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Aluminium in waters of the active exchange zone in the Karkonosze National Park (Western Sudetes, SW Poland)

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Abstract. The paper presents the variability of aluminum concentrations in groundwater of the main porous-fissured aquifer and surface waters in the area of the Karkonosze National Park (KPN), covering mainly the upper parts of the Karkonosze Mts. The analysis was based on the results of samplings carried out in the area of the KPN in August 2015 and supplemented with the results of water quality monitoring carried out during the period of 2010–2016 in selected catchments of the Karkonosze Mts. Significant spatial variability of aluminium concentrations was observed, from several dozen to over 1,090 μg/L, increasing along with the height of the measurement points. The highest concentrations were recorded in the ridge zone of the Karkonosze Mts, where the pH is the lowest.

Key words:
aluminum,
active exchange zone,
water chemistry,
Karkonosze Mts.

Introduction

Aluminium is one of the elements commonly found in the Earth's crust, but in the aquatic environment it occurs mainly in small amounts (usually up to several mg/L) and is not very mobile (Macioszczyk 1987; Macioszczyk and Dobrzyński 2002). One of the main factors affecting the release of Al into the waters is the pH reaction of the environment. Al is most soluble in acidic and strongly alkaline waters. In shallow systems of groundwater occurring in the upper part of hard rocks of the Karkonosze massif, aluminium is one of the basic microelements. The range of concentrations recorded in waters is significant, from several dozen to over 1,090 μg/L (Marszałek 2007; Marszałek and Rysiukiewicz 2015). The close contact between shallow local groundwater flows and surface waters also causes its presence in the waters of the streams. The acidic pH, typical for Karkonosze waters, promotes the release of aluminium from the rock environment to groundwater. Higher concentrations of Al are recorded in the ridge parts of the Karkonosze Mts, where waters are characterised by a lower pH. These parts of the Karkonosze Mts are protected in the 5,500 ha area of the Karkonosze National Park (KPN) established in 1959.

An important source of Al may be the so-called "exchangeable fraction" (Macioszczyk and Dobrzyński 2002), which consists of Al^{3+} and $AlOH_2^+$ ions, adsorbed on negatively charged particles of clay minerals and organic substances in soils and weathering residuals.

Elevated concentrations of Al in groundwater have been recorded in different parts of the Sudetes, including in gneisses of the Sowie Mts (Chudy and Marszałek 2010), granites of the Karkonosze Mts. (Kryza et al. 1994, 1995; Marszałek, 1996; Marszałek and Rysiukiewicz 2017), Rudawy Janowickie Mts and Intra-Sudetic Synclinorium (e.g. Dobrzyński 1995, 2009) and other aquifers of Poland

and the world (e.g. Frankowski et al. 2011; Batayneh 2012; De Meyer et al. 2017; Marin et al. 2010).

The knowledge of aluminium concentrations in waters is significant, because some water intakes for supplying the local population (e.g. Karpacz and Szklarska Poręba) are located within the KPN. So, the main purpose of the article is to present the aluminium content in groundwater of shallow circulation and surface waters within the Karkonosze National Park and to determine the influence of naturally lowered pH of water on the Al content.

Geological and hydrogeological background

The hydrogeological massif of the Karkonosze Mts is mainly built by Variscan Upper Carboniferous granite. Only in its eastern part do metamorphic series occur, predominantly consisting of Early Palaeozoic gneisses and schists (Fig. 1). In the upper part of the main ridge of the Karkonosze Mts, medium grain granite predominates, but in the lower parts of the massif porphyritic coarse granite (monzogranite) with large and pink crystals of potassium feldspar occur. The entire massif is cut by aplites, pegmatite, quartz and lamprophyres and a network of faults. Characteristic for dislocation zones within granite, mainly with NW–SE and SW–NE orientations, is the presence of cataclasites, mylonites and breccia (Mierzejewski 2005).

The granite massif which builds the vast majority of the KPN area is not petrographic or chemically homogeneous. The ridge parts of the mountains are composed mainly of equigranular granite and to a lesser extent of aplogranite, containing the highest respective average amounts of such elements as: Si (34.8%), Al (7.0%) and K (4.03%). On the other hand, they contain the lowest amount of Ca (0.79% on average), Mg (0.15%) and Fe^{2+} (0.15%) (Sachanbiński 1995). Most of the elements building the hard rocks of the Karkonosze Mts are mainly associated with silicates and aluminosilicates. They are released from minerals in the hypergenic zone only as a result of mainly chemical weathering. This type of weathering occurred in the Karkonosze massif in the Tertiary but most of the existing weathering residuals were formed in the Quaternary (Sachanbiński 1995).

