine, iodine, and magnesium in brines in the Cretaceous deposits

Sandstones and glauconite sands of the Lower Cretaceous and sandstones of the Upper Cretaceous occurring on the slope of the East European platform have very good hydrogeological properties. Aquifers in the Lower Cretaceous profile are composed of a complex of discontinuous, alternating sandy, sandy-marl, and sandy-mudstone layers. This level is hydraulically connected with both the underlying aquifers of the Jurassic formations and the overlying Upper Cretaceous deposits (Bojarski and Sadurski 2000; Hajto 2008).

The mineralization of waters in the Lower Cretaceous formations is low and generally ranges from 0.2 (outcrop zone) to 20 g/L, locally up to 50–100 g/L in deeper parts of the basin, the Łódź Trough at the contact zone with the Mogilno Trough, and in the Szczecin Trough (almost the whole area). The lowest mineralization (1–10 g/L) was found in the case of Kuyavian Swell, in the SE part of the Warsaw Trough, Miechów Trough, and in the SE and W part of the Mogilno–Łódź Trough. The Lower Jurassic formations contain water of the Cl-Na and HCO<sub>3</sub> type (Bojarski and Sadurski 2000; Hajto 2008).

The analyzed samples were dominated by waters of the Cl-Na type (37), followed by the Cl-HCO<sub>3</sub>-Na (5) and Cl-HCO<sub>3</sub>-Na-Ca types (5). The concentrations of magnesium, bromine, and iodine are highly variable. The concentrations of bromine and iodine in water in the Cretaceous formations are concentrated around the mean. The concentrations of magnesium are dispersed in relation to the mean (Table 3). Most of the concentrations of the analyzed elements are above the mean, which is evidenced by a right-sided asymmetry.

As already mentioned, the content of lithium and strontium was analyzed in total for waters occurring in all of the Mesozoic aquifers (Table 4). The concentration of lithium varies in a wide range, while the concentration of strontium is characterized by even higher variability. As in the case of the other analyzed elements, the distributions of lithium and strontium concentration in the Mesozoic waters indicate that their values are centered around the mean (kurtosis greater than zero – leptokurtic distribution), and most of the results are above the mean (right-handed asymmetry).



In order to indicate aquifers that are the most suitable for the extraction of bromine, iodine, lithium, magnesium, and strontium, the relationship between concentrations and the depth of retention was analyzed. Correlations were analyzed for both the set of all Mesozoic waters and sets containing the results obtained from the individual aquifers. The analyzes were performed using the Statistica PL software and involved the examination of the Pearson correlation coefficient. The parameters correlated with each other were those for which the values of correlation coefficients were statistically significant at the confidence level of  $\alpha < 0.05$ . In addition, the distribution of points corresponding to these parameters in the coordinate system has been analyzed. The contents of lithium and strontium increase with the depth of the sampled horizons (Figs. 1 and 2). In the case of strontium, the correlation is stronger ( $R = 0.648$ ; critical value of 0.3388), while in the case of lithium it is weaker ( $R = 0.326$ ; critical value of 0.3246).

The relationship between selected chemical components in waters of the Mesozoic formations has also been analyzed. A very strong correlation ( $R = 0.8530$ ) (a critical value of 0.3388) between the strontium and bromine content (Fig. 3) has been found for the data set covering all water samples from the Mesozoic formations. Furthermore, a correlation between strontium and magnesium ( $R = 0.5722$ ) (critical value of 0.3388) (Fig. 4) has also been confirmed.

The correlation between the content of bromine and magnesium for the whole research set is weaker ( $R = 0.5919$ ;  $n = 285$ , not compared to the critical value) (Fig. 5) and increases

