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Research paper

## Chemistry of water from the inflows to the “Franciszek” dipheading in the “Pomorzany” Zn-Pb mine in the Olkusz Area (SW Poland)

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## ABSTRACT

The “Franciszek” dipheading is one of the main components of the transportation infrastructure in the “Pomorzany” zinc and lead mine in the Olkusz ore district. The heading was cut out of the aeration zone, created by mine drainage in Quaternary sands and Middle and Lower Triassic carbonates. This study presents the results of the examination of the chemical composition of water leaks identified in the dipheading. It was found that the chemical composition of the water under examination depends on geogenic factors, mainly the mineralogical composition of the rocks that are infiltrated by the meteoric waters which feed the leaks, as well as the geochemical processes associated with metal sulphate weathering in the carbonate rock environment (with dolomites and limestones). The significant influence of anthropogenic factors was also identified, including the most important one linked to the migration of polluted waters from the surface mine facilities.

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## 1. Introduction

The “Franciszek” dipheading is one of the main components of the transportation infrastructure of the “Pomorzany” Zn-Pb Ore Mine. The volume of the inflow to the mine over the last 20 years, was between 200 and 280 m<sup>3</sup>/min, depending on the precipitation level (Motyka, Adamczyk, & Juško, 2016). The dipheading connects the surface with the underground workings of the mine. It is 940 m long, and, considering that the altitude difference at the dipheading's entrance on the land surface and at the place of connection with the underground working network equals 74.5 m, an approximate slope of the dipheading can be estimated at 7.9%. The facility is cut into dolomites, with a short section cut into the limestones of the Middle and Lower Triassic. 19 water inflows were recorded in the dipheading, the majority of which appear temporarily as a consequence of increased rainfall or thick snow cover melting. Water samples were collected for the purpose of chemical testing in 1997–2016, and the test results are presented in this study.

The chemical composition of leak water samples from the “Franciszek” dipheading was formed under the influence of

operation of geogenic and anthropogenic factors. The main geogenic factor was identified as the mineral composition of the rocks infiltrated by meteoric waters. This is another essential geogenic factor consisted in the metal sulphate weathering process in the carbonate rock environment, with the presence of dolomites and limestones. The migration of pollution from the surface mine facilities, situated around the “Dąbrówka” shaft, was an anthropogenic factor that was also significant in the chemical composition of leak waters collected from the “Franciszek” dipheading.

It was technically difficult to examine the leak waters of the “Franciszek” dipheading. Owing to the present function of that facility, the traffic of heavy mining machines is ongoing there and thus the possibility of conducting any kind of work inside, including examinations associated with the mining operations and industrial safety, is quite limited. That is further augmented by temporary copious leaks, depending on the rates of meteoric waters migrating through the aeration zone, in which the dipheading is situated, into the saturation zone. High instability of the water flow conditions in the aeration zone creates considerable difficulties in the local interpretation of the results of leak-water chemical composition testing. Such difficulties are, however, quite typical for underground mine workings and this needs to be taken into account in such conditions.

There are four aquifers in the Olkusz zinc and lead mining area: Quaternary, Jurassic, Triassic, and Carbonian-Devonian. The

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Quaternary aquifer is formed by fluvio-glacial sands, with the inclusion of gravel and rubble. This underground aquifer is of the porous type. The Jurassic aquifer is composed of Upper Jurassic (the Malm formation) limestones. This occurs in the northern and eastern sections of the Olkusz Area (Fig. 1).

The Jurassic aquifer is of the fissured-karstic type. The Triassic aquifer is composed of the dolomites and limestones of the Middle and Lower Triassic (Muschelkalk and Upper Bundsandstein). Owing to its high porosity of diporous dolomites (Middle Muschelkalk) and cell dolomites (Upper Bundsandstein – Röt formation), the carbonate Triassic formations build an aquifer of the porous-fissured-karstic type (Motyka, 1998; Zuber & Motyka, 1998). Outcrops of Triassic aquifer formations on the land surface or under the Quaternary deposits are in the western section of the Olkusz area (Fig. 1). The Carboniferous-Devonian aquifer is built by limestones and dolomites. This aquifer is of the fissured-karstic type.

The “Franciszek” dipheading, runs from the land surface to the underground “Pomorzany” mine workings, cutting through older and older carbonate rocks, belonging to Middle and Lower Triassic that is the Middle Muschelkalk and Upper Bundsandstein (Röt formation). The initial dipheading section is cut into the diporous dolomites and ore-bearing rocks (Middle and Lower Muschelkalk), the short middle section in Gogolin beds (Lower Muschelkalk), and the final section in Röt dolomites (Upper Bundsandstein). In the upper part of the initial section of the dipheading, diporous dolomites are covered by a thin layer of clay formations of the Upper Triassic (the Keuper formation). The Triassic rocks are covered by fluvio-glacial Quaternary sands, with its maximum thickness reaching nearly 55 m in the lower section of the dipheading (Fig. 2).