The latter are covered with a thin layer of crystalline fissured basement and are built of well permeable sandy gravel grus saprolite covered by deluvial clayey slope material and organogenic deposits. Peat bogs are frequent on both ridges and slopes of the Karkonosze Mts. Typical for the ridge zone of the Karkonosze Mts is rock debris covering the majority of summits. Alluvial sediments fill the river valleys. Their thicknesses – of up to a few metres – are greater in the valleys of the main rivers: the Kamienna and Łomnica rivers draining the northern Polish part of the Karkonosze Mts and flowing into the Bóbr River in the morphological depression of the Jelenia Góra Basin.

The Karkonosze Mts form an elevated hydrogeological massif, where the forming of groundwater resources is strongly related to rock fractures and the climatic features of the area. The basic porous-fissure water aquifer occurs within a well-developed network of fractures in the upper part of the massif covered by a weathering layer to a depth of about 30 m. This upper, most fractured part of the rock massif, with well-permeable weathering cover, forms an active exchange zone which is characterised by high values of filtration parameters. Values of hydraulic conductivity exceed 87 m/d (Marszałek 2007). The most intensive water exchange covers the upper part of the profile (max. 10 m). To the depth of about 30 m there is a zone with a limited exchange rate, and below this depth the exchange rate clearly decreases (Kryza et al. 1995). The high recharge from precipitations (reaching even 1,400 mm/a in the upper part of the massif) and intensive fissuring in the near-surface zone cause the main amount of renewable groundwater resources to form. The values of groundwater runoff are extremely high (10–15 L/s km^2) in the small river catchments of the upper parts of the mountains. Their strong morphological diversity favours the existence of numerous springs of mainly low discharge that during a dry period is usually in the range of 0.1–0.5 L/s, but during spring thaws can reach maxima even above 16 L/s (Marszałek 2007). The values of hydraulic conductivity estimated for fissured granite by pumping tests at a depth of several dozen metres are rather low and amount to 0.1–0.8 m/d on average. Their transmissivity is mainly within 1–40 m/d^2 and rarely reaches 100 m/d^2 (Marszałek 2007).

Methods

The chemical composition of water was determined based on 40 water samples collected during the dry season of August 2015 over the whole KPN area (Fig. 1). Water samples were taken from the spring zone in the upper parts of the park and from streams at the boundary of the protected area. This series of samples was completed with the results of water chemistry analyses for 24 water samples collected within the two monitored catchments (of the Wrzosówka and Łomnica rivers) at the beginning of July and at the end of October 2015. In this case, water was taken from springs, piezometers and streams.

The basic physico-chemical parameters of water such as temperature, pH, and electrolytic conductivity (EC) were measured on-site using a calibrated portable WTW 340 multiparametric meter with precision of measurements: 0.01 μS/cm for EC and 0.01 for pH. Chemical analyses of the water sample were made at the Chemical Laboratory of the Institute of Geography and Regional Development of the University of Wrocław using various analytical methods. The basic ions SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, NH_4^+, PO_4^- were determined by spectrophotometry and alkalinity was measured in the laboratory by colorimetric titration with HCl. For other major ions such as Ca^{2+}, Mg^{2+}, Na^+, K^+ and metals, including Al, Fe, Mn, plus selected trace elements, Atomic Absorption Spectrometry (AAS) was used.

The chemical composition of waters in the KPN was described in detail by Marszałek and Rysiukiewicz in 2017. Measurements of the concentrations of such gases as carbon dioxide and radon were not made in the KPN waters. The long-term dry period during the summer of 2015 did not allow rainwater to be sampled.

Geochemical modelling with PHREEQC version 3 was used to calculate the distribution of species and the values of the saturation index (SI) for selected minerals (Parkhurst and Appelo 1999). During modelling the Phreeqc.dat thermodynamic database was used and the oxidising redox potential, expressed as pe=4.0, was assumed.

