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Geochemical relationships in CO_2-rich therapeutic waters of the Sudetes (Poland)

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ABSTRACT:

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Geochemical studies of CO_2-rich therapeutic waters in the Sudetes have provided new data on a wide range of trace elements, going beyond standard chemical analyses of such waters. A consistent set of physicochemical data obtained using the same analytical methods was subjected to statistical analyses, including hierarchical clustering, factor analysis and nonparametric tests (Kruskal-Wallis, Tau Kendall), to reveal geochemical relationships between physicochemical and chemical parameters in the waters, and their relationships with the aquifer lithology. Distinct differences in the composition of waters found in crystalline rocks (mainly gneisses and mica schists) and sedimentary rocks were identified. The wide range of elements can be associated with the hydrolysis of silicate minerals, including alkali and alkali earth metals (Li, Na, K, Rb, Cs, Be) and (mostly) transition elements (Fe, Mn, Zn, Co, W, Mg). Carbonate equilibria are the next important factor as it determines the aggressiveness of the water towards the minerals of aquifer rocks and affects the concentrations of numerous solutes. The probable common origin of chlorides, bromides and sulphates together with Li, Na, Sr may be related to the relict saline component of deep circulating waters, a hypothesis that requires further investigations.

Key words: Groundwater geochemistry; Trace elements; Therapeutic water; CO_2-rich water; Sudetes.

INTRODUCTION

Groundwater naturally enriched in carbon dioxide (CO_2) is relatively common. Waters of high CO_2 concentration (above 250 mg/L) have a long tradition of being used in balneology (also referred to as medical hydrology or thermalism) as a valuable natural healing resource. In Poland, this type of CO_2-rich (named acidulous) therapeutic water occurs in the Carpathians and the Sudetes mountains. The chemical composition of these therapeutic waters is periodically examined within a range of physicochemical and chemical parameters required by regulation (Order 2006).

The subject of this study is the chemical composition of CO_2-enriched therapeutic waters occurring in the Sudetes (Text-fig. 1; Table 1), studying those components widely outside the area of those legally required for regular analyses, in particular in terms of trace elements. Such in-depth studies of the geochemistry of therapeutic waters results from various needs, such as better documentation of adverse and toxic components, recognition of the presence of previously unexplored or rarely studied components, more complete understanding of the genesis of the chemical composition of groundwater chemistry, and finally more effective protection of these groundwaters.

Locality	Intake name (symbol)	Aquifer lithology	Type of intake	Depth ** [m b.g.l.]
Waters in crystalline aquifers				
Świeradów-Zdrój	Górne (SW1)	gneisses	spring	nd
	1A (SW2)	granitogneisses	bore-hole	60
	2P (SW3)	granitogneisses	bore-hole	360
	Maria Skłodowska-Curie (SW4)	gneisses	well	6
Czerniawa-Zdrój	Jan II (CZ1)	mica schists	bore-hole	197
Duszniki-Zdrój	Jan Kazimierz (DU1)	mica schists	bore-hole	159
	Pieniawa Chopina (DU2)	mica schists	bore-hole	73
	B-39 (DU3)	mica schists	bore-hole	180
	B-4 (DU4)	mica schists	bore-hole	56
Długopole-Zdrój	Renata (DL1)	mica schists	shaft	nd
	Emilia (DL2)	mica schists	adit	nd
	Kazimierz (DL3)	mica schists	shaft well	nd
Waters in mostly sedimentary aquifers				
Szczawno-Zdrój	Marta (SZ1)	conglomerates, sandstones and shales	spring	nd
	Młynarz (SZ2)	conglomerates, sandstones and shales	spring	nd
	Dąbrówka (SZ3)	conglomerates, sandstones and shales	spring	nd
	Mieszko (SZ4)	conglomerates, sandstones and shales	spring	nd
Polanica-Zdrój	Wielka Pieniawa (PO1)	sandstones, marls	bore-hole	31
	Józef 2 (PO2)	sandstones, marls	bore-hole	43
	P-300 (PO3)	sandstones	bore-hole	269
Kudowa-Zdrój	Śniadecki (KU1)	sandstones	bore-hole	18
	Marchlewski (KU2)	sandstones	bore-hole	approx. 80
	K-200 (KU3)	sandstones	bore-hole	205
Jeleniów	J-150 (JE1)	sandstones	bore-hole	85

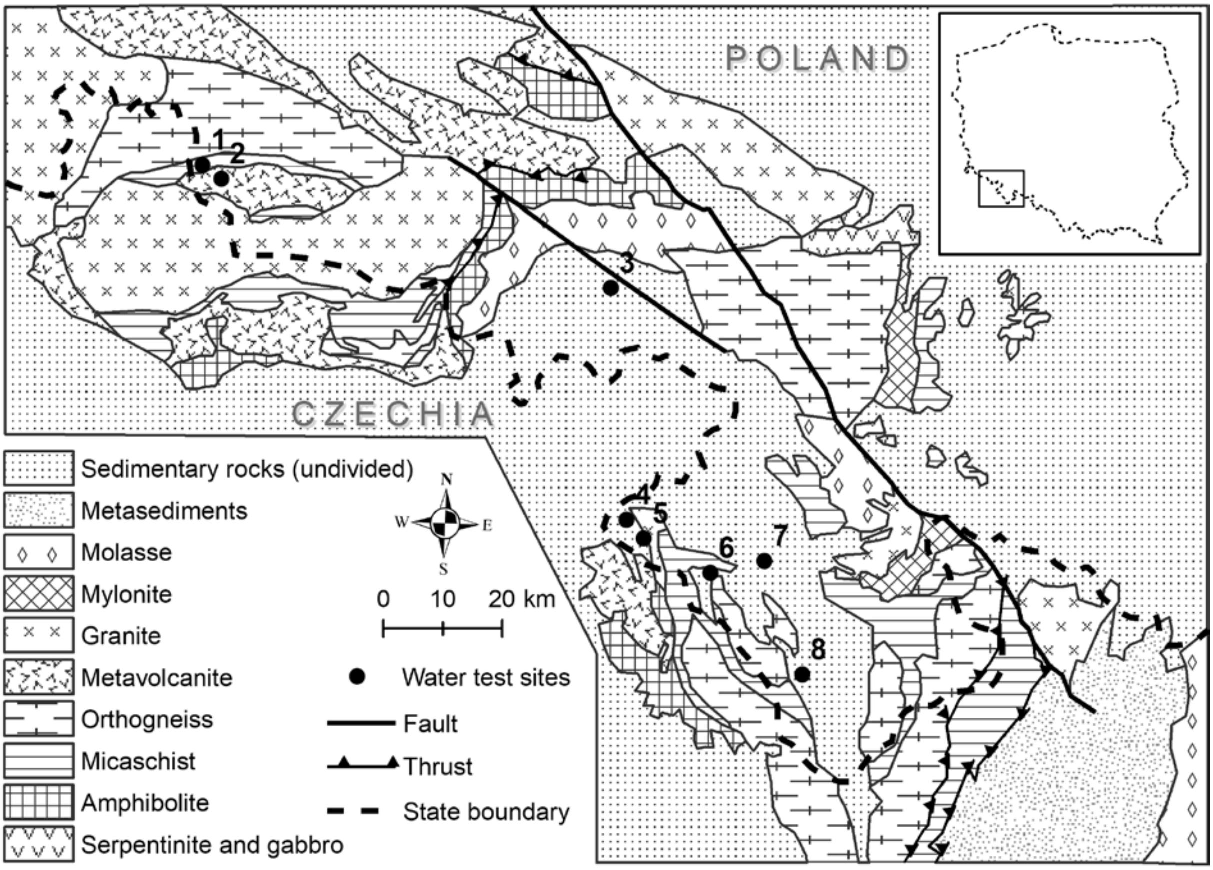
Table 1. General characteristics of the studied water intakes; * – based on data from Fistek (1967), Liber-Makowska and Kiełczawa (2021), and Mineral Groundwater Data Bank PGI-NRI (http://spd.pgi.gov.pl/PSHv8/). ** – in the case of a well or borehole, the value indicates its depth. nd – no depth in the case of captured outflow from a spring or adit.

The goals of this paper are: (1) to determine geochemical relationships involving trace elements rarely studied in therapeutic acidulous waters, and (2) to identify the main regional geochemical patterns related to the highly variable lithology of the local aquifer rocks.

GEOLOGY AND HYDROGEOLOGICAL SETTINGS

The Polish part of the Sudetes, representing the north-eastern fragment of the Bohemian Massif, differs in its geological structure and hydrogeology from other parts of Poland (Oberc 1972; Żelaźniewicz *et al.* 2011). The Sudetes mineral water province is also distinctly different (Paczyński and Płochniewski 1996), with water types and conditions of their occurrence differing from the neighbouring areas. The most characteristic feature of the Sudetes province is the occurrence of dislocated crystalline rocks and hard sedimentary rocks directly below the surface or at small depths, resulting in the large role that tectonic zones played in groundwater flow and spring formation, as well as the presence of waters characteristic of Miocene volcanic activity and with high tectonic impact, i.e. acidulous (CO_2-rich) waters and thermal waters, coupled with the almost complete lack of chloride waters.

The Sudetes are largely built of strongly folded Proterozoic and Palaeozoic igneous and metamorphic rocks. Only the Fore-Sudetic and Intra-Sudetic basins contain Carboniferous, Permian, Triassic and Upper Cretaceous sedimentary rocks. The variable and mosaic geological structure of the Sudetes results in different waters, i.e. fresh and mineral, cold and thermal, occurring in the subsurface even in the vicinity of each other. Deep tectonic dislocation zones play an important role in the development of mineralized waters. Uplifted areas represent zones along which precipitation and surface waters infiltrate, and the fault lines represent pathways of groundwater flow, which may often be quite deep. As a result, waters attain higher temperatures, are enriched in lithospheric CO_2 and specific components. Dislocation zones favour also enhanced radon emission from reservoir rocks (Ciężkowski 1990; Przylibski 2005; Ciężkowski *et al.* 2016). The chemical composition



Text-fig. 1. Location of water test sites against geological structure. Geological map adapted after Mazur and Aleksandrowski (2001). Sites: 1 – Czerniawa-Zdrój, 2 – Świeradów-Zdrój, 3 – Szczawno-Zdrój, 4 – Kudowa-Zdrój, 5 – Jeleniów, 6 – Duszniki-Zdrój, 7 – Polanica-Zdrój, 8 – Długopole-Zdrój.

of CO_2-rich waters may result from the mixing of highly mineralized deep-circulating waters with modern fresh shallow-circulating waters. The portion of the component of the waters of the deep circulation system can be determined by chemical or isotopic analysis (e.g., Ciężkowski and Zuber 1996; Kozłowski 1999). With regard to the geological setting, the occurrence of CO_2 waters in the Polish part of the Sudetes can be subdivided into two groups: (1) present in fissure aquifers of crystalline massifs (of the Izera, Bystrzyckie, and Orlickie mountains); and (2) related with pore-fissure aquifers in Palaeozoic and Mesozoic sedimentary rocks of the Intra-Sudetic Basin (Ciężkowski *et al.* 2016).

Intakes of studied CO_2-rich waters connected with crystalline aquifers occur in Świeradów-Zdrój, Czerniawa-Zdrój, Duszniki-Zdrój and Długopole-Zdrój. The term "zdrój" means spa or health resort.

The presence of CO_2-rich waters in the vicinity of Świeradów-Zdrój and Czerniawa-Zdrój is related to the Izera Mountains, composed of strongly folded lower Palaeozoic gneisses. Within the gneisses occur parallel zones of mica schists, in some cases amphibolites. Locally, there occur intrusions of Rumburk granite and hydrothermal mineral veins (Dowgiałło and Fistek, 2007). In Świeradów-Zdrój particular springs are related to the intersection between a large NW-SE-oriented fault zone and transverse faults (Fistek *et al.* 1975; Bażyński *et al.* 1986). The therapeutic waters of Świeradów-Zdrój are of infiltration origin. They are recharged on the slopes of the Kwisa valley. The recharge zone is located mainly within the gneisses, but the chemical composition of the acidulous waters is influenced mostly by the mica schists (Ciężkowski 1983). Radon acidulous waters characteristic of Świeradów-Zdrój are formed due to mixing of deep-circulation waters rich in CO_2 with shallow, low-mineralized waters containing high radon concentrations (Ciężkowski and Zuber 1996; Ciężkowski 2003; Ciężkowski *et al.* 2016). The chemistry of the therapeutic waters from Czerniawa-Zdrój is, similarly as in Świeradów-Zdrój, the result of mixing of waters of the deep and shallow circulation systems and develops also within the Izera Mountains (Ciężkowski *et al.* 2016).

The CO_2-rich waters of Duszniki-Zdrój are linked with the northern part of the Bystrzyckie Mountains. They flow out from paragneisses and mica schists in the vicinity of the intersection of a large deep-seated fault zone with transverse faults. Dry exhalations of free CO_2 occur also in this area. The main element of the deep-seated dislocation zone is the Pstrążna-Gorzanów Fault, running slightly to the north of Duszniki-Zdrój and passing in Czechia into the Hronov-Pořiči dislocation zone (Oberc 1972; Kiełczawa *et al.* 2018). Stable oxygen and hydrogen isotopes indicate that the Duszniki water recharge zone may occur in the northern part of the Bystrzyckie Mts., as well as in the Orlickie Mts. (in the Bystrzyca Dusznicka river valley) The Duszniki CO_2-rich waters may also be recharged by waters flowing through the karst systems developed in marbles occurring near Duszniki-Zdrój. Dowgiałło and Fistek (2007) hypothesised that CO_2 may have its source in the thermal decomposition of carbonate rocks occurring within the mica schists. In Duszniki, thermal CO_2-rich water with a temperature of approx. 36 °C has been also found in the (unused) well of a depth of 1695 m (Dowgiałło and Fistek 2003).

The CO_2-rich waters of Długopole-Zdrój occur in the southern part of the Bystrzyckie Mts. close to transverse faults (Ciężkowski 1990). Intakes of these waters are located within an old shaft constructed in mica schists searching for alum shales and ores. The shaft is located close to the complex tectonic boundary between the Upper Cretaceous sedimentary rocks of the Upper Nysa Kłodzka Graben and the basement mica schists. The CO_2-rich water recharge zone is located on the eastern slopes of the Bystrzyckie Mountains, in the upper part of the Ponikwa stream catchment (Ciężkowski *et al.* 1996; Dowgiałło and Fistek 2007).