Fissures and bedding planes provide the main water flow paths in Triassic dolomites and limestones and they were cut through by the “Franciszek” dipheading. We can also observe numerous small

caverns, with diameters of up to several centimetres. This rock environment is characterised by high heterogeneity of hydro-geological properties. The values of carbonate hydraulic conductivity relating to the Triassic rocks usually amounts to  $10^{-5}$  m/s, although several orders of magnitude are covered by their range (Motyka & Wilk, 1976). In natural conditions, the groundwater level remained at the interconnected Quaternary-Triassic aquifer of the dipheading area at the altitude of ca. +312 m asl. As a result of the dewatering of carbonate Triassic rocks and Quaternary sands, owing to the effects of the “Pomorzany” mine’s workings, the groundwater level was lower in that area, to an altitude of +180 m asl. Consequently, a young aeration zone was developed and the “Franciszek” dipheading was cut out of it.

Analyses of water chemical composition in the “Franciszek” diphead were performed to assess the impact of natural factors. Including: the mineral composition of rocks infiltrated by waters flowing into the diphead, pyrite weathering processes, and neutralization of acid drainage (AMD) in the carbonate rocks and the presence of contaminants from the surface (anthropogenic factor).

## 2. Materials and methods

The water inflows in the “Franciszek” dipheading originate from the aeration zone. For that reason, their discharge, reaching 1 L/min in the most productive inflows, depends to a large extent on the rate of the fluxes meteoric waters. 19 leaks were recorded in the dipheading the majority of which appear temporarily either after high rainfalls spread over time or during a short amount of time but with intense rainfall or thaw. The appearance of temporary inflows and the time of their operation is stochastic in nature.

Investigations of water inflows’ (leakages) chemistry started in the “Franciszek” dipheading in 1997, as part of the Polish-American

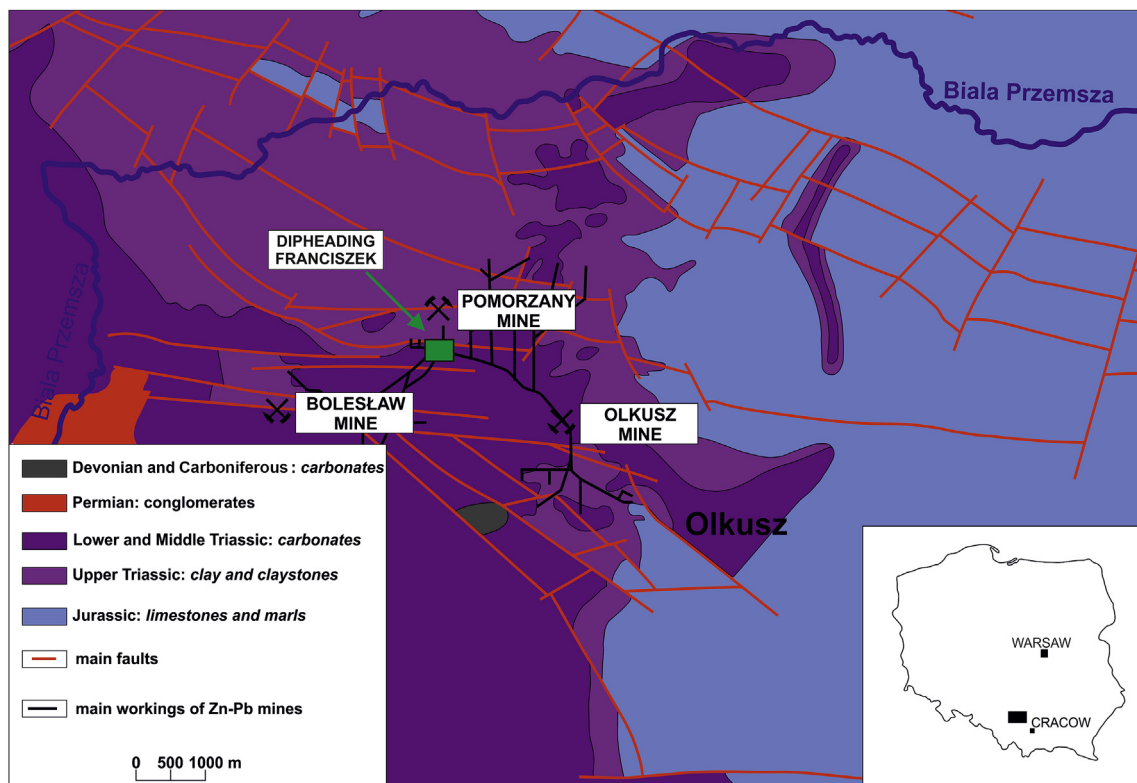


Fig. 1. Geological map of the Olkusz area.