Results an discussion

Hydrochemical investigations were carried out in the upper parts of the Karkonosze massif, and covered the spring areas of the streams network, where the chemical composition of groundwater and surface water is very uniform. This is due to the recharge of streams during dry periods by groundwater of shallow, local circulation. The water tem-

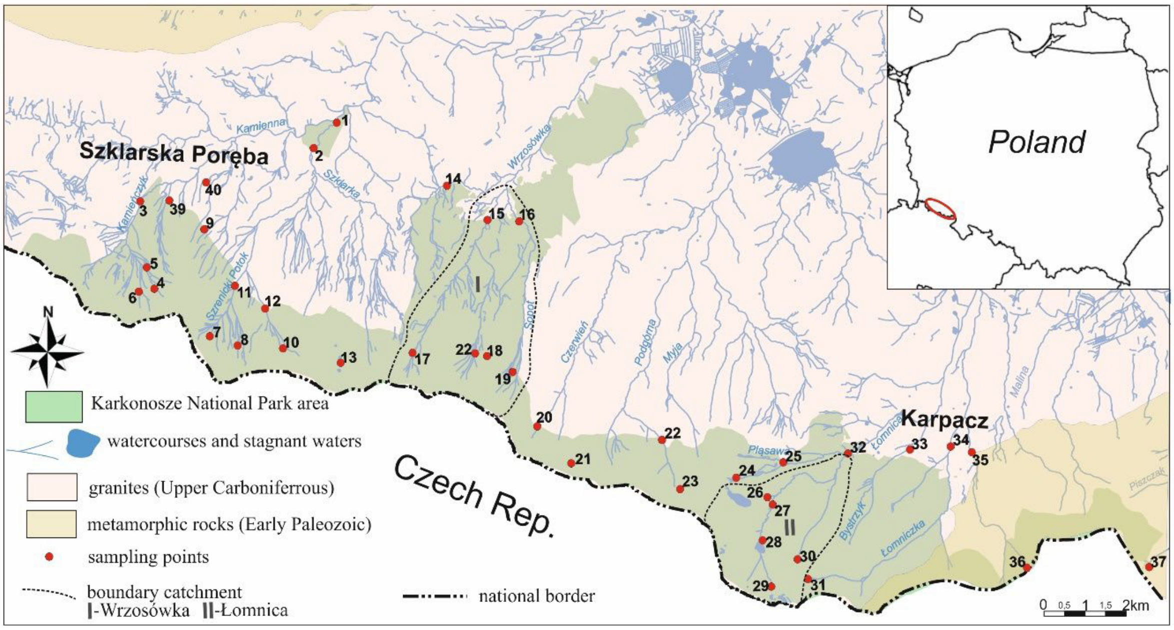

Fig. 1. Location of sampling points in the Karkonosze National Park on the geological background

perature measured in the field was within the range of 7.4–16.1°C, but for groundwater the range was much smaller (7.4–9.9°C).

The mineralisation of waters in most investigated points was very low and ranged from 10 to 67 mg/L (14.1–137 μS/cm). Only at one point located in the western part of the Karkonosze Mts, below the tourist shelter on the Hala Szrenicka, was the TDS higher, reaching 160 mg/L (Table 1). Anomalously high electrical conductivity EC (equal 365 μS/cm) was registered there, and this significantly differs from the other values and is much higher than the highest mineralisation found for the remaining 39 water samples, amounting to 137 μS/cm. By omitting this point, the average TDS was 21.79 mg/L (37.89 μS/cm). High concentration of nitrates (47.15 mg/L) indicates anthropogenic pollution of water below the shelter (Table 1). The low TDS results from the short residence time of groundwater flowing in the well-permeable near-surface heavily fractured hard rocks lying under a weathering cover, represented mainly by rock debris and sandy gravel grus saprolite. They also confirm the shallow and local circulation of groundwater in the active exchange zone.

The pH of water is a very important factor affecting the release of aluminium from the rocks. The pH of waters measured in the 40 samples in August 2015 ranged from 4.68 to 6.98 (6.21 in average; Table 1). Only at two points was the pH value below 5.0. Such slightly acidic and near-neutral values indicate an increase in groundwater pH in the research area compared with results obtained in the last few decades. Hydrogeochemical investigations carried out in the mid-1980s and 1990s, generally at the same points, showed average pH values of 4.84 in 1985 and 4.96 in 1995 (Kowalski and Marszałek 1985; Marszałek 1996). This indicates a clear improvement in water quality. The periodic measurements of water pH carried out since the 1980s at various points of the Karkonosze Mts showed a slight falling tendency in water pH with increasing altitude. Low pH values (even below 4) were measured in the highest watershed parts of the mountains, while there was a near-neutral value (6.5–7.0) for water occurring in the zones of intramontane depressions and river valleys. The pH of spring waters measured in the 1980s in the western parts of the Karkonosze ridge was often below 3.0 (Marszałek 1996).