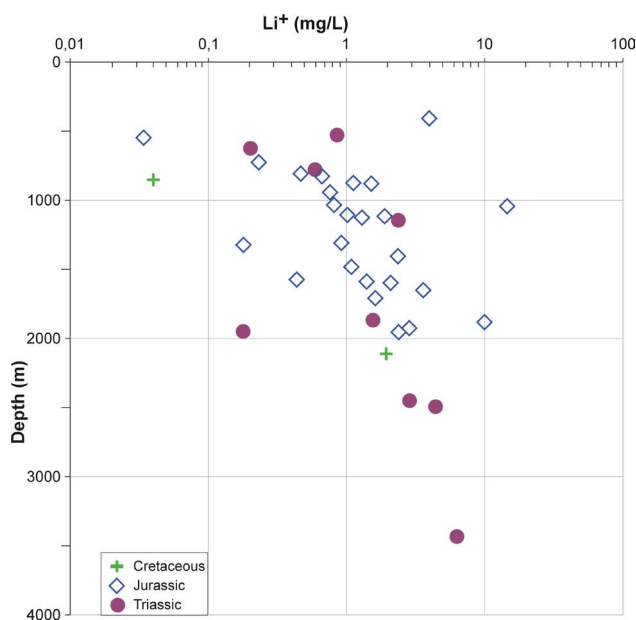


Fig. 1. Lithium content in waters in the Mesozoic deposits depending on the depth

Rys. 1. Zawartość litu w wodach w utworach mezozoiku w zależności od głębokości ich zalegania

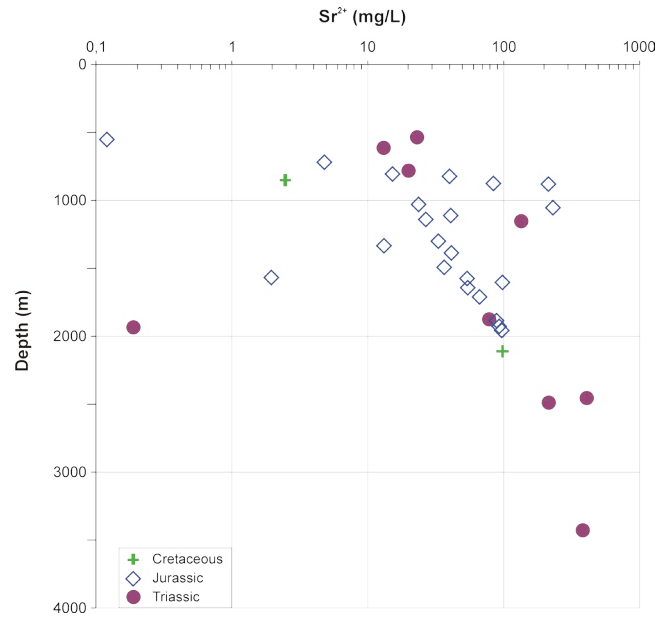


Fig. 2. Strontium content in waters in the Mesozoic deposits depending on the depth

Rys. 2. Zawartość strontu w wodach w utworach mezozoiku w zależności od głębokości ich zalegania

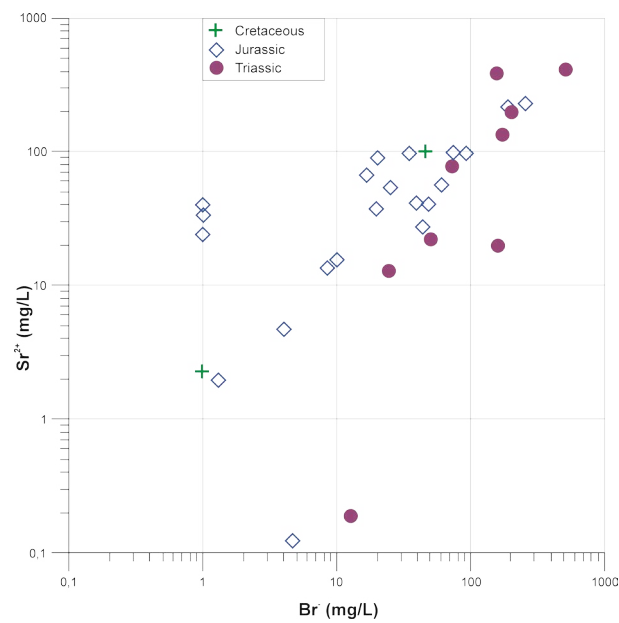


Fig. 3. The relationship between the content of bromine and strontium in waters in the Mesozoic deposits

Rys. 3. Zależność między zawartością bromu i strontu w wodach w utworach mezozoiku