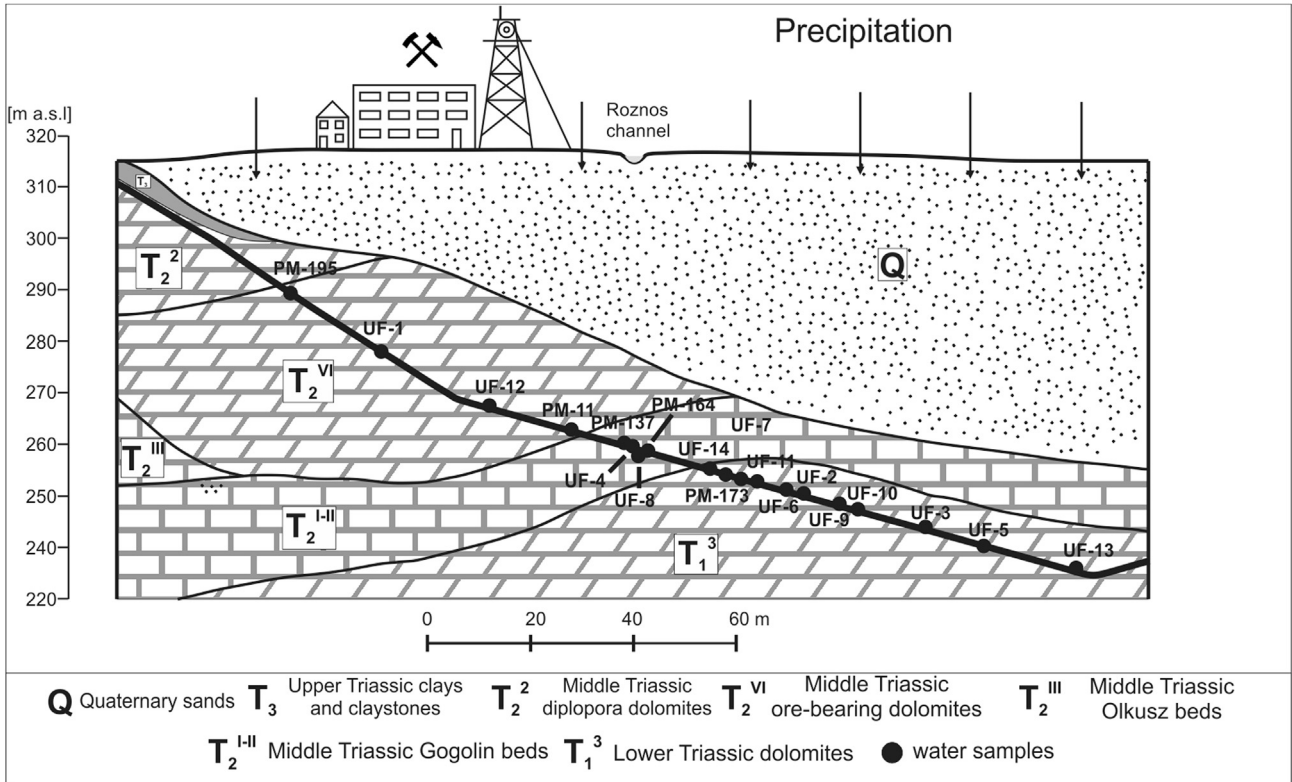


Fig. 2. Geological cross-section of the “Franciszek” dipheading.

regional project relating to the geochemistry of Zn-Pb ore deposits in the Olkusz and Chrzanów areas. At that time, sample PM-11 (Fig. 2) was collected for hydrochemical tests. The results of the analysis were published in Wirth et al. (2003). Owing to technical reasons, discussed above, leak water samples were, otherwise, rarely collected. In 2012, water samples were collected from 4 inflows. In 2014, when rainfall rates were below the average long-period values (a dry period), it was possible to collect water samples from 3 inflows only: samples UF-1, UF-2, and UF-3 (Fig. 2). Only in 2015 and 2016, after a period of increased rainfall, did numerous leaks appear and water samples were collected for chemical composition testing. In total, 36 samples were collected during that period. In August 2017, water samples were collected from the “Dąbrowka” and “Roznos” channels that are situated above the “Franciszek” dipheading (Fig. 3).

Electrical conductivity (EC) was measured in the field, as well as the pH, using proper instruments. Alkalinity was measured by the volumetric method in our laboratory, using a mixed indicator. At a pH reaction of up to 8.6, alkalinity was practically identical to the bicarbonate ion (HCO<sub>3</sub>) concentration. In addition, the authors determined the chloride ion (Cl) concentration by the argentometric method. A Perkin-Elmer ICP AES Plasma 40 inductively coupled plasma atomic emission spectrometer was used in the Laboratory of the Department of Hydrogeology and Engineering Geology of the AGH University of Science and Technology to determine the total sulphur (S), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), iron (Fe), strontium (Sr), and colloidal silica (SiO<sub>2</sub>) contents. The total sulphur content was converted into sulphate concentration. The concentration of trace elements was determined by the use of an ICP MS mass spectrometer, and also by Perkin-Elmer. The nitrate concentrations were determined by the colorimetric method, using a Hach Lange colorimeter. Analytical errors were calculated as the difference between the sum of cation

miliequivalents and the sums of anion miliequivalents, divided by the total sum of cation and anion miliequivalents.