The ionic composition of the waters is dominated by sulphates (often over 60% of the anion composition), bicarbonates, sodium and calcium. The sodium cation was sometimes displaced by magnesium and the concentration of chlorides were very low (3.21 mg/L on average; Table 1). This anion is not typical of the rock environment of the Karkonosze Mts and its origin is associated with its supply to waters as a result of human activity. Due to the low mineralisation of the analysed waters, they represent various hydrogeochemical types, from 3- to 5-ionic, with the predominant SO_4-HCO_3-Ca-Na-Mg type (Fig. 2) (Marszałek and Rysiukiewicz 2017).

The concentrations of such analysed metals as Al, Fe, Mn, Cu, Pb and Zn were generally low. Considering the quality of the analysed samples with regards to the standards for drinking water, only a few points located mainly in the central part of the KPN showed excessive contents of Fe (up to 0.91 mg/L) and Mn (up to 0.15 mg/L) (Table 2). Among the other metals there were found small amounts of Cu (10.25 μg/L maximum), Pb (10.45 μg/L) and Zn (over 89 μg/L). The maximum concentrations of these microelements were measured at one point in the upper part of the Wrzosówka River catchment (Marszałek and Rysiukiewicz 2017).

Apart from the exceeded concentrations of Fe and Mn, high Al ion contents were also recorded in a wide range from 7.93 to 831.2 μg/L. The average concentration of aluminium in the KPN waters was 177.8 μg/L (Table 2). In eight samples the concentration of Al ion exceeded the acceptable value for drinking water of 200 μg/L (Dz.U. z 2017r. poz. 328, 1566 I 2180). Hydrochemical studies carried out in July 2015 in the monitored Wrzosówka River catchment showed maximum concentrations of Al reaching 1,091.12 μg/L (Marszałek and Rysiukiewicz 2015, 2017).

The occurrence of this component in increased amounts in the waters of the ridge zone of the Karkonosze Mts is associated with its leaching from the rock environment with a low water pH, whose value decreases with increasing terrain altitude. The linear correlation of aluminium concentrations versus pH of water is -0.60 for the analyzed 40 samples, while for samples taken from springs it is much higher, amounting to -0.69 (Fig. 3). However, there is practically no relation between aluminium content and water mineralisation (R=0.15). The corre-

Table 1. Chemical composition of waters in the Karkonosze National Park (August 2015)

Statistical parameters	**EC**	**pH**	**TDS**	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**HCO_3^-**	**SO_4**	**Cl^-**	**NO_3^-**	**PO_4**	**NO_2**	**NH_4+**
n=40	µS/cm	mg/L												
min	14.1	4.68	10.00	0.63	0.34	1.16	0.09	2.68	4.01	0.38	0.13	0.00	0.00	0
max	365	6.98	160.0	10.82	4.93	26.16	9.27	11.78	19.49	41.54	47.15	3.47	2.99	4.03
mean	46.06	6.21	26.0	2.41	1.15	3.21	0.91	6.05	8.53	3.21	2.05	0.18	0.11	0.14
median	31.6	6.35	18.00	1.85	0.85	2.30	0.46	5.80	7.72	0.99	0.60	0.04	0.01	0.03
standard deviation	43	0.57	11.56	2.17	0.96	3.95	1.88	2.43	3.53	7.53	7.41	0.61	0.47	0.63