The CO_2-rich waters in sedimentary rocks of the Intra-Sudetic Basin can be grouped in two regions: in the NE basin margin and in the SW basin margin. CO_2-rich waters from the vicinity of Wałbrzych town belong to the first region. The springs can be observed both on the surface where these waters are exploited, mainly in the Szczawno-Zdrój, as well as at considerable depths exceeding several hundred meters below the surface, e.g., in, now abandoned, coal mines (Dowgiałło and Fistek 2007). Lower Carboniferous sedimentary rocks play a significant role in the occurrence of the Szczawno-Zdrój therapeutic waters. The springs occur in lower Carboniferous greywackes or at their contact with dark slaty mudstones (Ciężkowski 1990; Kiełczawa and Liber-Makowska 2017). Upper Carboniferous sedimentary rocks, which are cut by faults and strongly fractured, greatly influence the circulation of therapeutic waters; in this case CO_2-rich waters are usually associated with porphyry intrusions (Ciężkowski 1990). All springs in Szczawno-Zdrój are located close to the Szczawnik fault and the Struga tectonic zone, which is the main dislocation in this area (Fistek *et al.* 1975; Dowgiałło and Fistek 2007; Liber-Makowska and Kiełczawa 2021). The therapeutic waters are recharged on the neighbouring hills (Ciężkowski *et al.* 1996).

The CO_2-rich waters occurring in the vicinity of Polanica-Zdrój belong to the second region. Here the waters flow out from Upper Cretaceous sedimentary rocks, mainly from strongly fractured sandstones. Springs with CO_2 waters are linked with intersecting fault zones. The recharge area of these waters was considered to be both in the Middle Turonian sandstones of Stołowe Mts. and Bystrzyckie Mts., as well as in the fault zones at the foot of these mountain ranges (Fistek 1977; Ciężkowski *et al.* 1996). In recent years it has commonly been accepted that the acidulous waters in Polanica-Zdrój are a mixture of deep-circulation waters occurring in the metamorphic system of the Upper Nysa Kłodzka Graben and waters occurring in the Upper Cretaceous sedimentary rocks, infilling this structure (Kiełczawa *et al.* 2018).

The CO_2-rich waters from the Kudowa Trough, known from Kudowa-Zdrój and Jeleniów, are characterized by a more complex geological and hydrogeological setting (Dowgiałło and Fistek 2007; Ciężkowski *et al.* 2016). The Kudowa Trough is a WNW-ESE-oriented synclinal tectonic graben. The trough is bordered to the north by the Variscan Kudowa granite massif, and to the south by the crystalline rocks of the Orlickie Mts. and the Carboniferous Nový Hrádek granitoid intrusion (Gierwielaniec 1965). A relatively thin succession of Carboniferous, Permian and Upper Cretaceous sedimentary rocks situated on metamorphic schists and phyllites occurs in the trough. In the depression margins Rotliegend deposits dominate, in parts covered with Quaternary sediments, whereas Upper Cretaceous deposits occur in the axial part of the Kudowa Trough. All sedimentary series are cut by a number of faults allowing for the migration of CO_2 towards the surface and the formation of CO_2 waters. The recharge zone is located in the Stołowe Mountains but it is commonly considered that the main process of acidulous water formation takes place within the crystalline basement, and their final composition is influenced by sedimentary rocks (Ciężkowski 1990; Ciężkowski *et al*. 1996; Wiktorowicz 2009; Ciężkowski *et al*. 2016). The Kudowa-Zdrój therapeutic waters occur both in the Quaternary terrace deposits, in which the primary springs occur, and in Upper Cretaceous sandstones (Dowgiałło and Fistek 2007). CO_2 waters occurring in tectonically deformed Upper Cretaceous sandstones were captured in nearby Jeleniów. Their temperature of 20.5 °C allows them to be classified as thermal waters (Dowgiałło and Fistek 2003).

MATERIALS AND METHODS

This paper is based on the authors' field research and analysis of CO_2-rich (acidulous) therapeutic waters carried out in the years 2004–2010. In total, 50 analyses were carried out on water from 23 intakes located in the following localities in the Sudetes: Świeradów-Zdrój, Czerniawa-Zdrój, Szczawno-Zdrój, Polanica-Zdrój, Duszniki-Zdrój, Jeleniów, Kudowa-Zdrój and Długopole-Zdrój. The studied waters meet the criteria to be qualified as therapeutic waters according to Polish regulations. Water from Jeleniów (J-150 well), which is not used in balneotherapy, was investigated because of its similarities to therapeutic waters in Kudowa-Zdrój.

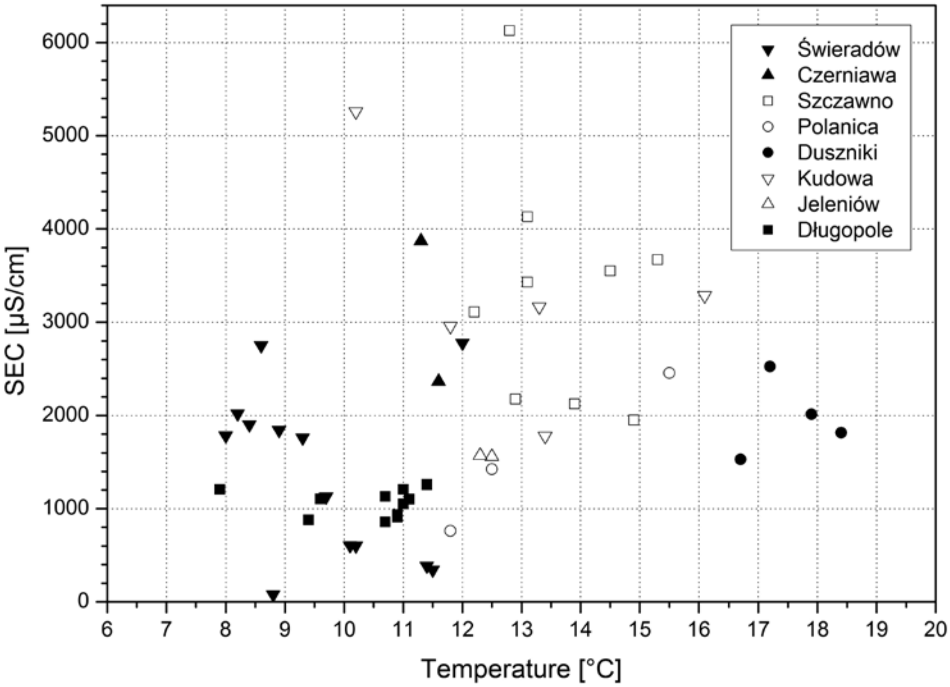
Field measurements of the physicochemical indicators covered temperature, pH, redox potential (E_H) and specific electric conductivity (SEC) measured in flow-through cell (Eijkelkamp). pH and E_H were measured with a PW9424 meter (Philips) accompanied with temperature probe PW9516/08 ATC, combined electrode CE50 and Pt-Ag/AgCl redox electrode (Corning). Specific electric conductivity (SEC) was measured by an L21 conductometer (Eijkelkamp). The field E_H measurements were corrected to a standard hydrogen electrode. Water samples were filtered in-situ by cellulose nitrate membrane filters with 0.45 μm pore size (Sartorius), preserved by ultra-pure nitric acid (Merck), and stored in LDPE containers (Nalgene). Hydrogencarbonates and chlorides were analysed volumetrically, while sulphates, fluorides, nitrates, phosphates, ammonium nitrogen and sulphides were spectrophotometrically analysed. Other components, including trace elements, were determined by ICP-MS (ACME, Canada).

Of the 79 parameters studied in the waters (4 physicochemical indicators and 75 solutes), data on 50 parameters (4 physicochemical indicators and 46 solutes), summarised in Supplementary Material 1 (Supplementary Material available only in the online version), were used for statistical analyses. Data for elements that were only detected in single samples were not used in the statistical analyses. The following elements were not detected (below the indicated detection limits) by using ICP-MS in most of the 50 water samples tested: <10 μg/L – Ti; <1 μg/L – Sc; <0.5 μg/L – Cr, Se; <0.2 μg/L – V, Pd; <0.1 μg/L – Hg, Pb; <0.05 μg/L – Th, Ru, Au, Bi, Te, Ag, Cd, Ga, Sb; <0.02 μg/L – Hf, Ta; <0.01 μg/L – Nb, Re, Rh, Pt, In, Eu, Tb, Tm, Lu, Tl. The specific electric conductivity (SEC) was not included in the set of parameters tested by the statistical analyses due to the fact that it is a collective, indicative parameter whose value depends on the content of all dissolved and dissociated solutes.

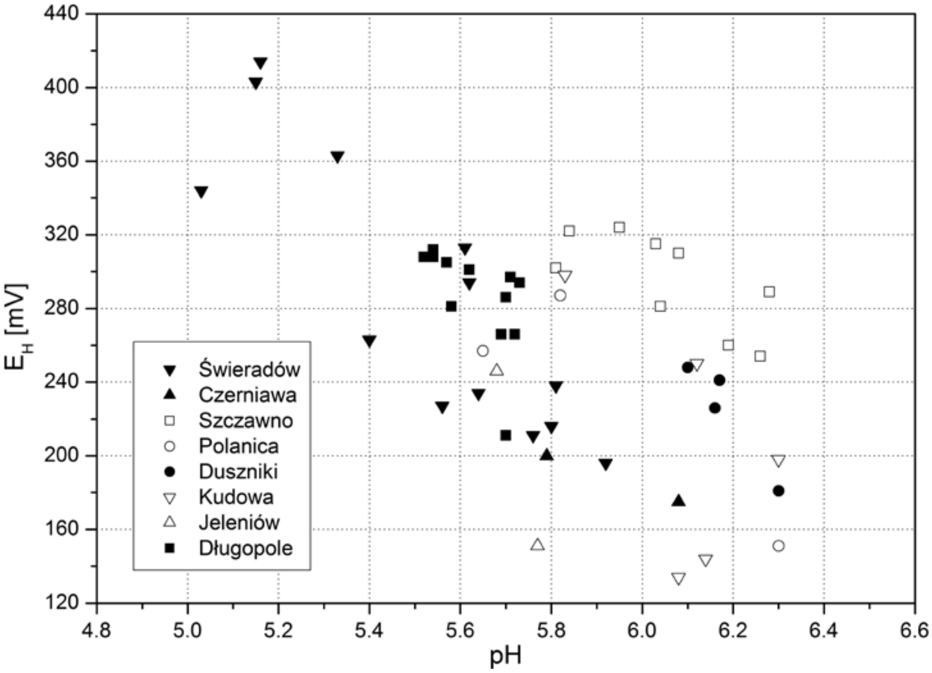
Statistical calculations were performed using STATISTICA (ver. 7.1) programme. Various statistical tests were performed on the data (hierarchical clustering, Tau Kendall, factor analysis (FA), Kruskal-Wallis). Due to the lack of normal distribution for the majority of analysed parameters (variables) and inability to normalise them, nonparametric tests and methods that do not require a normal distribution were selected. In order to initially reveal the relationships between the results of analysis according to their location and between the variables, hierarchical clustering with Ward's clustering method and the Manhattan distance as a measure of distance were used. Internal relations were also examined with nonparametric Tau Kendall and Kruskal-Wallis tests. Statistical analyses were supplemented by the FA, performed with the principal component method for variable grouping, and replacing the missing data with mean values. In FA, normalized varimax rotation was used in order to maximize variance.

GENERAL CHEMICAL CHARACTERISTICS OF THE STUDIED WATERS

The studied CO_2-rich waters are of the hydrogencarbonate type with varied cationic composition, dominated by Ca, Mg, Na, and sometimes with a high Fe content. The temperature of these waters ranges from 7.9°C to 18.4°C, pH from 5.03 to 6.30, E_H varies between +134 and +414 mV. The SEC is between 78 μS/cm and 6130 μS/cm (Supplementary Material 1), which is consistent with the fact that the acidulous therapeutic waters of the Sudetes usually have mineralisation (total dissolved solids) up to 4 g/L (Dowgiałło *et al*. 1973). In most studied waters SEC is between 800 and 4000 μS/cm (Text-fig. 2). The carbon dioxide in sudetic mineral waters was proposed to be of deep lithospheric origin, mainly associated with the final phases of Tertiary magmatic



Text-fig. 2. Specific electric conductivity (SEC) versus temperature in studied waters.



Text-fig. 3. Redox potential (E_H) versus pH in studied waters.

processes, and only locally, if at all, associated with the thermal decomposition of carbonate rocks or under the influence of organic carbon (Pačes 1972; Dowgiałło 1978). The Maria Skłodowska-Curie therapeutic water from Świeradów, which is the only one not enriched in CO_2, has the lowest SEC. The "classic" pattern of an increase in the value of E_H with a decline in pH is noted (Text-fig. 3).

GEOCHEMICAL PATTERNS. RESULTS AND DISCUSSION

The investigated waters occur in the two types of rocks, crystalline rocks (mostly metamorphic – gneisses and mica schists) and sedimentary rocks (usually conglomerates, sandstones, shales, marls). This is reflected in the picture emerging from the cluster analysis. Two main groups of case clusters were defined: (1) waters from the sedimentary aquifers of Szczawno (SZ) and waters of (mainly) Kudowa (KU), and (2) waters from metamorphic rocks (Świeradów (SW), Czerniawa (CZ), Długopole (DL)), and, indicating their proximity to them, waters of the Polanica (PO)-Duszniki (DU)-Jeleniów (JE)-Kudowa (KU) area (Text-fig. 4A).

The SW and CZ waters, although occurring in similar metamorphic rocks, are chemically different, probably due to differences in the depth of the circulation zones and the depth of the wells. An internally differentiated pattern also occurs in the waters of the Polanica-Duszniki-Jeleniów-Kudowa (PDJK) group. In this case, the diversity is most likely due to the highly varied lithology in the groundwater recharge (alimentation) and transition zones.