### 3. Results

Water inflows in the “Franciszek” dipheading displayed pH from 6.67 to 8.26, with the average value (arithmetic average) of 7.62 (Table 1). Electrical conductivity (EC) was identified as ranging

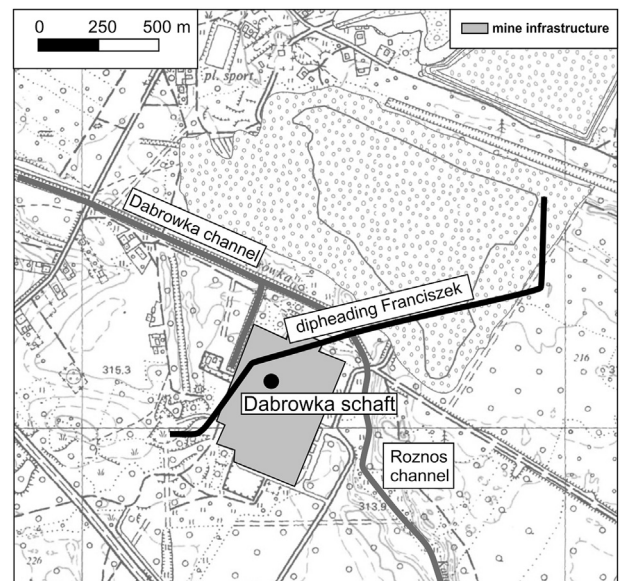


Fig. 3. Area of the “Dąbrowka” schaft.

**Table 1**  
Basic statistics of the physicochemical properties of the inflows into the “Franciszek” dipheading and the “Roznos” and “Dąbrówka” channels.

Parameter	Concentration [mg/L]				Parameter	Concentration [mg/L]	
	MIN	MAX	AVER	MED		“Dąbrówka”	“Roznos”
pH [–]	6,92	8,26	7,615	7,715	pH [–]	7,78	7,88
EC [μS/cm]	761	3080	1481,11	1261,5	EC [μS/cm]	908	890
TDS [g/L]	0.628	3024	1354	1129	TDS [g/L]	0.767	0.669
Ca	97.94	476.70	219.37	193.60	Ca	130.4	118.9
Mg	39.35	245.30	92.35	60.48	Mg	45.18	42.13
Na	4.96	107.10	23.963	10.643	Na	11.37	20.69
K	1.214	13.58	3.311	1.925	K	2.06	5.21
HCO <sub>3</sub>	183.1	460.3	293.88	300.2	HCO <sub>3</sub>	306.8	250.9
SO <sub>4</sub>	169.3	1685,00	649.2	507.9	SO <sub>4</sub>	184.9	178.3
Cl	1,76	130.6	29,97	16,47	Cl	19,76	29,35
NO <sub>3</sub>	0.05	34.1	6,64	3,80	NO <sub>3</sub>	2,30	13,80
Fe	0.002	2.778	0.475	0.231	Fe	0.191	0.083
Sr	0.1	1.597	0.338	0.206	Sr	0.275	0.132
Ba	0.00268	0.112	0.0211	0.011	Ba	0.0699	0.0225
Fe	0.002	2.778	0.475	0.231	Fe	0.191	0.083
Mn	<0.001	0.703	0.123	0.026	Mn	0.0992	0.0107
Zn	0.005	12.135	1.930	0.524	Zn	0.096	0.117
Ni	0.000749	0.356	0.0531	0.0134	Ni	0.00509	0.00269
Co	0.000133	0.0275	0.00361	0.000768	Co	0.00108	0.000558
As	<0.0002	0.449	0.0376	0.00328	As	0.0158	0.00438
Tl	0.000233	0.0898	0.0159	0.00562	Tl	0.00163	0.000543
Mo	0.000203	0.421	0.0428	0.00718	Mo	0.0211	0.00665
Sb	<0.00002	0.0349	0.00337	0.000498	Sb	0.000457	0.000372
Cd	<0.000005	0.00421	0.000491	0.000024	Cd	0.000238	0.000526
Bi	<0.000002	1.714	0.0686	0.000191	Bi	0.000012	<0.000002
Ga	0.000071	0.00504	0.000731	0.000316	Ga	0.00326	0.000998
W	<0.00001	0.557	0.0617	0.000873	W	0.00304	0.00136
Zr	0.000042	0.037	0.00365	0.000794	Zr	0.00139	0.000392
U	0.000052	0.0377	0.00529	0.00169	U	0.000761	0.000516
Cs	0.000085	0.00522	0.000885	0.000286	Cs	0.000341	0.000298

widely from 761 to 3080 μS/cm, with an average value of 1481 μS/cm, and total dissolved solids (TDS) ranged from 0.63 to 3.02 g/L.

The water collected from the inflows appearing in the “Franciszek” dipheading were mostly four-ion of the Ca-Mg-SO<sub>4</sub>-HCO<sub>3</sub> type, the Ca-Mg-SO<sub>4</sub> or Mg-Ca-SO<sub>4</sub> type and TDS was 1.5 g/L. The hydrochemical types of the tested waters were arranged along Ca-Mg and HCO<sub>3</sub>-SO<sub>4</sub> lines, although certain samples indicated deviation towards Na and Cl directions (Fig. 4).

The highest macro-component concentrations were observed in the inflows of the central section of the dipheading (Fig. 5).

The extreme and average values of pH, EC, and TDS, as well as the main component concentrations, are shown in Table 1.