n - number of analyzes

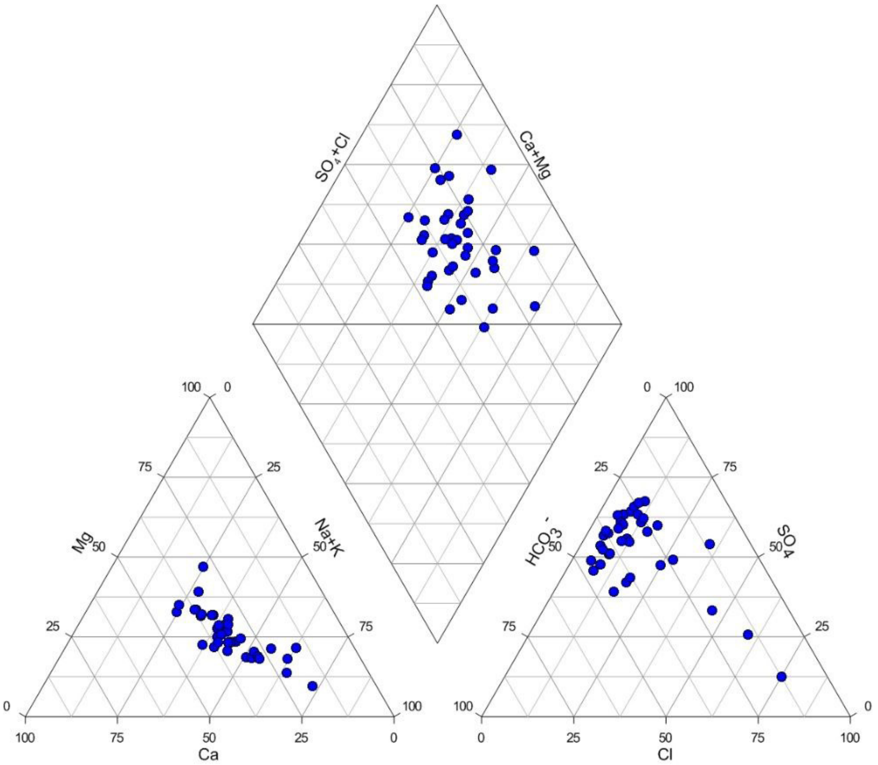

Fig. 2. Chemical composition of waters in the Karkonosze National Park for the period of August 2015, presented as a Piper diagram (after Marszałek and Rysiukiewicz 2017)

lation between Al concentration and the altitude of sampling points, estimated for the whole Karkonosze Mts, showed a similar value of -0.52 (Kryza et al. 1994, 2005). A slightly higher negative correlation of Al content and pH of water (-0.55) was obtained for the entire Western Sudetes in the mid -1990s (Bocheńska et al. 1997). The presence of peat bogs in the ridge zone of the mountains contributes to lower pH of the waters. It is also possible to supply Al to groundwater from atmospheric precipitation, but the decrease in pollution load observed in the Karkonosze Mountains since the early 1990s (Błaś et al. 2008) also limits this factor for supplying Al to groundwater. The aluminium concentration in precipitations measured in the Karkonosze Mts in the mid-1990s reached a value of 121 µg/L (Zwoździak et al. 1995).

Table 2. Concentration of selected microelements in waters of the Karkonosze National Park (August 2015)

Statistical parameters n=40	Fe	Mn	Cu	Pb	Zn	Al
	mg/L		µg/L			
min	0.005	0.005	0.5	1.0	0.5	7.93
max	0.91	0.15	10.25	10.45	89.43	831.20
mean	0.08	0.01	0.77	0.48	3.89	177.80
median	0.03	0	0.23	0.07	0.84	88.57
standard deviation	0.18	0.03	1.83	1.67	14.16	203.90

Speciation analysis showed that $Al(OH)_2^+$ is the dominant form of aluminium occurrence in various proportions, both in surface- and groundwater (Table 3). The similarity of the participation of this form in the two types of water results from water having been sampled in the high parts of the Karkonosze Mts, where groundwater with a short residence time has a similar chemical composition to surface waters. Other ionic complexes, often occurring in the water environment of KPN are $Al(OH)_4^-$ more often found in surface waters, and $AlOH^{2+}$ found mainly in springs. Al^{3+} is a secondary form of aluminium, whereas $Al(OH)_3$ and $AlSO_4^+$ were of marginal significance (Table 3).