The Polanica and Kudowa water recharge zones (on the southern slopes of the Stołowe Mountains) are built of Cretaceous sedimentary rocks on the surface. In the Duszniki groundwater recharge zones (located in northern parts of Bystrzyckie and Orlickie mountains), metamorphic and sedimentary rocks occur. In the case of Kudowa and Jeleniów, the situation is further complicated due to the presence of various crystalline rocks. The basement and surroundings of Kudowa Trough (KT) are built of Early Paleozoic metamorphic rocks (mainly of schists, phyllites, and amphibolites of Stronie and Nové Město formations) and Carboniferous granitoids (Kudowa-Olešnice granitoids from E, Nový Hrádek granitoids from SW) (Gierwielaniec 1965; Żelaźniewicz 1977; Bachliński 2002). The influence of various crystalline rocks would explain the similarity of some of PDJK waters to the SW and CZ waters from metamorphic rocks (Text-fig. 4A).

The clustering of variables organises them into the four core clusters (Text-fig. 4B) that are internally bi- or tri-partite. The cluster of REEs, which is the most distanced from the clusters grouping the other variables, is clearly divided into the light and heavy REEs. The other three core clusters show linkage distances at a similar level. The first of them cluster groups mostly alkali metals and other elements sourced from silicate minerals (Si, Ge). The next cluster is very diverse, including numerous transition and/or redox-sensitive elements. The last cluster groups mostly anions (HCO_3, SO_4, Cl, Br) and important physicochemical parameters (pH, temperature).

Kendall's Tau coefficients (Supplementary Material 2) expose the most positive and negative rank correlations. The strongest (>0.5) positive correlations comprise mainly: (a) REEs, (b) alkali metals (Li, Na, K, Rb, Cs), (c) pH with Na, K and Sr, (d) Ge with Li, K, Rb and Cs, (e) B with Li, Na and Sr, (f) Si with Be. Strong negative relationships (<-0.5) are much fewer and include: (a) Al versus SO_4 and temperature, and (b) Ge versus E_H.

In the FA, based on the scree plot criterion, the first five factors are selected, which together explain 68.4% of the total variability (Table 2). These factors together, at factor loads $\geq |0.5|$, comprise most of the variables considered in the FA (41 of the 49 variables).

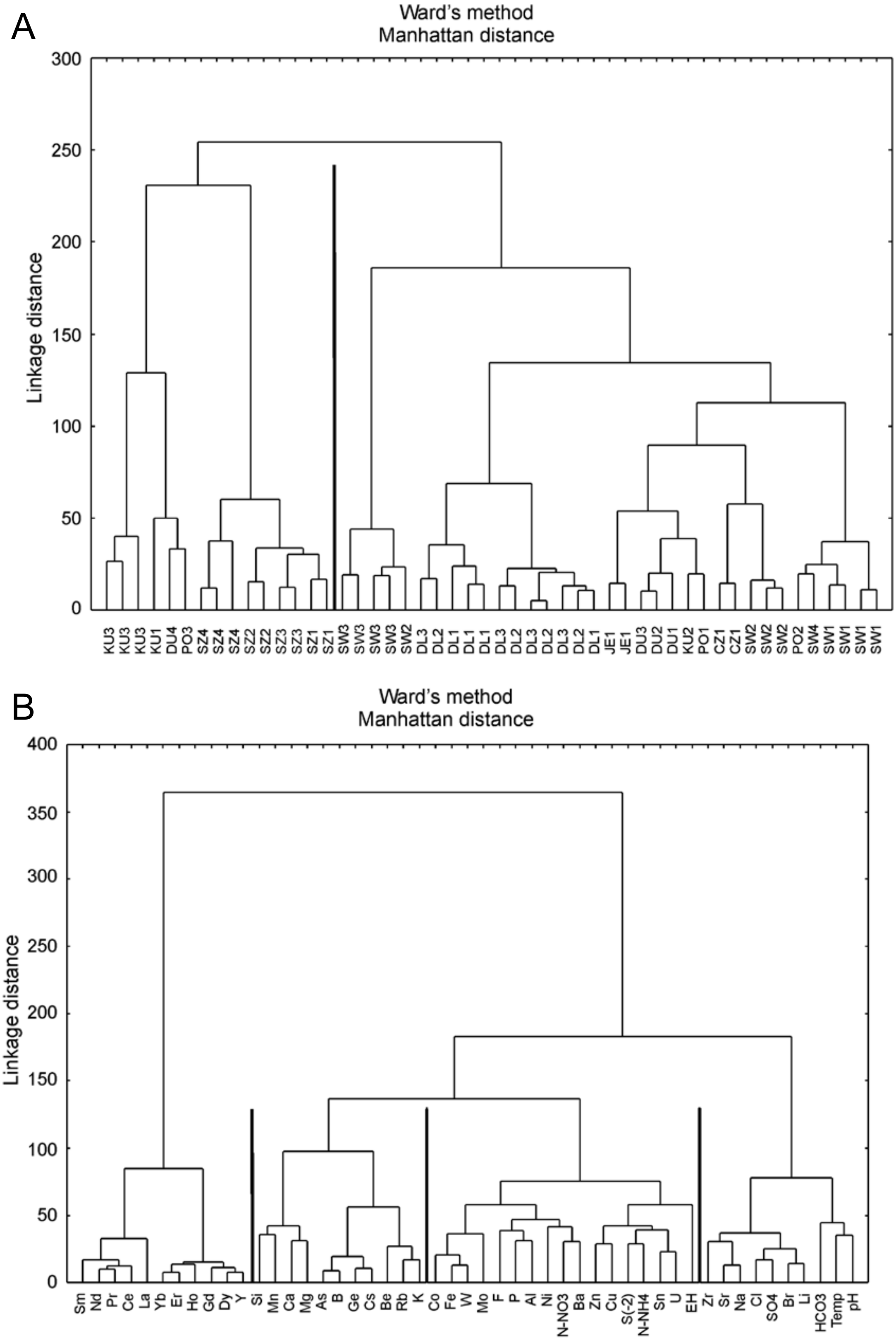
The REEs alone form one of the two strongest factors. The factor 2 mainly consists of alkali metals (Li, K, Rb, Cs, Be), metalloids (B, Si, Ge, As) and non-metal (P). Alkali metals with B and P are often associated with minerals such as apatite, tourmaline, biotite, lepidolite. Germanium shows various affinities, such as for silicon in silicate minerals, as well as a strong affinity for sulphur which is manifested by Ge occurrence e.g., together with Zn, Cu, Ag, As in sulphide minerals.

The variables included in the factor 3 (Fe, Mg, Mn, Zn, Si, Al) indicate decomposition of ferromagnesian silicate minerals. In this context, the strong W and Co factor loads are of interest. Both elements, W and Co, are very poor water migrants. Aqueous migration of cobalt is limited by co-precipitation and adsorption on Mn and Fe oxides/hydroxides, as well as by the low solubility of Co carbonate. Tungsten is very easily immobilised in secondary solid phases formed in the weathering zone. There is no evidence that the same process controls the concentrations of both elements in the studied waters. Lack of data on the content of the two elements under consideration in the aquifer rocks does not warrant further consideration. Factor 4 clearly illustrates the effect of a carbonate equilibria (pH, HCO_3, Ca), including the role of temperature. Factor 5 combines anions (Br^-, SO_4^{2-}, Cl^-) and some alkali metals (Li, Na, Sr). The presence of Zr and Cu in this factor is puzzling and difficult to explain.

The Kruskal-Wallis nonparametric test was applied to identify variables whose distribution of values differ significantly between the grouping variables, which were taken to be lithology (metamorphic, sedimentary), locality (i.e. all the waters in

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Eigenvalue	10.630	10.263	6.454	3.708	2.478
% of explained variation	21.694	20.946	13.172	7.568	5.058
Cumulated eigenvalue	10.630	20.893	27.347	31.056	33.534
Cumulated % of explained variation	21.694	42.639	55.811	63.379	68.437
pH	0.061	0.287	-0.050	**0.642**	-0.486
Temp	0.050	0.012	0.315	**0.744**	-0.167
E_H	-0.217	**-0.581**	0.283	-0.463	0.020
Li	-0.153	**0.573**	0.090	0.022	**-0.761**
Na	-0.175	0.180	0.152	0.275	**-0.880**
K	0.270	**0.632**	-0.014	0.491	-0.104
Rb	0.130	**0.813**	-0.242	0.280	0.014
Cs	0.004	**0.941**	0.056	-0.026	-0.227
Be	0.181	**0.817**	-0.242	0.202	0.038
Mg	0.116	0.282	**-0.532**	0.350	-0.362
Ca	0.458	0.422	-0.110	**0.589**	-0.125
Sr	-0.158	0.043	0.138	0.354	**-0.807**
Ba	0.016	-0.139	0.009	-0.204	0.285
Y	**0.869**	0.363	0.121	0.105	0.091
La	**0.682**	-0.396	-0.186	0.068	-0.244
Ce	**0.847**	-0.268	-0.007	-0.037	0.137
Pr	**0.868**	-0.253	0.045	-0.105	0.114
Nd	**0.923**	-0.153	0.076	-0.014	0.173
Sm	**0.915**	-0.055	0.101	-0.014	0.190
Gd	**0.904**	0.227	0.161	0.042	0.157
Dy	**0.894**	0.292	0.161	0.133	0.156
Ho	**0.909**	0.166	0.116	0.070	0.134
Er	**0.879**	0.315	0.165	0.147	0.141
Yb	**0.860**	0.254	0.166	0.206	0.214
U	-0.220	-0.090	0.106	0.215	-0.121
Zr	-0.093	-0.196	0.017	0.273	**-0.655**
Mo	-0.274	0.040	-0.479	0.086	0.140
W	-0.184	0.025	**-0.845**	-0.089	0.086
Mn	0.430	0.140	**-0.691**	0.259	0.177
Fe	-0.206	0.080	**-0.816**	-0.065	0.165
Co	-0.225	-0.047	**-0.808**	-0.050	0.135
Ni	0.164	0.067	-0.319	0.256	0.186
Cu	-0.101	-0.377	-0.021	0.077	**-0.664**
Zn	-0.029	-0.227	**-0.645**	-0.105	-0.310
B	-0.039	**0.796**	0.202	-0.004	-0.480
Al	-0.087	0.018	**-0.556**	-0.361	0.300
Si	0.127	**0.550**	**-0.614**	-0.156	0.021
Ge	-0.097	**0.878**	-0.206	-0.052	-0.262
Sn	0.363	-0.194	-0.080	-0.280	-0.113
P	-0.041	**0.511**	-0.153	-0.468	0.034
As	0.004	**0.886**	0.164	-0.014	-0.293
Br	-0.188	0.340	0.185	-0.004	**-0.838**
HCO_3	0.019	0.262	0.002	**0.636**	-0.158
SO_4	-0.207	0.326	0.234	0.140	**-0.818**
Cl	-0.090	0.248	0.129	0.034	**-0.778**
F	-0.324	0.305	-0.477	0.011	0.207
$N\text{-}NO_3$	-0.097	0.318	0.052	**-0.511**	-0.075
$N\text{-}NH_4$	-0.072	0.002	-0.038	0.339	-0.148
S(-2)	-0.061	0.039	0.011	-0.132	-0.223

Table 2. Factor loads of physicochemical data matrix and eigenvalues for the studied waters. Significant values (≥ |0.5|) are in bold.



Text-fig. 4. Hierarchical clustering dendrograms of the studied waters for cases (water samples) (A) and physicochemical variables (B). Symbols of water intakes (e.g., KU3) as given in Table 1.

a given locality; 8 localities) and water intake (totally 23 intakes).

Data diversity due to the effect of lithology is something to be expected. The Kruskal-Wallis test reveals a wide set of variables (30 variables), which are affected (differentiated) by the lithology (Table 3). Most of them (23 of 30 variables) are also found as variables differentiated by the location, which is related to the expected differences in lithology between the individual recharge and transition zones. However, REEs that do not differentiate lithology clearly appear among the variables that differentiate locations. This is probably due to the fact that in the relatively large and internally differentiated sets of analyses of waters from metamorphic and sedimentary rocks, differences in REE contents did not show up strongly enough. At the same time, REEs do not differentiate the individual water intakes in the location. This can be understood as the absence of any significant influence of the construction (material, screened interval, depth) of a particular intake on the composition of the water. This suggestion would be supported by the fact that as many as 30 variables do not differentiate intakes. It should be remembered that the statistical test results are influenced by the smaller size of the data for an individual intake.

The presence of a group of variables (Li, Na, K, Ca, Sr, Ba, Al, Si, Ge) can be considered as resulting from the hydrolytic decay of aluminosilicate minerals whose inventory depends on the mineralogical characteristics of the aquifer rocks. Six of these elements (Li, Na, K, Sr, Al, Ge) are effective as indicative variables for each of the grouping variables (lithology, location, intake).

The Kruskal-Wallis test might also help to reveal the strongest differences in the distribution of variables occurring between subpopulations distinguished according to the each grouping variable. For example, it can be shown how many variables differentiate the composition of waters from individual locations (Table 4).

The strongest differences (given the number of variables) are revealed when comparing intakes from sedimentary and metamorphic rocks. For example, there are as many as 20 statistically significant variables differentiating the waters from Szczawno (SZ) and Długopole (DL) and 16 for the Szczawno-Świeradów (SZ-SW) pair (Table 4). Strong variations (11 variables) are also evident for the Kudowa-

Grouping variable	Presence of statistically significant differences	Variables [number of variables]
Lithology	differences	pH, temperature, HCO_3, SO_4, Cl, Li, Na, K, Ca, Sr, Ba, Ce, Pr, Sm, U, Zr, W, Mn, Fe, Co, Cu, B, Al, Si, Ge, Sn, P, As, Br, NO_3 [30]
	no differences	E_H, Rb, Cs, Be, Mg, Y, La, Nd, Gd, Dy, Ho, Er, Yb, Mo, Ni, Zn, F, S(-2), NH_4 [19]
Locality	differences	pH, temperature, SO_4, Cl, Li, Na, K, Rb, Cs, Be, Ca, Sr, Ba, Y, Nd, Sm, Gd, Dy, Ho, Er, Yb, U, Zr, Mn, Fe, Co, Cu, B, Al, Si, Ge, P, As, Br, F [35]
	no differences	E_H, HCO_3, Mg, La, Ce, Pr, Mo, W, Ni, Zn, Sn [11]
Water intake	differences	Li, Na, K, Rb, Cs, Mg, Sr, Co, Al, Ge, F [11]
	no differences	pH, E_H, temperature, HCO_3, SO_4, Cl, Be, Ca, Ba, Y, La, Ce. Pr, Nd, Sm, Er, U, Zr, Mo, W, Fe, Ni, Cu, Zn, B, Si, Sn, P, As, Br [30]
Summary	differences in the case of all grouping variables	Li, Na, K, Sr, Co, Al, Ge [7]
	no differences in the case of all grouping variables	E_H, La, Mo, Ni, Zn [5]

Table 3. Physicochemical parameters (variables) showing statistically significant differences between particular grouping variables (after Kruskal-Wallis test).