In the background of the calcium and magnesium cations and sulphate and bicarbonate anions dominated in four water samples collected from inflows PM-11, PM-137, PM-164, and UF-8 in the central section of the dipheading (Fig. 2), increased concentrations of Cl and Na ions were found, ranging from 70 to 131 mg/L (Cl ions) and from 5 to 107 mg/L (Na ions). The nitrate (NO<sub>3</sub>) concentrations showed wide range of values (Table 1). Maximum concentrations of these ions were found in inflow UF-1 and UF-12, situated in the upper section of the dipheading (Fig. 2). The values amounted to 15.7 mg/L in 2015 and 34.1 mg/L in 2016 (UF-1), and 19.3 mg/L in 2016 (UF-12).

Zinc, lead, and iron sulphates occurred in the ore-bearing dolomites which were cut through by the upper section of the “Franciszek” dipheading. These three groups of sulphate minerals, being the main components of the Zn-Pb ores in the Silesia-Kraków Region, contained admixtures of such other metals as arsenic, antimony, cadmium, manganese, copper, nickel, silver, as well as thallium, chromium, and cobalt (Ekiert, 1970; Żabiński, 1963). Taking this into account, the authors paid special attention to the micro-elements associated with zinc and lead ores, as well as carbonate rocks that are cut through by the “Franciszek” dipheading,

i.e. barium and strontium, among all the analysed micro-elements. Additionally, zirconium, rubidium, caesium, and uranium were accounted for, since their concentrations were fairly high in comparison to those of the micro-elements (Table 1).

The concentrations of the analysed trace elements had a very broad ranges of values, from typical ones relating to groundwater to abnormal ones (Table 1). These concentrations also displayed considerable changeability over time, depending on the water residence time and the intensity of the meteoric water infiltration stream in the aeration zone above the “Franciszek” dipheading. Despite this, one can notice a certain regularity of changes in the micro-element concentrations along the working under discussion, from its entrance on land surface to its connection with the underground workings of the “Pomorzany” mine. The largest concentrations were reached by the micro-elements considered here in the water leaks situated in the central and lower sections of the “Franciszek” dipheading. This is demonstrated in the example of the selected micro-elements (Fig. 6).

The results of the chemical composition analyses concerning the water samples collected from the “Dąbrówka” and “Roznos” canals, are visible in Table 1. In both canals, water was poorly alkaline, with a mineralisation rate (TDS) of ca. 0.7 g/L, and it belonged to the Ca-Mg-HCO<sub>3</sub>-SO<sub>4</sub> type. The concentration values of both the main components and micro-elements were close to the lower boundaries of the concentrations relating to the water leaks of the “Franciszek” dipheading in the majority of cases (Table 1).

#### 4. Discussion

The chemical composition of water samples originating from the “Pomorzany” mine workings, cut out of the carbonate Triassic rocks, was shaped by both natural and anthropogenic factors. The significant natural factors included, primarily, the mineral

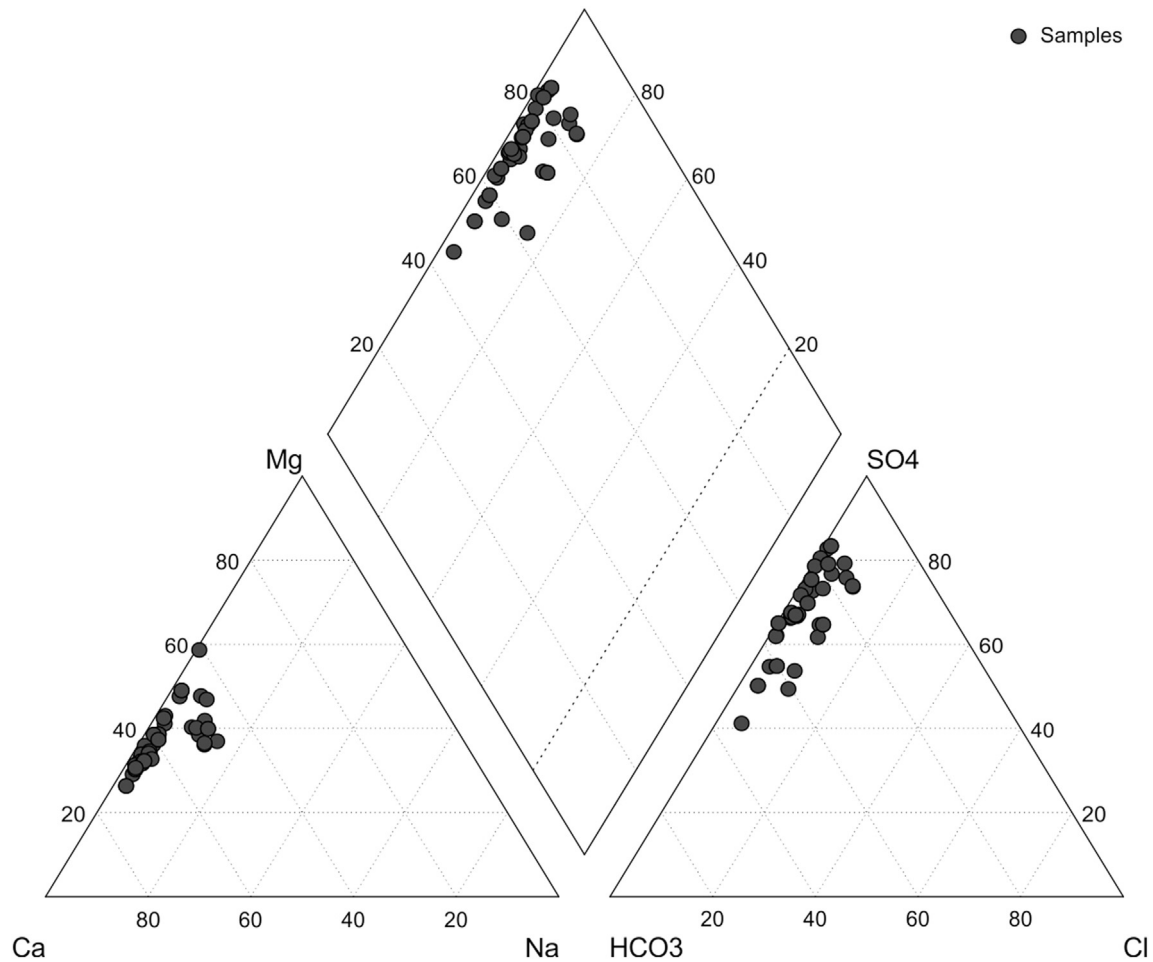
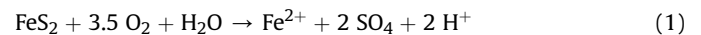