Concentrations of aluminium in the groundwater of the active exchange zone in the hard rocks of the Karkonosze Mountains are controlled by many factors. Aluminium enters environmental media naturally through the weathering of rocks and minerals. Weathering cover contains both primary minerals (such as quartz, feldspar and mica) and various clay minerals (illite, montmorillonite, kaolinite and lepidocrocoite). The clay minerals adsorb various elements that previously passed from the rock environment to aqueous solutions. According to Sachanbiński (1995) both main elements (Si, Al, Fe, Ca, Na, K, Mg) and trace elements occur in the weathering layer and soils of the Karkonosze Mts in several forms, including metal cations connected as

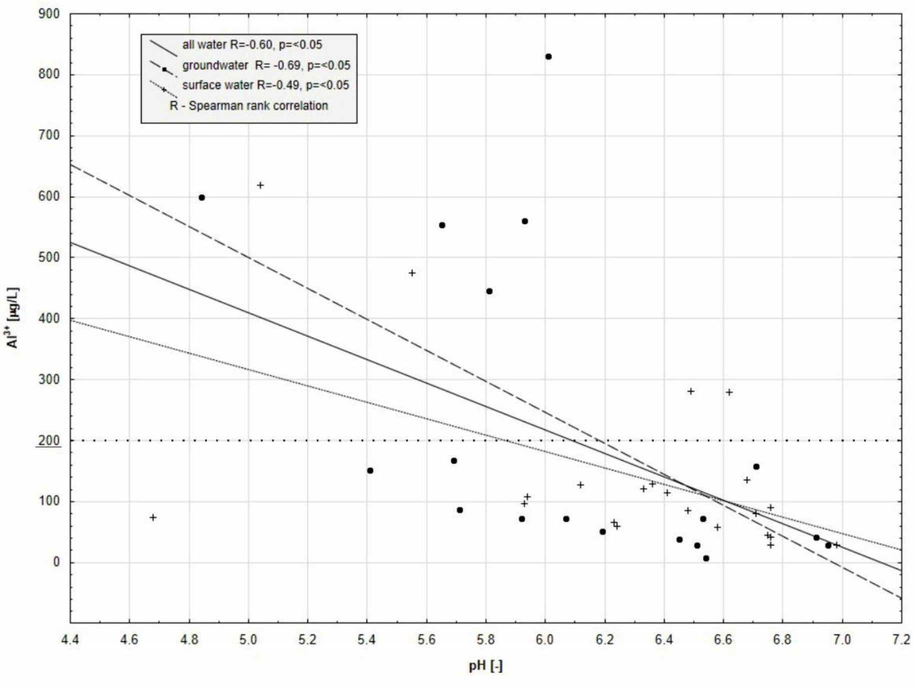

Fig. 3. Aluminium concentration vs pH of water in the Karkonosze National Park (200 µg/L – limit of Al for drinking water)

Table 3. Results of hydrochemical speciation modelling of surface- and groundwater in the area of KPN (in %)

Complex ions	**Statistical parameters**	**surface water**	**groundwater**
$Al(OH)_2^+$	min	1.44	2.09
	max	59.32	58.35
	mean	36.70	37.04
$Al(OH)_4^-$	min	0.01	0.01
	max	85.85	76.3
	mean	37.13	20.88
$AlOH^{2+}$	min	0.34	1.45
	max	36.32	39.93
	mean	10.95	22.10
Al^{3+}	min	0.01	0.06
	max	75.25	71.60
	mean	8.41	14.79
$Al(OH)_3$	min	0.01	0.01
	max	8.53	7.29
	mean	5.84	3.19
$AlSO_4^+$	min	9.85	10.36
	max	0.01	0.01
	mean	1.13	2.00

a result of ion exchange with clay minerals or as a result of bonds with organic matter. So, clay minerals and organic matter play a very important role in the circulation of elements in the upper weathered parts of the studied area. The strength of metals' bonds with organic matter (occurring in soils in the form of humic and fulvic acids binding cations of metals) has a large impact on the transport of metals in soil and waters (Sachanbiński 1995).

The main factor affecting aluminium mobility in the water–rock system is the pH of water. Metals can be released and pass into seepage and groundwater with decreasing environmental pH. The strong acidification of the environment, including water, caused the strong deforestation of the Karkonosze in the 1980s. The hydrogeochemical background determined at the beginning of the 1990s for aluminium occurring in waters in the highest parts of the Karkonosze Mts was 8.2–356.6 µg/L (Kryza et al. 1995).

The results of the hydrogeochemical modelling show that aluminium ions present in both groundwater of shallow circulation and surface waters are close to the solubility limit (Fig. 4).