	CZ (2)*	DL (12)	SW (13)	DU (4)	JE (2)	KU (5)	PO (3)	SZ (9)
CZ								
DL	0							
SW	2	9						
DU	0	5	4					
JE	0	1	1	0				
KU	0	11	11	1	0			
PO	1	0	0	0	0	1		
SZ	1	20	16	5	0	8	1	

Table 4. Number of variables that differ significantly between localities (after Kruskal-Wallis test). * – locality symbol as in Table 1. Number of analyses given in brackets.

Długopole (KU-DL) and Kudowa-Świeradów (KU-SW) pairs. This indicates significant differences in the geochemical distribution of a number of variables (physicochemical parameters and solutes) depending on the lithology. This effect is also probably due to the fact that the locations listed have the highest abundance of water analyses.

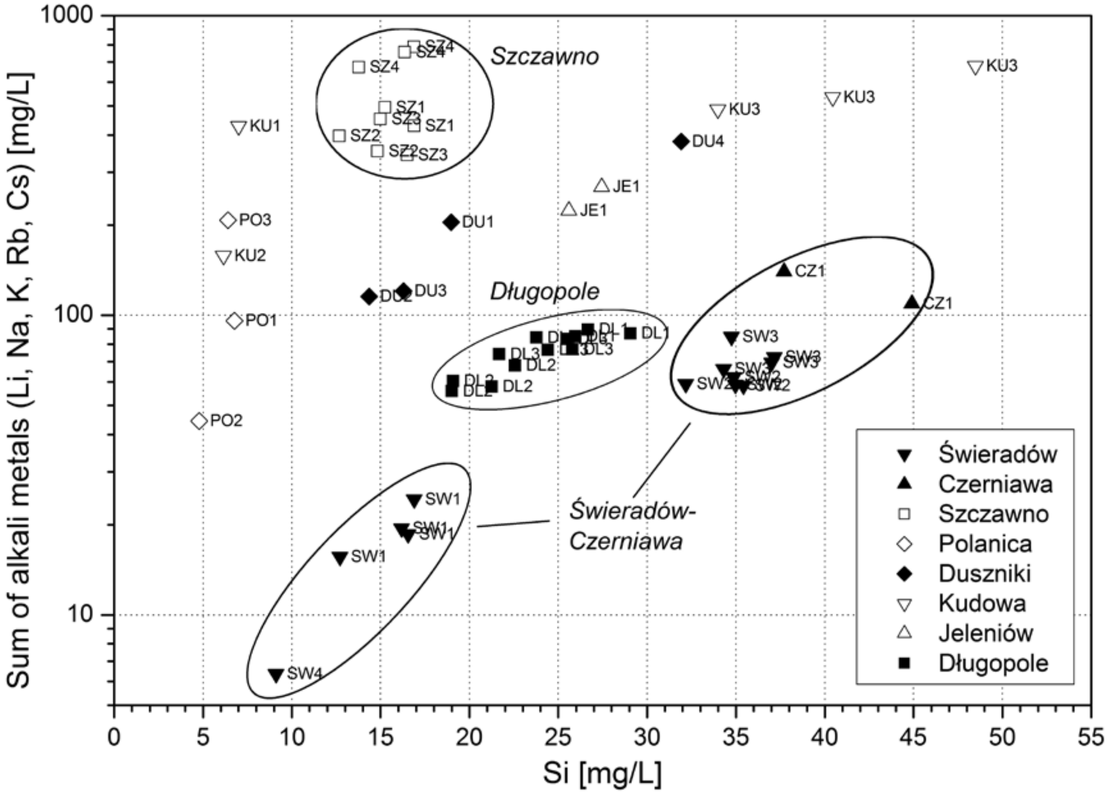
The small total number of chemical analyses from individual locations does not allow us to draw firm conclusions, but it is also evident that there are no significant differences for water pairs with similar hydrogeological conditions: PO-DU, PO-JE, JE-KU, JE-PO, JE-DU.

Relatively large number of differences for the SW-DL pair may be both an effect of the fact that they are the most numerous sets analysed and that within a given location (between intakes) there are statistically significant differences in the distribution of variables.

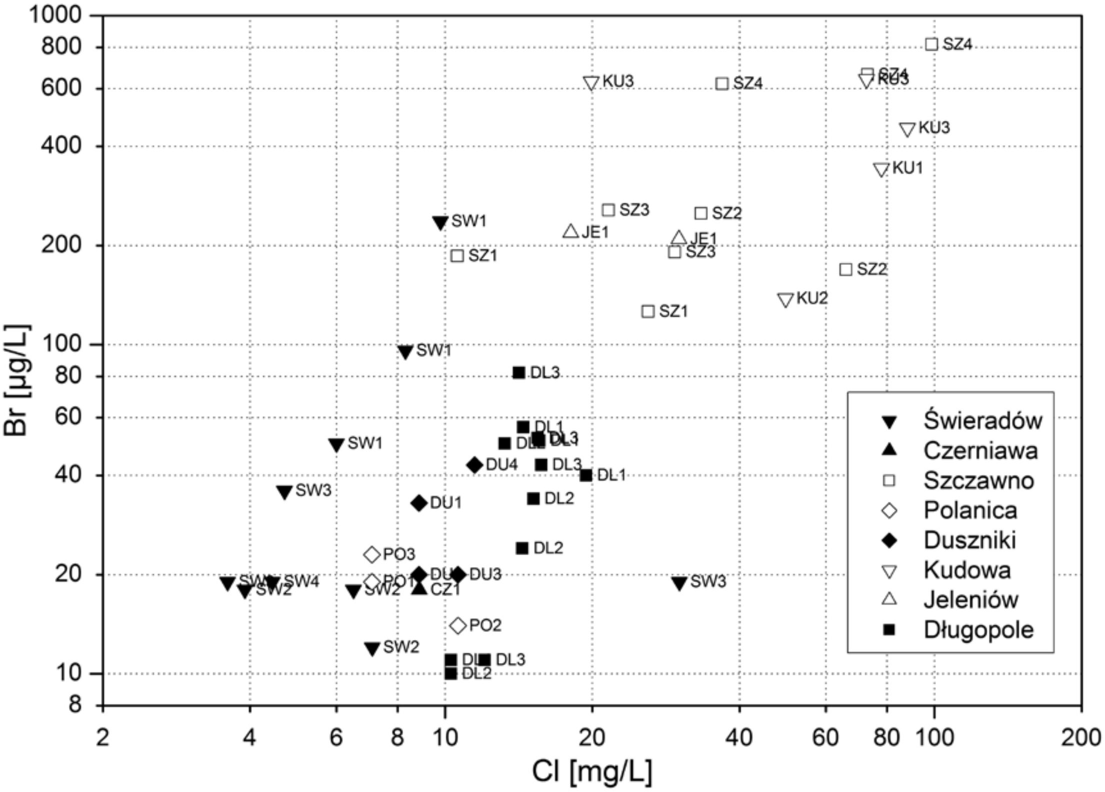
The CO_2 influx significantly increases the aggressiveness of groundwater against aquifer minerals. The hydrolytic breakdown of silicate minerals, which make up on average about 90% of the mass of the upper continental crust, is responsible, along with carbonate minerals, for supplying the largest load of dissolved substances to groundwater (e.g., Drever 1997; Appelo and Postma 2005). The effects of these factors are also seen in the studied waters.

A number of concurring suggestions regarding the relationships between (physico)chemical parameters emerged from the statistical tests. The set of elements that can be associated with the hydrolytic decomposition of silicate minerals stands out clearly. Within it, two subgroups can be distinguished: (1) alkali and alkaline earth metals (especially Li, K, Rb, Cs, and also Be), and (2) mostly transition metals (Fe, Mn, Zn, Co, W, Mg). Naturally, there are also Si, Al and Ge in the aforementioned set. The first subgroup may be primarily associated with the hydrolytic decomposition of primary silicates from the tectosilicates and phyllosilicates subclasses, like feldspars and muscovite. The sources of the second subgroup elements are likely ferromagnesian minerals, such as biotites, pyroxenes, amphiboles.

In the statistical tests performed, the alkali metals (Li, Na, K, Rb, Cs) were systematically revealed as one of the most important groups of solutes. Their common presence in water is mainly due to the hydrolytic decomposition of silicate minerals, usually silicates with a higher degree of polymerisation of silicon tetrahedra, such as tectosilicates and phyllosilicates.



Text-fig. 5. Alkali metals versus silicon in the studied waters. Symbols of water intakes as given in Table 1.



Text-fig. 6. Bromides versus chlorides in the studied waters. Symbols of water intakes as given in Table 1.

The relation between alkali metals and dissolved silicon is proving to be a good tool for the analysis of variation in water composition and the analysis of genetic relationships between studied waters (Text-fig. 5).

The SZ and DL waters show little diversity in composition and are clearly different from the other waters. The SW and CZ waters confirm their high diversity of composition resulting mainly from the influence of circulation conditions and the variation of CO_2 inflow to the water. The composition of waters of the PDJK group is even more varied. Here, the influence of lithological and circulation conditions varies greatly both between locations and between individual intakes.

The next group of elements that appear is the REEs. Studied waters from metamorphic rocks (SW, CZ, DL) contain on average higher concentrations of most REEs than other waters, the only exceptions being Er, Tm and Lu (Supplementary Material 1). REEs are mainly concentrated in silicates (hornblende, epidote, allanite, potassium feldspar, mica, titanite, garnets) and phosphates (apatites, monazite) (Lipin and McKay 1989; Sarbas and Töpper 1988; Ivanov 1997), which might explain the relative enrichment of waters from metamorphic rocks. LREEs failed to be detected more frequently than HREEs in the studied waters (Supplementary Material 1) due to the lower solubility of the former.

Another group consists of parameters (pH, temperature, HCO_3, Ca) with a strong direct link to carbonate equilibria in the water-CO_2-carbonate minerals systems. The geochemistry of carbonate systems is the subject of an immensely rich literature. Some of the best summary works include, for example, White (1988), Bakalowicz (1994), Appelo and Postma (2005).

Another distinctive group of components are Cl, Br, SO_4 along with metals (Li, Na, Sr). Chlorides, bromides and sulphates can originate from various sources, like atmospheric deposition, deep relict/saline groundwater components, inclusions in primary minerals, anthropic pollutions, and, in the case of bromides and sulphates, also from the decomposition of organic matter. Anthropic pollution can be ruled out in the case of the investigated therapeutic waters. The very poor recognition of the composition of atmospheric depositions in the Sudetes, including the lack of information on bromides, does not allow this potential source to be discussed. Similarly, consideration of the possible role of salts released from inclusions of decomposing primary minerals is impossible due to the lack of adequate research and data. In the Sudetes, the presence of groundwater enriched in chlorides, bromides or sulphates was rarely found (e.g., HCO_3-Cl-Na-Ca-Mg acidulous water with TDS of 4.7 g/L in Długopole Dolne, HCO_3-SO_4-Na acidulous water with TDS of 19 g/L in Nowa Ruda-Zdrojowisko, acidulous HCO_3-SO_4-Na-Ca (Fe) waters of TDS 4.1–6.7 g/L in Rochowice Stare, SO_4-Ca-Na mineral water of 1.7 g/L TDS in Sokołowsko). However, these rare waters have not usually been extensively studied. The common presence of Cl, Br, SO_4, Na and Li in this statistically recognized group can suggest that in studied waters constituents associated with deep circulation waters manifest.

In studied waters the concentration of bromides increases with increasing concentration of chlorides, indicating a likely common origin for both components (Text-fig. 6). Greater concentrations of both constituents in waters of sedimentary rocks (SZ, KU, JE) than in waters of metamorphic rocks (SW, CZ, DL) are clearly evident. This may confirm the possible association of components of this group of elements with migration of matter from deeper parts of the continental crust.

CONCLUSIONS

A study of the composition of CO_2-rich therapeutic waters in the Sudetes was carried out, including a broad set of trace elements not previously studied in these waters. The scope of water analyses performed widely exceeds the list of parameters required by legal regulations. Analysis of the data set leads to a number of conclusions.

The influence of the lithology of aquifer rocks is clearly visible in the composition of the studied waters. Among the studied CO_2-rich (acidulous) waters, three groups of waters stand out: (1) waters associated with metamorphic rocks (waters of Świeradów, Czerniawa and Długopole), (2) waters associated with sedimentary rocks (Szczawno), and (3) the internally very diversified group of waters from the Kudowa-Polanica region (Kudowa, Jeleniów, Duszniki, Polanica). The diversity of waters of the latter group results from very high lithological variability in recharge and transition zones of individual waters and the probable influence of deep-originated components migrating through deep-seated dislocations related to the seismically active the Hronov-Poříčí Fault zone, continuing in Poland in the Pstrążna-Gorzanów Fault, with accompanying faults. This system of dislocations is an inflow pathway for lithospheric CO_2 and may also facilitate the migration of other components of deep-seated origin. The mineral waters in the Kudowa-Polanica area require further detailed geochemical studies.

The most important processes and reactions responsible for forming the composition of waters, including trace elements, can be identified.

Hydrolysis of silicate minerals provides a very wide range of elements. Among these, the enrichment of waters in alkali metals – Li, Na, K, Rb, Sc (derived mainly from tectosilicates and phyllosilicates) and (mostly) transition elements – Fe, Mn, Zn, Co, W, Mg (derived from ferromagnesian minerals, such as biotites, pyroxenes, amphiboles) is most evident.

Another group are chemical reactions resulting from carbonate equilibria. These directly affect the pH of the waters and the concentrations of hydrogencarbonate and calcium, and indirectly affect the concentrations of numerous solutes as they determine the aggressiveness of the water against the minerals of aquifer rocks.