Fig. 4. Piper diagram.

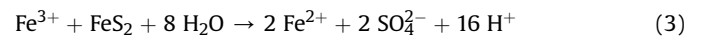
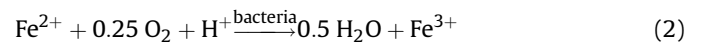
composition of the rocks penetrated by the mine waters and the water residence time in lithosphere. Anthropogenic factors distinguished by Motyka and Witkowski (2002) were divided into internal and external ones. Internal factors were associated with the natural geochemical processes, initiated by human activities. This category included the natural process of the chemical weathering of metal sulphides, initiated by mine drainage and the related change of redox conditions in the rock mass. The above quoted authors identified such external factors as the influences of various human pollution sources located on land surface. Such specific remarks are also true of the “Franciszek” dipheading.

The internal pollution sources, identified in the Triassic carbonate rocks in which the “Pomorzany” mine workings were cut out, including the “Franciszek” dipheading, were created as a result of the dewatering of the rock mass and the change of the original redox conditions, from near reduction to oxidation. This process, associated primarily with the deep and long-term dewatering of the mine, as well as metal sulphide weathering, was named acid mine drainage (AMD) and it occupies a separate and important place in mining hydrogeology.

The weathering of iron sulphides (pyrite and marcasite) was especially unfavourable because their oxidising reactions caused a considerable reduction of pH in the newly created solutions. Oxidation of pyrite and marcasite is taking place in accordance with the following reaction (Bethke, 2008; Clark, 2015; Singer & Stumm, 1970; Stumm & Morgan, 1996; Younger, Banwart, & Hedin, 2002):



with the participation of bacteria, bivalent iron is oxidised to trivalent, followed by a complex iron reduction process leading to a bivalent form. The following reactions occur:



Similar reactions occur in the case of the weathering of other sulphide minerals that are present in the deposit, i.e. sphalerite and galena in the presence of trivalent iron ( $\text{Fe}^{3+}$ ) and water (Dold, 2017). As a result of each of these reactions, the concentration of hydrogen ions is increased, accompanied by the decrease of the pH, equivalent to increased water acidity. Since, metals become increasingly mobile in an acid environment, their concentrations in water solution is also increasing. Depending on the rock types in which such chemical reactions occur, water acidity can be quickly neutralised as a result of the buffering process, which significantly decreases metal mobility. The buffering capability, i.e. in this case, the shift of pH towards an alkaline reaction, is displayed by, for example, carbonate rocks, limestones, and dolomites. The buffering process develops in limestones in accordance with the reaction in which carbon dioxide is one of the products (Bethke, 2008; Torres, West, & Li, 2014):