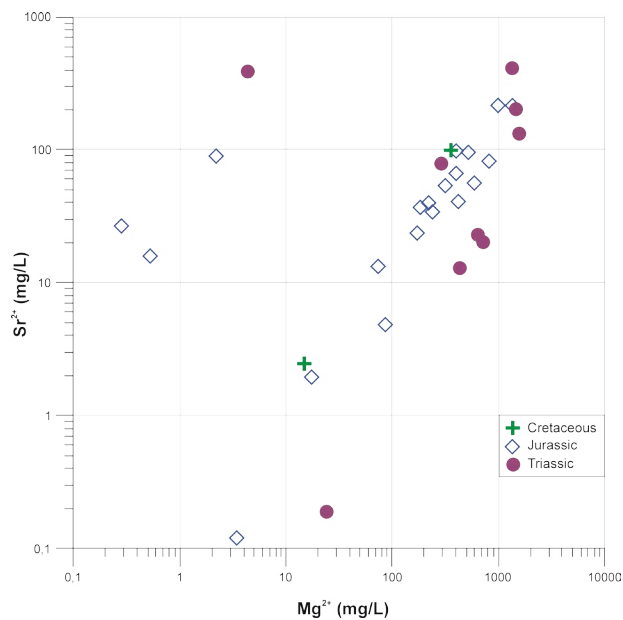


Fig. 4. The relationship between the content of magnesium and strontium in waters in the Mesozoic deposits

Rys. 4. Zależność między zawartością magnezu i strontu w wodach w utworach mezozoiku

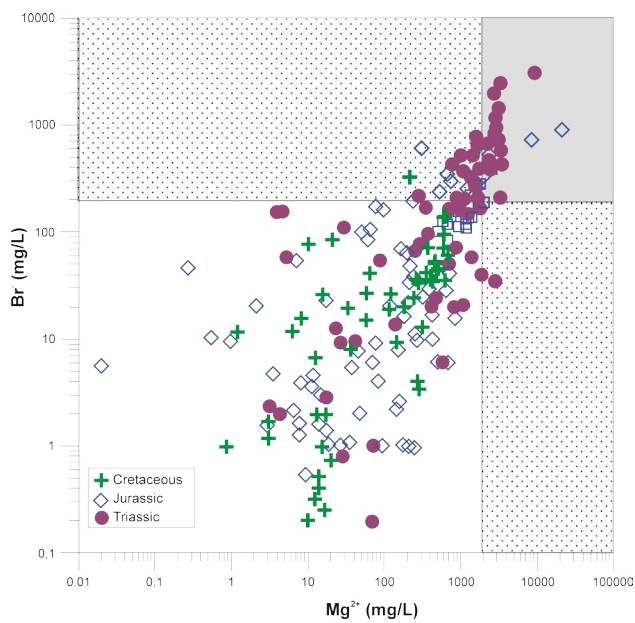


Fig. 5. The relationship between the content of bromine and magnesium in waters in the Mesozoic deposits

Rys. 5. Zależność między zawartością bromu i magnezu w wodach w utworach mezozoiku

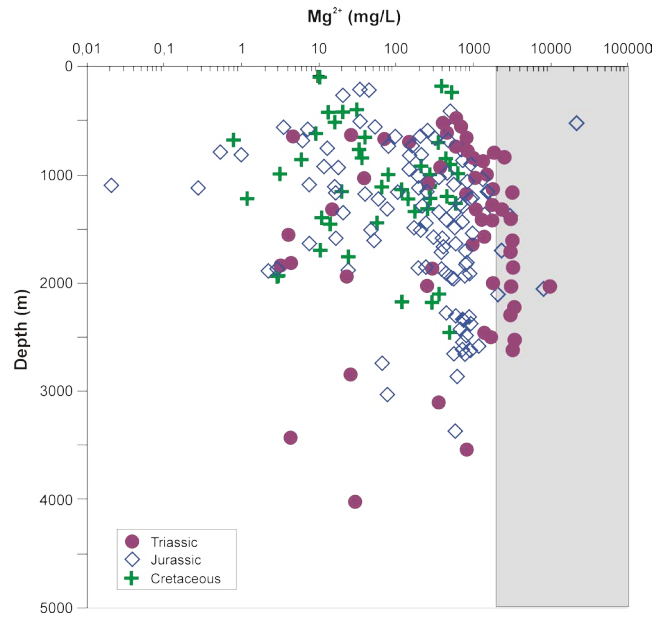


Fig. 6. Magnesium content in waters in the Mesozoic deposits against of their depth