The test results suggest a common origin of chlorides, sulphates and bromides together with Li, Na, Sr. Such an assemblage may indicate a relict, saline component of deep-circulating waters. In this context, it is evident that there is a lack of more complete geochemical information on rare acidulous waters in the Sudetes, which presumably contain waters and components of deeper circulation (like the enriched in Cl, SO_4 and/or Br waters of Długopole Dolne, Nowa Ruda-Zdrojowisko and Rochowice Stare).

Research into trace elements in therapeutic waters should be carried out more extensively. Alkali elements (Li, Na, K, Rb, Sc) can be used for studies to clarify the origin of water composition in individual intakes, and perhaps to assess the extent of mixing of water components.

The specificity and individuality of the REE group is very clearly revealed. However, the use of REE for detailed hydrogeochemical interpretations requires REE analyses in waters with much lower detection limits to be able to quantitatively characterise REE in all waters.

Investigations of trace elements provide the opportunity to carry out more detailed interpretations of the therapeutic waters in individual deposits, also in terms of water protection.

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Supplementary Material 1. Physicochemical and chemical parameters of studied waters.

				pH	Temperature	SEC	E_H	Li	Na	K	Rb	Cs	Be	Mg	Ca
Location	Water intake	Symbol of water intake	Year of sampling		*°C*	*µS/cm*	*mV*	*µg/L*	*mg/L*	*mg/L*	*µg/L*	*µg/L*	*µg/L*	*mg/L*	*mg/L*
Świeradów	Górne	SW1	2004	5.03	11.5	344	344	45.6	12.473	6.018	42.64	5.11	1.14	14.263	34.272
Świeradów	Górne	SW1	2010-1*	5.33	10.1	605	363	74.0	15.78	8.36	44.44	5.26	0.92	17.46	38.11
Świeradów	Górne	SW1	2010-2	5.16	10.2	603	414	50.3	13.26	6.1	41.67	4.81	0.44	15.79	38.57
Świeradów	Górne	SW1	2010-3	5.15	11.4	386	403	46.9	11.12	4.41	33.18	3.74	0.4	12.29	35.8
Świeradów	1A	SW2	2004	5.40	9.7	1129	263	228.4	40.27	17.576	156.22	16.71	4.79	74.602	115.158
Świeradów	1A	SW2	2010-1	5.76	8.0	1785	211	265.8	41.53	16.74	161.46	18.36	3.44	63.06	97.93
Świeradów	1A	SW2	2010-2	5.61	8.9	1842	313	207.6	43.74	17.93	177.53	16.92	3.56	67.79	98.02
Świeradów	1A	SW2	2010-3	5.62	8.4	1902	294	264.8	42.44	16.04	163.68	18.29	2.54	65.23	99.84
Świeradów	2P	SW3	2004	5.56	9.3	1760	227	214.7	60.03	24.472	137.5	13.48	2.3	84.807	128.134
Świeradów	2P	SW3	2010-1	5.92	8.2	2020	196	311.6	48.6	20.31	184.16	20.7	2.92	75,000	122.01
Świeradów	2P	SW3	2010-2	5.81	12.0	2780	238	237.9	50.13	21.93	199.61	18.84	2.43	78.71	118.42
Świeradów	2P	SW3	2010-3	5.80	8.6	2750	216	310.0	47.23	18.3	173.22	20.2	2.02	74.4	121.1
Świeradów	MCS	SW4	2004	5.64	8.8	78	234	1.2	5.323	1.027	3.02	0.23	0.08	2.492	6.458
Czerniawa	4 (Jan II)	CZ1	2004	5.79	11.6	2365	200	276.0	125.389	14.358	111.41	11.56	6,00	158.106	347.077
Czerniawa	4 (Jan II)	CZ1	2010	6.08	11.3	3870	175	326.6	93.13	15.71	123.44	13.71	6.19	128.44	295.27
Szczawno	Marta	SZ1	2004	5.81	12.9	2175	302	634.7	477.842	15.059	34.00	1.43	0.37	69.912	122.697
Szczawno	Marta	SZ1	2009	6.04	13.1	4130	281	751.6	412.781	15.236	36.21	1.69	0.14	66.993	122.436
Szczawno	Młynarz	SZ2	2004	5.95	14.9	1952	324	486.3	372.014	23.752	33.98	1.11	0.28	73.654	111.363
Szczawno	Młynarz	SZ2	2009	6.28	15.3	3670	289	589.4	332.112	19.718	36.18	1.31	0.13	70.578	110.908
Szczawno	Dąbrówka	SZ3	2004	5.84	13.9	2125	322	597.1	439.889	11.286	19.31	0.42	0.14	57.664	120.009
Szczawno	Dąbrówka	SZ3	2009	6.08	14.5	3550	310	604.9	330.814	10.849	18.63	0.42	0.13	52.704	116.802
Szczawno	Mieszko	SZ4	2004	6.03	13.1	3430	315	1398.2	761.531	24.057	61.92	2.46	<0.05	92.213	143.792
Szczawno	Mieszko	SZ4	2007	6.19	12.2	3110	260	1302.9	652.504	19.167	57.39	2.68	0.23	67.526	102.587
Szczawno	Mieszko	SZ4	2009	6.26	12.8	6130	254	1427.6	730.812	21.356	53.89	2.5	0.13	71.217	118.181
Polanica	Wielka Pieniawa	PO1	2004	5.65	12.5	1425	257	92.0	60.938	34.557	146.46	18.66	0.66	23.892	205.738
Polanica	Józef 2	PO2	2004	5.82	11.8	762	287	49.1	25.043	19.13	91.73	13.17	0.14	13.246	109.08
Polanica	P-300	PO3	2004	6.30	15.5	2455	151	254.7	147.441	59.826	166.81	15.87	1.33	61.226	502.432
Duszniki	Jan Kazimierz	DU1	2004	6.10	16.7	1529	248	117.7	129.479	74.464	286.97	27.74	4.16	42.603	170.556
Duszniki	Pieniawa Chopina	DU2	2004	6.16	17.9	2015	226	73.6	72.456	42.864	172.77	16.33	3.04	29.517	111.772
Duszniki	B-39	DU3	2004	6.17	18.4	1816	241	78.1	73.296	46.987	196.02	19.9	3.39	33.548	122.623
Duszniki	B-4	DU4	2004	6.30	17.2	2525	181	192.1	240.973	138.806	470.46	47.41	6.61	91.018	323.794
Kudowa	Śniadecki (2)	KU1	2004	6.14	16.1	3285	144	843.4	377.167	49.659	173.76	52.92	2.34	42.734	272.163
Kudowa	Marchlewski (3)	KU2	2004	5.83	13.4	1780	298	347.0	138.804	18.534	79.79	27.5	0.98	20.314	110.687
Kudowa	K-200	KU3	2004	6.3	13.3	3165	198	1807.1	591.483	86.327	412.00	175.13	11.28	112.529	298.902
Kudowa	K-200	KU3	2007	6.08	11.8	2960	134	2237.2	460.474	70.251	393.62	181.91	6.68	77.193	222.172
Kudowa	K-200	KU3	2010	6.12	10.2	5260	250	1608.7	425.92	58.43	303.77	139.18	5.52	73.59	215.4
Jeleniów	J-150	JE1	2004	5.68	12.5	1558	246	633.2	228.846	38.278	151.79	56.7	2.87	45.904	142.778
Jeleniów	J-150	JE1	2007	5.77	12.3	1571	151	1035.2	186.932	35.203	158.89	67.81	2.96	41.811	128.527
Długopole	Renata	DL1	2004	5.57	11.4	1261	305	173.8	74.807	9.262	41.4	1.49	1.33	57.972	130.58
Długopole	Renata	DL1	2007	5.70	11.4	1254	211	288.2	74.844	9.894	55.47	2.09	1.58	57.126	145.79
Długopole	Renata	DL1	2008	5.69	7.9	1207	266	254.3	75.009	14.303	51.82	2.7	1.48	57.854	144.09
Długopole	Renata	DL1	2009	5.72	11.0	1206	266	207.4	74.018	12.683	51.1	2.3	1.41	57.193	149.039
Długopole	Emilia	DL2	2004	5.54	10.9	937	312	128.9	59.72	8.013	33.83	1.13	1.26	49.129	122.563
Długopole	Emilia	DL2	2007	5.58	10.9	908	281	154.9	52.522	7.632	32.56	1.26	1.38	42.759	108.211
Długopole	Emilia	DL2	2008	5.62	9.4	880	301	141.0	46.612	9.081	31.8	1.3	1.07	37.073	97.826
Długopole	Emilia	DL2	2009	5.54	10.7	857	308	139.1	49.043	8.621	33.13	1.3	1.04	38.996	108.956
Długopole	Kazimierz	DL3	2004	5.52	11.0	1051	308	152.3	67.664	8.793	38.24	1.36	1.57	54.431	127.407
Długopole	Kazimierz	DL3	2007	5.70	11.1	1101	286	188.8	65.112	8.761	38.84	1.68	1.51	51.391	127.978
Długopole	Kazimierz	DL3	2008	5.71	9.6	1106	297	212.3	70.124	12.964	46.6	1.97	1.16	54.246	138.044
Długopole	Kazimierz	DL3	2009	5.73	10.7	1132	294	188.2	65.901	10.907	44.34	1.9	1.27	53.427	139.412

* – Number of the sampling session of the year. nd – not determined

Sr	Ba	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
µg/L	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*
72.31	20.56	<1	1.1	0.23	0.61	0.08	0.41	0.1	<0.01	0.13	0.01	0.13	0.03	0.12	0.01	0.12
77.27	51.63	<1	1.03	0.22	0.61	0.09	0.46	0.12	0.02	0.17	0.02	0.12	0.02	0.09	0.01	0.09
86.76	733.96	<1	0.92	0.2	0.44	0.06	0.24	0.07	<0.01	0.09	0.01	0.09	0.02	0.07	<0.01	0.07
70.03	659.96	7	0.46	0.07	0.1	0.02	0.07	0.03	<0.01	0.04	<0.01	0.03	0.01	0.03	<0.01	0.04
189.06	57.31	<1	1.97	0.16	0.33	0.06	0.34	0.09	0.01	0.2	0.02	0.21	0.04	0.13	0.01	0.12
203.52	85.03	<1	2.04	0.14	0.33	0.06	0.33	0.1	<0.01	0.18	0.03	0.17	0.04	0.11	0.01	0.1
203.07	55.58	<1	1.97	0.12	0.3	0.04	0.22	0.07	<0.01	0.14	0.02	0.16	0.03	0.11	0.01	0.09
197.36	450.57	17	0.02	0.01	0.01	<0.01	0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
181.41	54.18	<1	0.21	0.06	0.14	<0.01	0.04	<0.02	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
271.13	107.34	1	0.51	0.13	0.23	0.02	0.11	0.03	<0.01	0.04	<0.01	0.03	<0.01	0.02	<0.01	0.01
265.48	654.29	<1	0.38	0.41	0.21	0.02	0.08	<0.02	<0.01	0.01	<0.01	0.02	<0.01	0.01	<0.01	0.01
237.07	48.19	19	0.01	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
23.94	8.17	<1	0.53	0.14	0.18	0.03	0.2	0.06	<0.01	0.1	<0.01	0.08	0.01	0.06	<0.01	0.06
1000.18	183.52	1	1.93	0.28	0.4	0.04	0.28	0.07	0.02	0.12	0.01	0.18	0.04	0.16	0.02	0.16
1151.62	234.89	<1	2.23	0.26	0.42	0.04	0.26	0.07	<0.01	0.12	0.02	0.17	0.04	0.12	0.02	0.13
2122.71	36.98	1	0.92	0.06	0.11	0.02	0.13	0.04	0.01	0.11	0.01	0.1	0.02	0.07	<0.01	0.04
2482.18	37.29	1	0.16	0.13	0.22	0.03	0.12	0.02	<0.01	0.02	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
2022.17	26.93	1	0.52	0.31	0.42	0.08	0.38	0.08	<0.01	0.09	<0.01	0.06	0.01	0.03	<0.01	0.02
2273.46	29.94	1	0.11	0.24	0.87	0.09	0.37	0.1	<0.01	0.04	0.01	0.02	<0.01	<0.01	<0.01	0.01
1328.19	54.41	1	0.63	0.06	0.09	0.01	0.09	<0.02	<0.01	0.06	<0.01	0.06	0.01	0.03	<0.01	0.03
1371.5	64.08	2	0.12	0.01	<0.01	<0.01	0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2362.73	51.03	<1	0.51	1.11	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2219.01	41.49	4	0.52	0.02	0.09	0.01	0.08	0.02	<0.01	0.06	<0.01	0.07	0.01	0.03	<0.01	0.01
2122.54	40.16	2	0.09	0.02	0.04	<0.01	0.01	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01
434.01	64.22	<1	1.29	0.26	0.14	0.02	0.13	0.02	<0.01	0.09	0.01	0.12	0.03	0.1	0.01	0.1
240.84	864,00	<1	0.5	0.26	0.2	0.02	0.14	0.03	<0.01	0.04	<0.01	0.06	0.01	0.03	<0.01	0.04
950.28	206.28	1	4.48	0.81	0.82	0.1	0.61	0.14	0.04	0.31	0.04	0.44	0.11	0.37	0.04	0.33
423.81	52.32	<1	1.59	0.17	0.32	0.04	0.3	0.09	0.03	0.18	0.02	0.2	0.04	0.12	0.01	0.11
284.92	35.32	1	1.5	0.28	0.47	0.06	0.3	0.09	0.02	0.14	0.01	0.16	0.03	0.1	0.01	0.09
316.64	46.1	1	1.41	0.11	0.2	0.02	0.18	0.07	0.02	0.14	0.01	0.17	0.03	0.11	0.01	0.09
715.41	84.26	<1	4.52	0.52	0.87	0.13	0.78	0.26	0.09	0.49	0.07	0.52	0.11	0.32	0.04	0.29
984.8	163.47	1	4.04	0.21	0.38	0.06	0.34	0.11	0.03	0.29	0.03	0.39	0.09	0.29	0.03	0.24
495.24	29.66	1	0.84	0.07	0.11	0.01	0.09	0.02	<0.01	0.06	<0.01	0.08	0.01	0.06	<0.01	0.06
1643.61	29.19	<1	3.29	<0.01	<0.01	<0.01	0.11	<0.02	<0.01	0.24	<0.01	0.23	<0.01	0.18	<0.01	0.12
1751.89	31.88	13	3.1	0.02	0.11	0.01	0.13	0.08	0.02	0.22	0.03	0.3	0.06	0.19	0.02	0.12
1293.53	114.17	19	2.44	0.03	0.1	0.02	0.14	0.06	<0.01	0.18	0.03	0.21	0.06	0.16	0.02	0.12
665.58	50.97	<1	1.18	0.22	0.16	0.02	0.17	0.04	0.01	0.11	0.01	0.12	0.02	0.08	0.01	0.07
789.99	60.17	9	1.3	0.06	0.18	0.02	0.17	0.06	0.02	0.13	0.01	0.13	0.02	0.09	0.01	0.08
330.71	152.06	<1	2.49	0.19	0.36	0.06	0.37	0.1	0.03	0.23	0.03	0.24	0.06	0.14	0.01	0.13
430.07	242.97	11	3.13	0.23	0.47	0.07	0.46	0.14	0.11	0.36	0.04	0.37	0.08	0.23	0.03	0.19
430.84	359.92	3	3.44	0.6	0.92	0.13	0.63	0.16	0.03	0.36	0.06	0.37	0.08	0.22	0.02	0.2
406.58	228.69	4	3.98	0.72	1.22	0.2	1.02	0.27	0.04	0.44	0.07	0.42	0.09	0.27	0.03	0.19
316.39	139.54	<1	2.16	0.19	0.32	0.04	0.29	0.1	0.03	0.2	0.02	0.21	0.04	0.12	0.01	0.1
272.59	211.96	6	2,00	0.13	0.28	0.03	0.23	0.08	<0.01	0.2	0.01	0.21	0.03	0.1	0.01	0.09
279.81	204.08	2	2.16	0.37	0.32	0.08	0.37	0.11	0.02	0.21	0.03	0.21	0.04	0.16	0.01	0.11
293.21	157.13	3	2.58	0.68	0.92	0.11	0.56	0.13	0.01	0.23	0.04	0.26	0.07	0.17	0.02	0.12
322.09	1616.04	<1	2.28	0.19	0.26	0.03	0.27	0.09	0.02	0.19	0.02	0.2	0.04	0.13	0.01	0.11
333.57	160.33	7	2.29	0.14	0.27	0.02	0.22	0.07	0.01	0.18	0.02	0.21	0.03	0.12	0.01	0.09
414.71	226.94	3	2.99	0.26	0.34	0.06	0.33	0.09	0.02	0.22	0.03	0.24	0.07	0.17	0.02	0.13
378.52	213.57	4	2.9	0.5	0.67	0.1	0.51	0.13	0.01	0.3	0.04	0.27	0.07	0.2	0.02	0.16