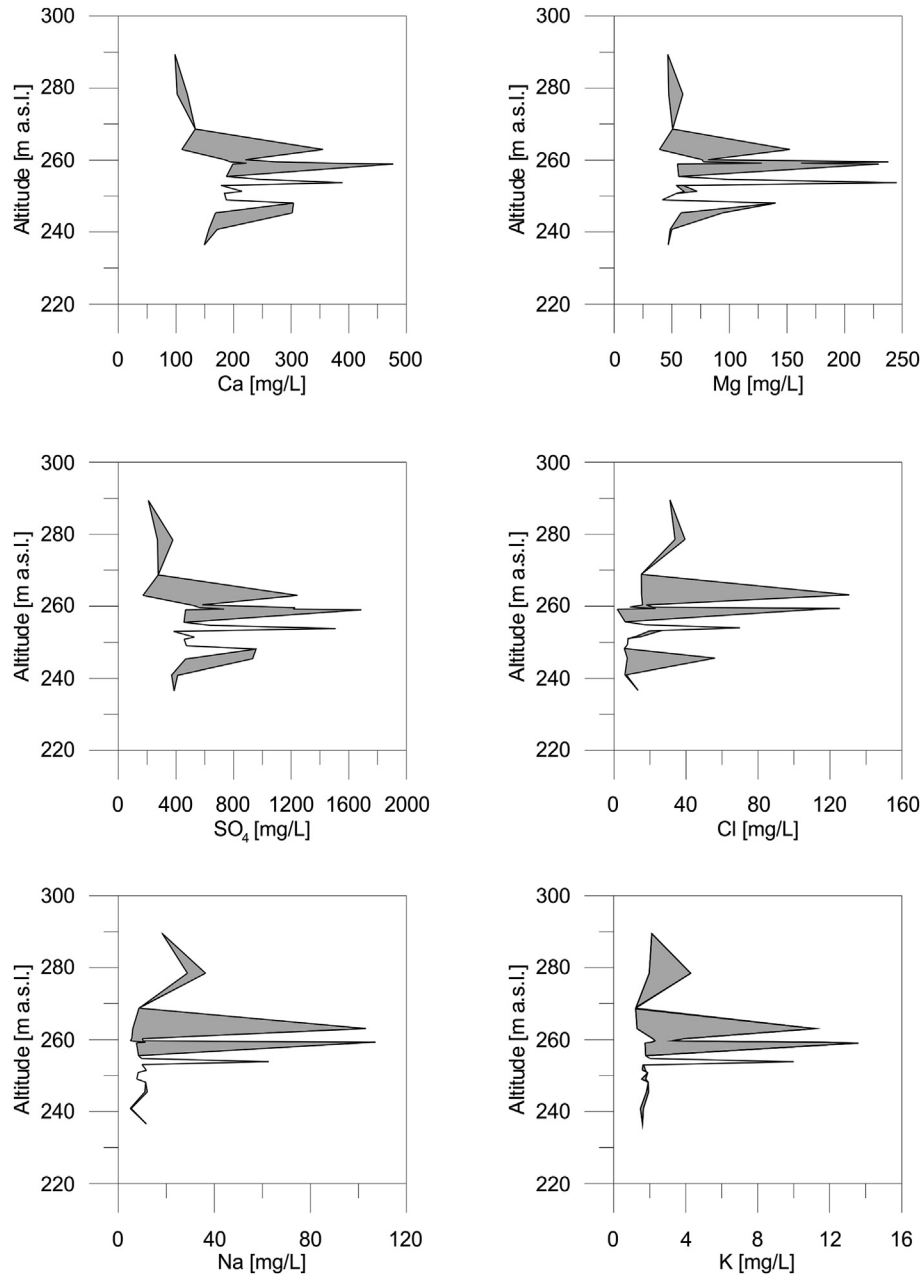
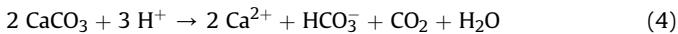
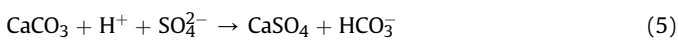


Fig. 5. Macroelements variability with depth.



In the presence of sulphate ion ( $\text{SO}_4^{2-}$ ), calcium sulphate (gypsum and anhydrite) is developed. The solubility of those minerals is higher than that of calcium carbonates by which the concentrations of calcium and sulphates is increasing in the solution. These processes are developing in accordance with the following reaction:



In the samples of water in which such a reaction occurs, one can also observe an increased bicarbonate ion concentration, in addition to increased sulphate content. With adequate water quantity, this reaction produces gypsum ( $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ).

In the dolomite environment, in which the Olkusz zinc and lead ore deposits occur, the buffering process develops in accordance

with the following reaction (Fernandez-Rubio, Fernandez Lorca, & Estaban Arlequi, 1986):



The process of the geochemical transformation in the aeration zone, occurring for metal-sulphide containing rocks is much more complex than that described above. In the dehydrated and oxidised section of the deposit, complex mineralogical forms were developed, usually with the participation of bacteria, and such forms are characteristic for sulphide deposit zone weathering (Kubisz, 1964; Źabiński, 1963). Calcium (gypsum), magnesium (hexahydrate and epsomite), and iron (melanterite) sulphates are the most important