Rys. 6. Zawartość magnezu w wodach mezozoiku na tle głębokości ich zalegania

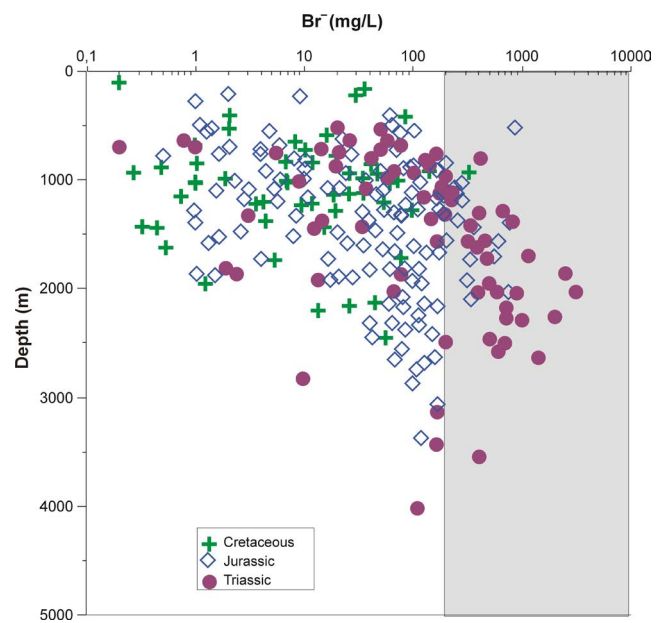


Fig. 7. Bromine content in the Mesozoic deposits against of their depth

Rys. 7. Zawartość bromu w wodach mezozoiku na tle głębokości ich zalegania

with the age of aquifers. In the case of waters from the Cretaceous formations, the correlation is moderate ( $R = 0.4009$ ) ( $R$  critical = 0.2759), while in the case of the Jurassic deposits, the correlation is strong ( $R = 0.6951$ ,  $n = 164$ , the critical correlation coefficient is not analyzed). When it comes to waters of the Triassic deposits, the correlation is high  $R = 0.8109$  ( $R$  critical = 0.236).

The possibility of using groundwater for the recovery of chemical raw materials on an industrial scale is determined by the concentration of selected elements. The elements can be recovered from waters containing lithium at a concentration of at least 10 mg/L, iodine (15 mg/L), bromine (200 mg/L), strontium (500 mg/L), and magnesium (2000 mg/L) (Bukowski and Czapowski). The analyzed data show that the elements whose concentration exceeds these thresholds are bromine and magnesium. In some groundwaters both bromine and magnesium occur in quantities that may indicate the possibility of recovery of these elements on an industrial scale. Waters from the Triassic formations may be considered as the most suitable for recovery of these elements, although in individual cases water from the Jurassic deposits is also promising. The aquifers prospective for the recovery of Br and Mg occur at depths of approximately 1000 m to 2500 meters below ground level (Figs. 6 and 7).

## Conclusions

Waters occurring in the Mesozoic deposits of central and northern of Poland are characterized by normal hydrogeochemical zonation. The mineralization and the concentration of magnesium, bromine, and iodine are increasing with the increasing age and depth of aquifers. This is evidenced by median values of the content of individual elements in the groundwaters from Triassic, Jurassic, and Cretaceous formations. The increase in the amount of iodine, magnesium, and bromine is associated with the occurrence of these waters in zones that are isolated from the contemporary water cycle, as evidenced by their chemical composition.

In the case of bromine, the standard deviation increases with the increasing age of the tested horizon; this suggests a greater variation in the concentration of this element in older aquifers. In contrast, waters from the Jurassic deposits are characterized by the highest variability in magnesium and iodine content.

The Triassic formations contain brines with bromine and magnesium concentrations of above 200 and 2000 mg/L respectively. This indicates that these groundwaters are the most suitable for the recovery of bromine and magnesium among all analyzed aquifers.

The correlation between the content of bromine, strontium, and magnesium has been confirmed. Based on the analysis of the relationship between these elements in individual aquifers, it can be concluded that the relationship between bromine and magnesium increases with their increasing age, which (as evidenced by the increasing value of the correlation coefficient).

The directly proportional relationship between bromine, magnesium, and strontium can be used to predict the above-average occurrence of these elements in water. However, limited data and the lack of waters with a strontium content above 500 mg/L may indicate that the suitability of brines for the recovery of strontium is low. The lithium, strontium, and bromine content increases with the increasing depth of the aquifer, which may indicate that waters occurring at significant depths (more than 1500 m) are rich in the abovementioned elements.