Lu	Th	U	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W	Mn	Re	Fe	Ru	Co
μg/L	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*mg/L*	*μg/L*	*μg/L*
0.01	<0.05	0.21	<10	0.11	<0.02	<0.2	<0.01	<0.02	<0.5	0.1	0.04	107.24	<0.01	4.358	<0.05	0.68
0.01	<0.05	0.22	<10	<0.02	<0.02	0.6	<0.01	<0.02	0.9	<0.1	0.03	136.00	<0.01	4.802	<0.05	0.61
0.01	<0.05	0.21	<10	<0.02	<0.02	<0.2	<0.01	<0.02	1.7	0.4	<0.02	133.07	<0.01	4.917	<0.05	0.56
0.01	1.29	0.13	<10	0.46	0.03	<0.2	0.02	<0.02	<0.01	0.1	<0.02	85.17	<0.01	0.004	<0.05	0.5
0.01	<0.05	0.1	13	0.94	<0.02	1,0	<0.01	<0.02	1,0	0.1	0.13	534.67	<0.01	35.328	<0.05	0.23
0.01	<0.05	0.12	<10	<0.02	<0.02	1.8	0.01	<0.02	2.1	<0.1	0.16	554.48	<0.01	31.648	<0.05	0.17
0.01	0.13	0.19	<10	<0.02	<0.02	1.6	0.04	<0.02	1.6	0.2	0.31	557.28	<0.01	34.636	<0.05	0.12
<0.01	0.27	0.11	<10	0.57	0.02	<0.2	0.02	<0.02	<0.01	0.3	<0.02	496.51	<0.01	7.661	<0.05	0.24
<0.01	<0.05	<0.02	16	0.33	<0.02	<0.2	0.07	<0.02	19.4	0.3	0.62	828.74	<0.01	290.378	<0.05	6.78
<0.01	<0.05	0.03	<10	<0.02	<0.02	0.6	0.09	<0.02	26,0	0.8	1.49	1065.89	<0.01	180.763	<0.05	11.48
<0.01	<0.05	<0.02	<10	0.24	<0.02	0.4	0.09	<0.02	22,0	1.1	1.2	984.63	<0.01	183.214	<0.05	10.67
<0.01	0.19	<0.02	12	0.49	<0.02	<0.2	0.07	<0.02	0.7	0.6	0.2	859.6	<0.01	152.026	<0.05	9.82
<0.01	<0.05	2.43	<10	0.07	<0.02	<0.2	<0.01	<0.02	<0.5	0.1	0.02	3.26	0.01	0.202	<0.05	0.14
0.02	<0.05	0.92	13	12.48	0.02	0.8	0.64	<0.02	0.7	0.1	0.1	527.38	<0.01	19.78	<0.05	1.11
0.02	<0.05	1,00	<10	12.86	<0.02	1.3	0.83	<0.02	1.6	<0.1	0.14	594.48	<0.01	18.743	<0.05	0.99
<0.01	<0.05	44.02	<10	1.81	<0.02	<0.2	<0.01	<0.02	<0.5	0.3	<0.02	356.67	0.03	4.139	<0.05	2.36
<0.01	0.12	47.47	<10	7.77	0.03	<0.2	<0.01	<0.02	<0.5	0.4	<0.02	369.2	<0.01	<0.010	<0.05	2.76
<0.01	<0.05	0.93	<10	4.79	0.02	<0.2	0.01	<0.02	<0.5	0.1	<0.02	408.93	<0.01	2.491	<0.05	0.48
<0.01	0.16	1.09	<10	5.57	<0.02	<0.2	<0.01	<0.02	<0.5	0.1	<0.02	424.98	<0.01	<0.010	<0.05	0.41
<0.01	<0.05	0.56	<10	8.04	0.03	0.6	<0.01	<0.02	<0.5	0.3	0.02	375.46	<0.01	3.694	<0.05	0.33
<0.01	<0.05	0.6	<10	8.59	0.04	<0.2	<0.01	<0.02	<0.5	0.2	<0.02	313.96	<0.01	<0.010	<0.05	0.17
<0.01	<0.05	0.76	<10	10.89	<0.02	<0.2	<0.01	<0.02	<0.5	<0.1	<0.02	324.39	<0.01	4.977	<0.05	0.61
<0.01	<0.05	0.54	<10	19.47	0.16	0.4	<0.01	<0.02	<0.5	0.2	0.03	270.28	<0.01	3.79	0.08	0.42
<0.01	0.09	0.5	<10	19.3	0.11	0.3	<0.01	<0.02	<0.5	0.4	<0.02	261.52	<0.01	0.106	<0.05	0.37
0.01	<0.05	0.32	<10	0.44	<0.02	<0.2	<0.01	<0.02	<0.5	0.1	0.02	238.04	<0.01	4.776	<0.05	0.04
<0.01	<0.05	0.42	<10	0.14	<0.02	0.2	<0.01	<0.02	<0.5	0.1	0.02	114.3	<0.01	2.3	<0.05	0.22
0.04	<0.05	0.53	<10	4.74	<0.02	<0.2	<0.01	<0.02	0.7	0.1	0.02	1000.63	<0.01	9.046	<0.05	0.07
0.01	<0.05	1.32	<10	0.68	<0.02	0.4	<0.01	<0.02	2.6	1.2	0.02	732.48	0.01	6.466	<0.05	0.96
<0.01	<0.05	0.07	<10	0.17	<0.02	<0.2	<0.01	<0.02	0.6	0.1	<0.02	451.94	<0.01	6.497	<0.05	1.89
0.01	<0.05	0.18	<10	0.22	<0.02	<0.2	<0.01	<0.02	<0.5	0.1	<0.02	422.71	<0.01	5.733	<0.05	0.39
0.03	<0.05	0.64	<10	1.34	<0.02	0.4	<0.01	<0.02	<0.5	0.2	<0.02	1075.77	<0.01	15.368	<0.05	1.22
0.02	<0.05	0.14	<10	0.96	<0.02	0.6	<0.01	<0.02	<0.5	<0.1	<0.02	313.91	<0.01	6.861	<0.05	0.07
<0.01	<0.05	0.17	<10	0.08	<0.02	0.3	<0.01	<0.02	<0.5	<0.1	<0.02	157.71	<0.01	2.647	<0.05	0.21
<0.01	<0.05	2.33	<10	2.16	<0.02	<0.2	<0.01	<0.02	<0.5	<0.1	<0.02	572.66	<0.01	13.208	<0.05	<0.02
0.01	<0.05	2.17	<10	2.73	<0.02	<0.2	<0.01	<0.02	<0.5	<0.1	<0.02	450.78	<0.01	11.368	<0.05	0.12
0.02	<0.05	1.51	13	2.37	0.02	0.4	<0.01	<0.02	<0.01	0.1	0.03	328.92	<0.01	8.496	<0.05	<0.01
<0.01	<0.05	2.86	<10	0.38	<0.02	0.6	<0.01	<0.02	<0.5	0.8	0.02	404.08	<0.01	8.088	<0.05	1.72
<0.01	<0.05	3.56	<10	0.31	<0.02	0.6	<0.01	<0.02	0.6	0.7	<0.02	379.93	<0.01	8.539	<0.05	1.88
0.01	<0.05	<0.02	<10	1.14	<0.02	0.3	<0.01	<0.02	<0.5	0.2	<0.02	585.22	<0.01	14.279	<0.05	0.37
0.02	<0.05	<0.02	<10	2.07	<0.02	<0.2	<0.01	<0.02	<0.5	<0.1	<0.02	692.08	<0.01	17.904	<0.05	0.47
0.03	0.14	0.03	<10	3.94	0.07	0.4	0.01	<0.02	1.4	0.3	0.06	681.04	<0.01	16.587	<0.05	0.41
0.03	0.13	0.02	12	2.66	0.04	0.8	0.01	<0.02	1.7	0.2	<0.02	696.33	<0.01	16.744	<0.05	0.42
0.01	<0.05	0.07	<10	0.28	<0.02	0.2	<0.01	<0.02	0.8	0.2	<0.02	552.97	<0.01	14.088	<0.05	2.38
0.01	<0.05	0.02	<10	0.84	<0.02	<0.2	<0.01	<0.02	<0.5	<0.1	<0.02	481.63	<0.01	11.987	<0.05	1.83
0.02	0.09	0.12	<10	2.03	<0.02	<0.2	<0.01	<0.02	0.6	0.2	<0.02	475.14	<0.01	12.35	<0.05	2.71
0.02	0.06	0.03	<10	0.7	<0.02	0.4	<0.01	<0.02	2.6	0.1	0.02	541.51	<0.01	13.146	<0.05	2.62
0.01	<0.05	0.08	<10	1,00	<0.02	<0.2	<0.01	<0.02	<0.5	0.1	<0.02	659.23	<0.01	13.792	<0.05	1.48
0.01	<0.05	0.03	<10	0.88	<0.02	<0.2	<0.01	<0.02	<0.5	<0.1	<0.02	710.61	<0.01	12.736	<0.05	1.44
0.02	<0.05	0.06	<10	0.94	<0.02	<0.2	<0.01	<0.02	0.6	0.2	<0.02	747.27	<0.01	14.968	<0.05	1.92
0.02	<0.05	0.07	<10	1.89	0.03	0.4	0.01	<0.02	1.9	0.1	0.02	725.24	<0.01	14.586	<0.05	1.67