The chemical composition of groundwater may change, among others as a result of precipitation of solid phases (minerals) in them. The tendency to precipitate specific substances can be assessed by calculating the saturation index (SI). The dissolved aluminium concentration in groundwater is controlled by the solubility of weathering products such as gibbsite and kaolinite (Appelo and Postma 2005). The SI calculation results showed that groundwaters of the local flow occurring in the ridge parts of the Karkonosze Mts are close to saturation with the $Al(OH)_3$(a) complex ion (SI close to 0; in most springs from -0.32 to 0.03). The weathering of soil results in the more rapid release of silica, and aluminium precipitates from hydrated aluminium oxides such as gibbsite. There is also the theoretical possibility of aluminium precipitation from water, reaching the saturation state, for such minerals as gibbsite (SI in the range 0.66–3.39), kaolinite (SI from 2.98 to 8.53) and Ca-montmorillonite (SI from 0.14 to 7.02).

It should be assumed that the increase in aluminium concentrations in water may be affected by the ability of exchange sorption by forming aluminium complexes with organic matter contained in soils. Compared to the weathering of primary and secondary minerals, this process is fast and reversible (Berggren and Mulder 1995).

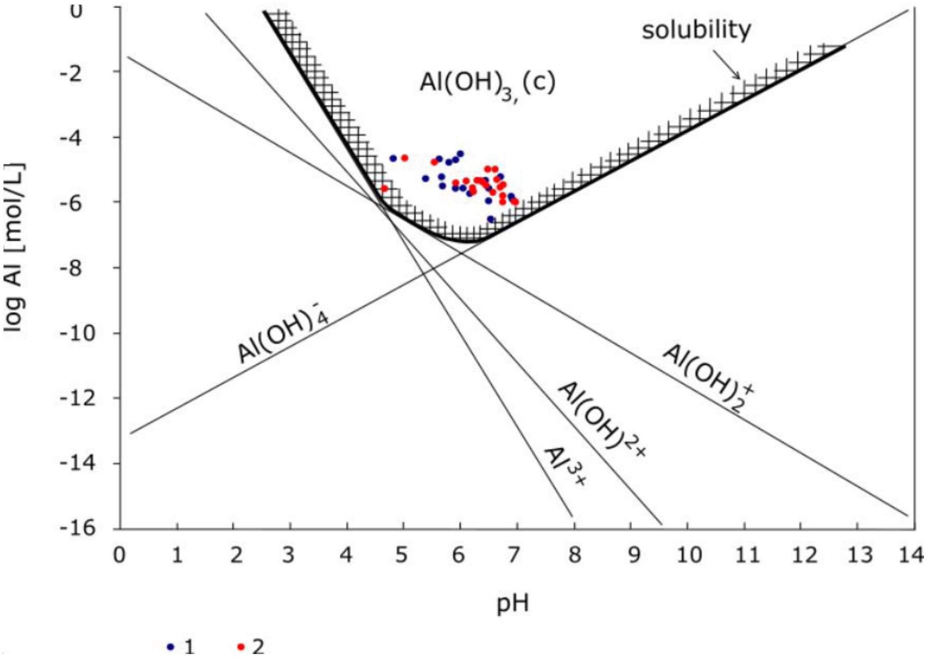

Fig. 4. The location of sampling points (1 – groundwater, 2 – surface water) on the graph of the solubility of total dissolved aluminium in equilibrium with gibbsite [$Al(OH)_3$] and aqueous Al-hydroxy complexes (after Apello and Postma 2005)

Conclusions

Low-mineralised waters in the upper parts of the Karkonosze Mts contain elevated amounts of aluminium. They are of sulphates-bicarbonates-calcium-sodium hydrochemical type and represent groundwater of shallow circulation. When compared against lower average values in recent decades, their slightly acidic and near-neutral pH confirm an improvement in water quality. The results of the research indicate that the content of aluminium concentrations in the waters of the active exchange zone in the KPN is influenced by the presence of clay minerals in the weathering residuals and soils covering the crystalline basement. The pH of water plays an important role in activating aluminium in the aquatic environment. The presence of organic matter in soils, which was not analysed in this work, can also influence the amount of this element in waters.

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Disclosure statement

No potential conflict of interest was reported by the authors.

Author Contributions

Study design: H.M.; data collection H.M., M.R.; statistical analysis H.M., M.R.; interpretation of results H.M., M.R.; preparation of manuscript H.M.; literature review: H.M.

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