Due to the limited scope of this study (a small amount of information on the concentrations of lithium, strontium and iodine), the analyzed historical data allow only an approximate estimation of the content of these elements. With more data (e.g. from collecting samples from aquifers during drilling), the determination of the relationships would allow further research on the suitability of saline water as a source of chemical raw materials.

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#### BRINES FROM THE MESOZOIC FORMATIONS OF NORTHERN AND CENTRAL POLAND AS A PROSPECTIVE SOURCE OF CHEMICAL RAW MATERIALS

##### Abstract

Polish brines are highly mineralized and can potentially be used for recovery of selected useful elements such as magnesium and potassium. They also contain a number of other elements, including iodine, bromine, boron, and strontium. The results of the examination of the chemical composition of groundwater from the Mesozoic formations (bromine, iodine, lithium, magnesium, and strontium content) of northern and central Poland were analyzed. The basic statistical parameters of the content of these elements (Br, I, Mg) in brines of the Triassic, Jurassic, and Cretaceous deposits and the content of lithium and strontium in waters of the entire Mesozoic formations were determined. In order to indicate aquifers that are the most suitable for the recovery of bromine, iodine, lithium, magnesium, and strontium, the relationship between concentrations and the depth of retention and dependencies between selected chemical components of these waters were analyzed.

It has been found that the mineralization and concentrations of magnesium, bromine, and iodine increase with the age of aquifers, where these waters occur. Triassic waters are the most prospective for bromine and magnesium recovery among all analyzed aquifers. Furthermore, a relationship between the content of bromine, strontium, and magnesium has also been observed. The increase in the

content of individual elements observed for lithium, strontium, and bromine with the increasing depth indicates a potential abundance of waters occurring at significant depths. The presented analysis is an approximation of the content of bromine, iodine, lithium, magnesium, and strontium; however, it may be the basis for further studies on the perspectives of using brines from the Mesozoic deposits of central and northern Poland as a source of chemical raw materials.

**Key words:** brine, Mesozoic, Poland, recovery, chemical raw materials

#### SOLANKI Z UTWORÓW MEZOZOICZNYCH PÓŁNOCNEJ I ŚRODKOWEJ POLSKI JAKO POTENCJALNE ŹRÓDŁO SUROWCÓW CHEMICZNYCH

##### Streszczenie

W Polsce występują solanki o wysokich mineralizacjach, które mogą być potencjalnie wykorzystywane do odzysku wybranych pierwiastków użytecznych takich jak np. magnez, potas. Mogą one również zawierać szereg innych pierwiastków, jak np. jod, brom, bor, stront. Przeanalizowano wyniki badań chemizmu wód podziemnych z utworów mezozoicznych z obszaru Polski północnej i środkowej pod kątem zawartości: bromu, jodu, litu, magnezu i strontu. Obliczono podstawowe parametry statystyczne zawartości tych pierwiastków w solankach w utworach triasu, jury i kredy oraz litu i strontu łącznie w wodach w utworach mezozoiku. W celu wskazania najbardziej perspektywicznych pięt wodonosnych pod kątem występowania bromu, jodu, litu, magnezu i strontu przeanalizowano zależności pomiędzy stężeniami a głębokością zalegania, a także zależności między wybranymi składnikami chemicznymi tych wód.

Stwierdzono wzrost mineralizacji oraz stężeń magnezu, bromu i jodu wraz z wiekiem pięt wodonosnych, w których te wody występują. Spośród analizowanych pięt wodonosnych wody w utworach triasu są najbardziej perspektywiczne pod kątem odzysku bromu i magnezu. Zaobserwowano również zależność między zawartością bromu, strontu i magnezu. Wzrost zawartości poszczególnych pierwiastków obserwowany dla litu, strontu i bromu wraz z głębokością świadczy o potencjalnej zasobności wód występujących na znacznych głębokościach. Przedstawiona analiza ma charakter orientacyjnej prognozy zawartości bromu, jodu, litu, magnezu i strontu (ze względu na ograniczoną liczbę istniejących oznaczeń) może jednak stanowić podstawę dalszych badań nad perspektywicznością wykorzystania wód zasolonych z utworów mezozoiku środkowej i północnej Polski jako źródła surowców chemicznych.

**Słowa kluczowe:** solanka, mezozoik, Polska, odzysk, surowce chemiczne