Rh	Ni	Pd	Pt	Cu	Ag	Au	Zn	Cd	Hg	B	Al	Ga	In	Tl	Si	Ge
µg/L	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*mg/L*	*µg/L*
<0.01	1.7	<0.2	<0.01	3.7	1.39	<0.05	16.1	3.22	<0.1	<20	723	0.39	<0.01	<0.01	16.546	0.14
<0.01	1.6	<0.2	<0.01	19.6	<0.05	<0.05	59.4	9.11	<0.1	18	476	0.24	0.07	0.02	16.888	0.14
0.01	2.9	<0.2	<0.01	<0.1	0.51	<0.05	15.6	<0.05	0.3	<5	389	0.26	<0.01	0.01	16.173	0.13
0.09	1.4	<0.2	0.01	1.7	<0.05	<0.05	<0.5	0.33	<0.1	13	272	0.24	<0.01	0.02	12.71	0.08
<0.01	12.1	<0.2	<0.01	1,0	1.71	<0.05	38.8	0.11	<0.1	<20	1590	<0.05	<0.01	<0.01	35.421	0.76
<0.01	10.2	<0.2	<0.01	4,0	<0.05	<0.05	23,0	<0.05	<0.1	16	1479	<0.05	<0.01	<0.01	34.963	0.78
0.02	9.8	<0.2	<0.01	0.4	<0.05	<0.05	25.6	<0.05	0.2	<5	1471	<0.05	<0.01	<0.01	34.881	0.81
0.03	5.6	<0.2	0.01	0.2	<0.05	<0.05	3.4	<0.05	0.4	12	812	<0.05	<0.01	<0.01	32.181	0.5
<0.01	4.7	<0.2	<0.01	1.2	2.22	<0.05	19.4	<0.05	<0.1	<20	727	0.09	<0.01	<0.01	34.742	4.33
<0.01	6.1	<0.2	<0.01	6.3	5.4	<0.05	124.7	0.24	<0.1	20	1023	0.07	<0.01	<0.01	37.016	4.61
0.01	8.4	<0.2	<0.01	<0.1	8.3	<0.05	95.9	<0.05	0.4	<5	1031	0.09	<0.01	<0.01	37.161	4.21
0.03	4.8	<0.2	<0.01	0.1	<0.05	<0.05	36.0	<0.05	0.6	14	373	0.09	<0.01	<0.01	34.311	2.77
<0.01	1.4	<0.2	<0.01	1.7	0.36	<0.05	7.4	0.27	<0.1	<20	159	<0.05	<0.01	<0.01	9.12	<0.05
<0.01	47.0	<0.2	<0.01	2.6	0.61	<0.05	6,0	0.74	<0.1	<20	199	<0.05	<0.01	<0.01	37.707	0.87
<0.01	18.3	<0.2	<0.01	3,0	<0.05	<0.05	10.3	<0.05	<0.1	30	237	<0.05	<0.01	<0.01	44.896	1,00
<0.01	2.0	<0.2	<0.01	15.1	0.68	<0.05	12.0	0.14	<0.1	199	59	<0.05	<0.01	<0.01	15.243	0.59
0.08	3.6	<0.2	<0.01	3,0	<0.05	<0.05	2.4	<0.05	0.2	231	11	<0.05	<0.01	<0.01	16.892	0.63
0.01	0.2	<0.2	<0.01	22,0	0.49	<0.05	2.1	<0.05	<0.1	172	58	<0.05	<0.01	<0.01	12.681	0.3
0.08	0.7	<0.2	<0.01	12.2	<0.05	<0.05	0.2	<0.05	0.3	197	18	<0.05	<0.01	<0.01	14.821	0.32
<0.01	<0.2	<0.2	<0.01	35.7	1.02	<0.05	2.2	0.43	<0.1	169	80	<0.05	<0.01	<0.01	14.998	0.4
0.04	0.7	<0.2	<0.01	44.7	<0.05	<0.05	6.8	<0.05	0.2	176	3	<0.05	<0.01	<0.01	16.497	0.38
<0.01	5.3	<0.2	<0.01	89.4	1.67	<0.05	160.1	<0.05	<0.1	389	7	<0.05	<0.01	<0.01	16.869	0.68
<0.01	0.2	0.6	<0.01	6.1	<0.05	<0.05	4.9	0.07	0.2	281	<1	<0.05	<0.01	<0.01	13.767	0.74
0.06	1.1	0.3	<0.01	4.8	<0.05	<0.05	4.8	<0.05	0.2	348	19	<0.05	<0.01	<0.01	16.364	0.62
<0.01	<0.2	<0.2	<0.01	0.3	5.92	<0.05	0.1	<0.05	<0.1	33	13	<0.05	<0.01	0.04	6.767	0.41
<0.01	19.7	<0.2	<0.01	2.3	3.01	<0.05	34.1	<0.05	<0.1	<20	323	<0.05	<0.01	0.03	4.792	0.13
<0.01	1.8	<0.2	<0.01	1.1	0.06	<0.05	<0.5	<0.05	<0.1	52	26	<0.05	<0.01	<0.01	6.406	1.01
<0.01	8.7	<0.2	<0.01	3.1	0.28	<0.05	13.8	<0.05	<0.1	51	34	<0.05	<0.01	1.59	18.97	0.88
<0.01	8.0	<0.2	<0.01	0.7	0.24	<0.05	21.6	0.09	<0.1	28	10	<0.05	<0.01	0.93	14.361	0.43
<0.01	1.7	<0.2	<0.01	3.8	3.42	<0.05	16.9	<0.05	<0.1	28	2	<0.05	<0.01	0.97	16.283	0.67
<0.01	18.6	<0.2	<0.01	4.1	2.1	<0.05	29.4	<0.05	<0.1	68	20	<0.05	<0.01	1.8	31.928	1.16
<0.01	8.4	<0.2	<0.01	6.4	<0.05	<0.05	13.2	<0.05	<0.1	992	8	<0.05	<0.01	<0.01	7.013	3.94
<0.01	4,0	<0.2	<0.01	13.3	<0.05	<0.05	24.3	<0.05	<0.1	428	13	<0.05	<0.01	<0.01	6.153	2.03
<0.01	2.7	<0.2	<0.01	5.2	0.51	<0.05	14.2	<0.05	<0.1	2060	34	<0.05	<0.01	<0.01	48.484	10.62
<0.01	<0.2	0.2	<0.01	<0.1	<0.05	<0.05	<0.5	<0.05	0.3	1544	21	<0.05	<0.01	<0.01	40.452	11.39
0.1	1.4	<0.2	<0.01	4.2	<0.05	<0.05	<0.5	<0.05	0.4	1273	28	<0.05	<0.01	<0.01	33.974	7.3
<0.01	11.4	<0.2	<0.01	1.2	<0.05	<0.05	2.0	<0.05	<0.1	712	11	<0.05	<0.01	0.63	27.45	3.54
<0.01	11.4	<0.2	<0.01	<0.1	<0.05	<0.05	1.2	1.38	0.2	738	17	<0.05	<0.01	0.78	25.606	4.5
<0.01	<0.2	<0.2	<0.01	1.2	1.48	<0.05	2.6	0.14	<0.1	57	89	<0.05	<0.01	<0.01	23.782	0.34
<0.01	<0.2	<0.2	<0.01	<0.1	<0.05	<0.05	<0.5	<0.05	0.1	69	30	<0.05	<0.01	<0.01	25.967	0.53
0.03	2.6	<0.2	<0.01	2.7	<0.05	<0.05	7.2	14.46	0.6	61	103	<0.05	<0.01	<0.01	26.682	0.51
<0.01	3.4	<0.2	<0.01	2.4	<0.05	<0.05	4.4	<0.05	<0.1	124	432	0.12	<0.01	<0.01	29.044	0.39
<0.01	6.0	<0.2	<0.01	13.7	1.61	<0.05	21.7	0.49	<0.1	43	31	<0.05	<0.01	<0.01	22.569	0.24
<0.01	4.6	<0.2	0.01	<0.1	<0.05	<0.05	7.7	0.38	<0.1	36	37	<0.05	<0.01	<0.01	19.08	0.27
0.02	8.4	<0.2	<0.01	4,0	<0.05	<0.05	12.3	<0.05	0.7	42	40	<0.05	<0.01	0.01	19.012	0.24
<0.01	12.1	<0.2	<0.01	9.2	<0.05	<0.05	61.9	<0.05	<0.1	79	144	<0.05	<0.01	0.02	21.261	0.28
<0.01	2.0	<0.2	<0.01	6.3	0.09	<0.05	5.9	<0.05	<0.1	44	30	<0.05	<0.01	<0.01	24.407	0.3
<0.01	2.7	<0.2	<0.01	<0.1	<0.05	<0.05	3.3	0.13	<0.1	40	26	<0.05	<0.01	<0.01	21.681	0.31
0.02	3.9	<0.2	<0.01	1.4	<0.05	<0.05	8.9	<0.05	0.8	56	51	<0.05	<0.01	<0.01	25.482	0.4
<0.01	5.9	<0.2	<0.01	7.9	<0.05	<0.05	11.3	<0.05	<0.1	77	187	0.1	<0.01	<0.01	25.807	0.34

Sn	Pb	P	As	Sb	Bi	Se	Te	Br	HCO3	SO4	Cl	F	N-NO3	N-NH4	S(-2)
μg/L	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*μg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*
0.08	<0.1	140	0.6	<0.05	<0.05	1.1	<0.05	237	2599.6	20.2	9.8	0.5	0.56	0.06	nd
0.09	5.9	107	3.8	0.07	<0.05	<0.5	<0.05	74	nd	nd	nd	nd	nd	nd	nd
0.16	2.6	13	<0.5	0.06	<0.05	0.7	<0.05	96	221.6	6.0	8.3	0.51	5.9	nd	nd
0.42	<0.1	70	<0.5	0.07	0.49	<0.5	<0.05	50	206.7	7.0	6,0	0.46	3.2	nd	nd
0.07	<0.1	281	2.4	<0.05	<0.05	<0.5	<0.05	12	3846.6	8.0	7.1	1.6	nd	nd	nd
<0.05	3.7	286	2.7	<0.05	<0.05	<0.5	<0.05	48	nd	nd	nd	nd	nd	nd	nd
0.62	1.2	13	2.2	<0.05	<0.05	<0.5	<0.05	18	787.2	<1	3.9	1.97	1.2	nd	nd
0.23	<0.1	170	<0.5	<0.05	<0.05	<0.5	<0.05	18	768.8	<1	6.5	1.94	0.7	nd	nd
0.34	<0.1	199	<0.5	<0.05	<0.05	<0.5	<0.05	19	5333.3	6.0	30.1	1.5	nd	nd	nd
0.26	0.3	247	0.9	0.07	<0.05	<0.5	<0.05	46	nd	nd	nd	nd	nd	nd	nd
0.58	4.9	16	0.6	0.16	<0.05	<0.5	<0.05	19	883.0	<1	3.6	1.27	1.3	nd	nd
0.24	<0.1	100	<0.5	<0.05	0.08	<0.5	<0.05	36	867.2	1.0	4.7	1.87	1.6	nd	nd
0.07	0.1	73	1.1	<0.05	<0.05	<0.5	<0.05	19	18.1	14.5	4.4	0.2	0.26	nd	nd
0.11	<0.1	42	0.6	<0.05	<0.05	<0.5	<0.05	18	4466.8	4.0	8.9	1.1	nd	nd	nd
0.09	55.7	41	0.8	<0.05	<0.05	<0.5	<0.05	26	nd	nd	nd	nd	nd	nd	nd
<0.05	0.6	24	<0.5	<0.05	<0.05	0.6	<0.05	126	4367.1	139.1	26.0	0.4	0.07	0.23	nd
0.18	0.2	<20	<0.5	0.16	<0.05	<0.5	<0.05	186	1691.5	108.0	10.6	nd	nd	nd	<0.01
0.1	1.9	10	<0.5	<0.05	<0.05	0.8	<0.05	169	2997.0	147.3	66.0	0.3	0.08	0.39	nd
0.2	0.2	<20	<0.5	0.13	<0.05	0.06	<0.05	250	1418.3	92.0	33.4	nd	nd	nd	<0.01
0.18	<0.1	3	0.6	0.1	<0.05	0.8	<0.05	191	3502.2	104.1	29.5	0.3	0.06	0.16	nd
0.07	0.1	<20	<0.5	0.11	<0.05	<0.5	<0.05	256	1401.1	83.0	21.6	nd	nd	nd	0.02
<0.05	0.2	10	<0.5	<0.05	<0.05	<0.5	<0.05	661	4709.4	226.3	73.0	0.4	0.06	0.31	nd
<0.05	0.2	40	2,0	<0.05	<0.05	3.1	<0.05	621	nd	235.0	36.9	0.55	0.05	0.01	0.01
0.08	1.6	<20	<0.5	0.11	<0.05	1.3	<0.05	817	2173.2	250.0	98.8	nd	nd	nd	0.01
<0.05	<0.1	20	86.6	<0.05	<0.05	<0.5	<0.05	19	4260.0	25.9	7.1	0.36	0.06	0.10	nd
0.07	1,0	129	10.6	<0.05	<0.05	<0.5	<0.05	14	1576.5	24.4	10.6	0.31	0.07	0.08	nd
0.11	<0.1	18	104.1	<0.05	<0.05	<0.5	<0.05	23	4430.2	29.5	7.1	0.55	0.06	0.18	nd
<0.05	<0.1	23	145.6	0.59	<0.05	<0.5	<0.05	33	3292.2	44.0	8.9	0.54	0.06	0.21	nd
<0.05	<0.1	13	87.2	0.08	<0.05	<0.5	<0.05	20	3801.7	52.7	8.9	0.52	0.06	0.40	nd
0.18	<0.1	10	132.3	0.19	<0.05	<0.5	<0.05	20	3316.1	47.1	10.6	0.86	0.06	0.22	nd
<0.05	<0.1	36	219.3	<0.05	<0.05	<0.5	<0.05	43	4295.1	53.9	11.5	0.4	0.01	0.09	nd
0.08	<0.1	16	1375.7	<0.05	<0.05	1.6	<0.05	344	5353.8	196.6	78.0	0.9	0.17	0.30	nd
<0.05	<0.1	1	337.3	<0.05	<0.05	0.6	<0.05	138	4351.5	143.6	49.6	0.59	0.06	0.18	nd
<0.05	<0.1	10	3532.7	<0.05	<0.05	<0.5	<0.05	641	4911.8	202.4	72.7	0.92	0.07	0.51	nd
<0.05	<0.1	400	2521.9	<0.05	<0.05	3.0	<0.05	630	nd	190.0	19.9	0.8	0.8	0.06	0.01
<0.05	<0.1	400	2006.3	<0.05	<0.05	2.9	<0.05	456	2096.8	248.0	88.1	0.58	9.8	0.06	0.01
<0.05	<0.1	504	1099.1	0.42	<0.05	0.8	<0.05	209	3985.2	89.1	30.1	0.4	0.02	0.14	<0.01
<0.05	<0.1	60	1125.6	0.47	<0.05	0.8	<0.05	219	nd	90.0	18.1	0.76	2.00	0.08	<0.01
0.12	0.9	30	2.8	<0.05	<0.05	<0.5	<0.05	11	3826.6	19.0	10.3	0.29	0.03	0.43	nd
<0.05	<0.1	36	3.8	<0.05	<0.05	<0.5	<0.05	56	nd	<1	14.5	0.34	0.86	0.05	<0.01
0.82	2.1	36	2.9	<0.05	<0.05	<0.5	<0.05	40	957.1	2.0	19.4	0.38	0.11	0.08	<0.01
36.8	0.2	62	2.8	<0.05	0.13	<0.5	<0.05	51	975.4	2.0	15.6	0.44	0.6	nd	nd
0.17	0.8	67	5.9	<0.05	<0.05	<0.5	<0.05	10	3127.0	35.0	10.3	0.2	0.02	0.26	nd
<0.05	2.7	no	4.6	<0.05	<0.05	<0.5	<0.05	50	nd	nd	13.3	nd	nd	0.1	<0.01
0.98	4.7	65	3.6	<0.05	<0.05	0.09	<0.05	24	600.9	28.0	14.4	0.29	0.2	0.08	0.01
371.92	2.1	91	5.6	<0.05	0.59	<0.5	<0.05	34	659.0	24.0	15.2	0.12	0.6	nd	nd
0.09	0.4	19	2.4	0.07	<0.05	<0.5	<0.05	11	3106.6	34.0	12.1	0.21	0.02	0.29	nd
<0.05	<0.1	no	3.3	<0.05	<0.05	<0.5	<0.05	82	nd	nd	14.2	nd	nd	0.07	<0.01
0.39	1.2	209	2.4	<0.05	<0.05	<0.5	<0.05	52	837.0	12.0	15.5	0.4	0.64	0.08	0.02
107.42	1.7	55	2.3	0.09	0.42	<0.5	<0.05	43	866.9	16.0	15.7	0.35	0.6	nd	nd

Supplementary Material 2. Matrix of Tau Kendall coefficients.

	pH	Temp	EH	Li	Na	K	Rb	Cs	Be	Mg	Ca	Sr	Ba	Y	La	Ce	Pr	Nd	Sm	Gd	Dy	Ho	Er	Yb	U	Zr	Mo	W	Mn	Fe	Co	Ni	Cu	Zn	B	Al	Si	Ge	Sn	P	As	Br	HCO3	SO4	Cl	F	N-NO3	N-NH4
Temp	0,453																																														
EH	-0,369	-0,078																																													
Li	0,460	0,132	-0,258																																												
Na	0,530	0,432	-0,181	0,605																																											
K	0,558	0,350	-0,467	0,402	0,419																																										
Rb	0,293	0,093	-0,489	0,185	0,140	0,623																																									
Cs	0,219	0,062	-0,440	0,213	0,109	0,542	0,780																																								
Be	0,092	-0,082	-0,435	0,115	0,010	0,323	0,557	0,508																																							
Mg	0,289	-0,004	-0,263	0,499	0,362	0,375	0,282	0,150	0,278																																						
Ca	0,316	0,212	-0,412	0,290	0,447	0,407	0,347	0,270	0,316	0,334																																					
Sr	0,516	0,411	-0,146	0,579	0,827	0,344	0,078	0,058	-0,065	0,309	0,437																																				
Ba	-0,240	-0,227	0,025	-0,197	-0,246	-0,216	-0,032	-0,030	0,077	-0,055	0,112	-0,203																																			
Y	-0,003	-0,030	-0,189	-0,007	0,085	0,056	0,155	0,106	0,383	0,051	0,388	0,088	0,254																																		
La	-0,067	0,049	0,045	-0,250	-0,092	-0,054	-0,059	-0,132	-0,051	-0,069	0,141	-0,012	0,239	0,305																																	
Ce	-0,131	-0,071	0,005	-0,264	-0,175	-0,145	-0,061	-0,134	0,100	-0,094	0,049	-0,109	0,208	0,410	0,643																																
Pr	-0,157	-0,093	0,060	-0,279	-0,183	-0,169	-0,115	-0,167	0,036	-0,141	0,010	-0,124	0,191	0,441	0,642	0,869																															
Nd	-0,123	-0,064	0,011	-0,236	-0,124	-0,109	-0,065	-0,121	0,108	-0,116	0,098	-0,090	0,154	0,544	0,573	0,798	0,881																														
Sm	-0,122	-0,092	-0,013	-0,232	-0,123	-0,116	-0,048	-0,092	0,142	-0,135	0,099	-0,086	0,193	0,598	0,507	0,739	0,822	0,870																													
Gd	-0,050	-0,059	-0,137	-0,090	0,007	0,008	0,091	0,047	0,325	-0,023	0,282	-0,007	0,209	0,850	0,301	0,490	0,549	0,657	0,721																												
Dy	-0,020	-0,042	-0,182	-0,057	0,043	0,020	0,132	0,088	0,372	0,000	0,338	0,045	0,235	0,909	0,308	0,455	0,495	0,608	0,662	0,914																											
Ho	-0,080	-0,076	-0,135	-0,110	0,001	-0,018	0,090	0,050	0,333	-0,050	0,314	0,011	0,303	0,841	0,399	0,529	0,582	0,651	0,723	0,811	0,868																										
Er	-0,028	-0,044	-0,194	-0,053	0,038	0,031	0,153	0,113	0,401	0,008	0,362	0,043	0,247	0,892	0,337	0,461	0,504	0,600	0,641	0,860	0,924	0,888																									
Yb	-0,047	-0,038	-0,196	-0,079	0,019	0,025	0,146	0,120	0,390	-0,005	0,353	0,024	0,247	0,817	0,384	0,517	0,537	0,626	0,647	0,797	0,849	0,868	0,908																								
U	0,285	0,311	-0,054	0,253	0,307	0,245	0,054	0,113	-0,102	0,040	0,067	0,370	-0,335	-0,127	-0,131	-0,174	-0,148	-0,142	-0,192	-0,163	-0,157	-0,173	-0,120	-0,115																							
Zr	0,319	0,217	-0,048	0,436	0,544	0,116	-0,098	-0,158	-0,119	0,403	0,344	0,594	0,007	0,129	0,055	-0,041	-0,016	-0,002	0,000	0,073	0,105	0,102	0,130	0,120	0,162																						
Mo	-0,013	-0,081	0,029	0,052	0,007	0,085	0,040	0,025	-0,039	0,080	-0,033	-0,031	0,023	-0,268	-0,094	-0,106	-0,097	-0,161	-0,194	-0,236	-0,247	-0,202	-0,249	-0,257	-0,019	-0,042																					
W	-0,098	-0,345	-0,163	-0,056	-0,246	0,058	0,246	0,219	0,198	0,179	-0,033	-0,236	0,025	-0,087	0,034	0,035	0,009	-0,026	-0,072	-0,110	-0,100	-0,033	-0,061	-0,002	-0,110	-0,177	0,132																				
Mn	0,065	-0,135	-0,273	0,006	-0,043	0,140	0,252	0,097	0,362	0,357	0,318	-0,047	0,216	0,348	0,168	0,224	0,179	0,223	0,237	0,319	0,328	0,286	0,304	0,273	-0,315	0,018	0,141	0,171																			
Fe	-0,125	-0,355	-0,254	0,059	-0,162	0,121	0,324	0,231	0,493	0,371	0,244	-0,208	0,271	0,378	0,124	0,189	0,154	0,194	0,216	0,360	0,359	0,347	0,358	0,350	-0,416	-0,065	0,046	0,353	0,600																		
Co	-0,151	-0,145	0,043	-0,108	-0,144	-0,151	-0,146	-0,138	0,012	0,018	-0,070	-0,131	0,069	-0,099	0,138	0,087	0,051	0,000	0,010	-0,064	-0,081	-0,071	-0,111	-0,144	-0,207	-0,086	0,314	0,039	0,254	0,207																	
Ni	-0,026	-0,120	-0,180	-0,063	-0,186	0,115	0,216	0,229	0,357	0,061	0,048	-0,143	0,171	0,079	0,194	0,160	0,117	0,088	0,074	0,051	0,082	0,102	0,096	0,109	-0,062	-0,198	0,099	0,210	0,209	0,328	0,274																
Cu	0,187	0,172	0,256	0,146	0,260	-0,016	-0,224	-0,234	-0,268	0,044	-0,026	0,270	-0,204	-0,065	0,033	-0,012	0,031	0,027	0,021	-0,045	-0,088	-0,080	-0,074	-0,089	0,195	0,199	-0,096	-0,080	-0,158	-0,243	-0,038	-0,093															
Zn	-0,073	-0,150	0,044	-0,178	-0,258	-0,011	0,143	0,112	0,084	-0,004	-0,178	-0,301	-0,020	-0,072	0,087	0,052	0,025	-0,002	-0,003	-0,047	-0,084	-0,092	-0,076	-0,082	-0,188	-0,328	0,000	0,260	0,117	0,235	0,225	0,422	0,149														
B	0,373	0,283	-0,096	0,564	0,665	0,296	0,033	0,041	-0,092	0,161	0,311	0,640	-0,219	0,202	-0,075	-0,092	-0,062	0,007	0,035	0,172	0,180	0,106	0,154	0,097	0,279	0,446	-0,053	-0,367	-0,099	-0,194	-0,125	-0,180	0,294	-0,289													
Al	-0,371	-0,504	0,116	-0,227	-0,483	-0,218	0,010	0,033	0,130	0,077	-0,216	-0,476	0,232	-0,063	0,043	0,163	0,153	0,101	0,050	-0,006	-0,044	-0,017	-0,025	0,035	-0,264	-0,280	0,104	0,449	0,185	0,376	0,089	0,212	-0,154	0,266	-0,479												
Si	-0,043	-0,320	-0,282	0,249	-0,022	0,118	0,332	0,254	0,567	0,489	0,273	-0,032	0,162	0,227	-0,065	0,018	-0,021	0,012	0,030	0,188	0,188	0,138	0,210	0,183	-0,144	0,026	0,103	0,274	0,453	0,608	0,165	0,288	-0,189	0,122	-0,074	0,308											
Ge	0,385	0,119	-0,549	0,521	0,382	0,629	0,621	0,589	0,465	0,477	0,425	0,292	-0,117	0,104	-0,176	-0,183	-0,242	-0,191	-0,169	0,008	0,059	0,010	0,076	0,047	0,126	0,104	0,127	0,225	0,273	0,306	-0,051	0,162	-0,077	0,044	0,267	-0,126	0,372										
Sn	-0,216	-0,279	0,212	-0,221	-0,259	-0,250	-0,184	-0,221	-0,106	0,013	-0,123	-0,212	0,243	-0,075	0,182	0,217	0,226	0,128	0,113	-0,035	-0,053	-0,002	-0,026	-0,022	-0,337	-0,032	0,279	0,160	0,195	0,164	0,215	0,085	0,040	0,095	-0,249	0,336	0,095	-0,176									
P	-0,292	-0,468	-0,130	-0,114	-0,341	-0,091	0,102	0,174	0,223	-0,033	-0,033	-0,335	0,143	0,096	-0,025	0,041	0,058	0,092	0,126	0,123	0,122	0,166	0,123	0,111	-0,135	-0,209	0,018	0,318	0,094	0,291	0,141	0,187	-0,219	0,058	-0,195	0,372	0,296	0,028	0,022								
As	0,105	0,136	-0,304	-0,074	0,145	0,234	0,331	0,371	0,347	-0,213	0,295	0,108	-0,013	0,483	0,070	0,099	0,125	0,225	0,279	0,474	0,502	0,407	0,464	0,415	0,057	-0,124	-0,246	-0,109	0,057	0,044	-0,173	0,117	-0,089	-0,020	0,241	-0,264	0,015	0,221	-0,287	0,109							
Br	0,310	0,237	-0,008	0,487	0,455	0,153	-0,018	0,059	-0,195	0,082	0,038	0,414	-0,274	-0,075	-0,209	-0,179	-0,172	-0,159	-0,148	-0,093	-0,101	-0,178	-0,104	-0,137	0,304	0,270	-0,092	-0,221	-0,243	-0,298	-0,131	-0,268	0,214	-0,188	0,547	-0,312	-0,121	0,158	-0,246	-0,127	0,008						
HCO3	0,309	0,386	-0,307	0,297	0,436	0,433	0,259	0,241	0,212	0,256	0,474	0,367	-0,208	0,143	-0,004	-0,082	-0,134	-0,039	-0,056	0,098	0,105	0,052	0,111	0,129	0,156	0,157	-0,221	-0,030	0,049	0,094	-0,114	0,027	0,179	0,014	0,266	-0,261	-0,021	0,428	-0,434	-0,158	0,262	0,080					
SO4	0,423	0,419	-0,048	0,367	0,614	0,291	0,000	0,060	-0,144	0,100	0,117	0,537	-0,403	-0,062	-0,189	-0,258	-0,230	-0,182	-0,159	-0,088	-0,086	-0,154	-0,120	-0,160	0,458	0,291	-0,168	-0,325	-0,308	-0,405	-0,169	-0,168	0,420	-0,117	0,594	-0,549	-0,268	0,188	-0,414	-0,267	0,256	0,473	0,351				
Cl	0,322	0,196	-0,021	0,487	0,551	0,229	-0,051	-0,042	-0,115	0,206	0,187	0,512	-0,208	0,073	-0,084	-0,129	-0,137	-0,061	-0,044	0,040	0,040	-0,043	0,022	-0,027	0,155	0,398	-0,132	-0,224	-0,152	-0,165	-0,082	-0,147	0,404	-0,137	0,651	-0,328	-0,038	0,190	-0,188	-0,124	0,085	0,536	0,257	0,553			
F	0,177	0,016	-0,285	0,243	0,052	0,344	0,533	0,542	0,399	0,277	0,111	0,018	-0,101	-0,096	-0,284	-0,193	-0,297	-0,263	-0,258	-0,157	-0,114	-0,174	-0,099	-0,089	0,033	-0,078	0,055	0,235	0,122	0,233	-0,118	0,169	-0,277	0,109	-0,059	0,095	0,274	0,507	-0,051	-0,004	0,041	0,073	0,162	-0,068	-0,075		
N-NO3	-0,207	-0,350	0,014	0,066	-0,221	-0,142	0,026	0,098	0,075	0,014	-0,169	-0,215	0,169	-0,113	-0,114	-0,052	-0,031	-0,077	-0,085	-0,094	-0,097	-0,095	-0,068	-0,065	-0,114	-0,116	0,042	0,121	-0,041	0,108	0,000	-0,002	-0,328	-0,081	-0,124	0,390	0,230	0,025	0,239	0,218	-0,210	0,152	-0,462	-0,313	-0,109	0,224	
N-NH4	0,090	0,350	0,117	-0,015	0,134	0,124	0,010	-0,090	-0,015	0,100	0,085	0,085	-0,204	-0,040	0,108	0,010	0,008	0,005	-0,054	-0,028	-0,092	-0,155	-0,091	-0,084	0,027	-0,030	-0,008	-0,345	0,065	-0,085	0,007	0,086	0,305	0,223	0,030	-0,075	-0,139	0,002	0,080	-0,496	-0,028	-0,190	0,363	0,187	-0,005	-0,035	-0,302	
S(-2)	0,255	-0,072	0,217	0,192	0,216	0,096	-0,024	-0,024	-0,158	0,192	-0,072	0,072	-0,024	-0,048	-0,367	-0,432	-0,402	-0,390	-0,245	-0,086	-0,112	0,013	-0,012	-0,012	0,000	0,288	-0,013	-0,035	-0,240	-0,122	-0,266	-0,219	0,404	0,293	0,120	0,000	-0,096	0,048	0,182	0,116	-0,111	0,264	-0,261	0,157	0,312	0,104	0,068	-0,272

1,00-0,75	🟦
0,75-0,50	🟦
0,50-0,25	🟦
0,25-0,00	🟦
0,00--0,25	🟨
-0,25--0,50	🟨
-0,50--0,75	🟧
-0,75--1,00	🟫