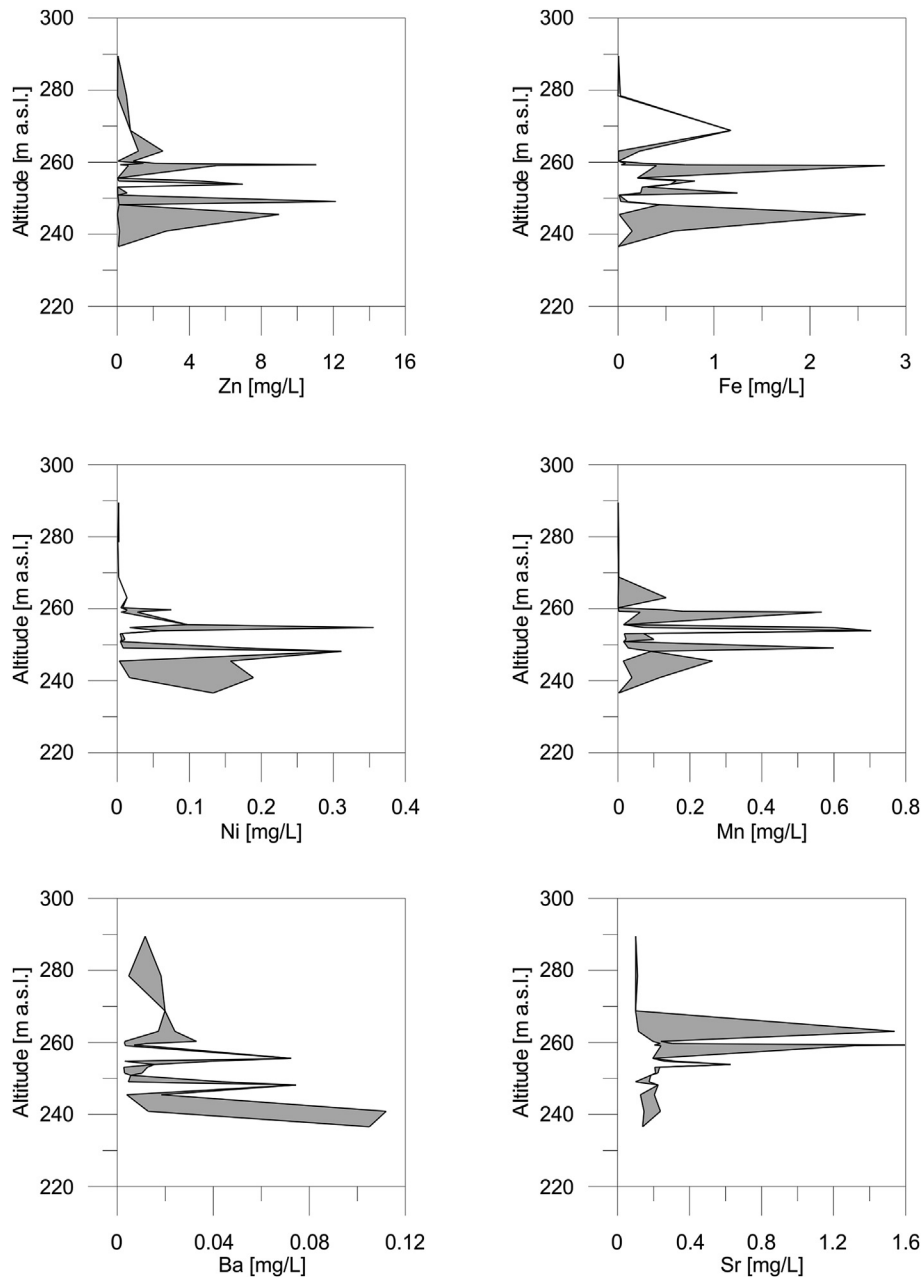


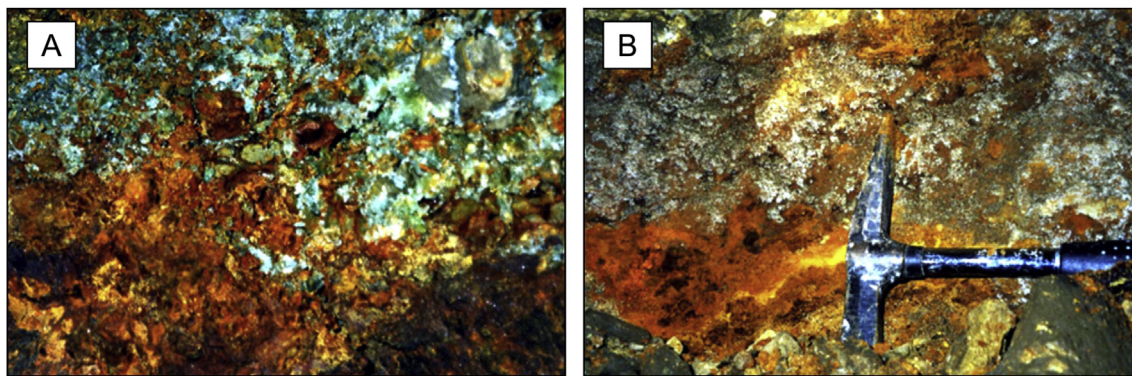
Fig. 6. Selected microelements variability with depth.

from the viewpoint of the shaping of the chemical composition of underground waters in the young aeration zone of the Triassic dolomites and limestones. These minerals commonly occur in the Olkusz ore mine workings (Fig. 7A and B) and they are easily or very easily soluble. The solubility values of certain minerals that are typical for the metal sulphate weathering zone environment in carbonate rocks are as follows (Lide, 2001): calcium sulphate  $\text{CaSO}_4$ : 2050 mg/L, magnesium sulphate  $\text{MgSO}_4$ : 357,000 mg/L, and iron sulphate  $\text{FeSO}_4$ : 295,000 mg/L.

The presence of magnesium and iron sulphates, which are common in the sulphide weathering zone in a dolomite environment, causes an increase of sulphate and magnesium concentrations in the waters migrating through that zone. The ion concentrations in the inflows in the mine workings depend on the groundwater flow rate and the total flow volume.

The infrastructure existing around the “Dąbrówka” shaft (Fig. 3), consisting of office buildings, miner’s social facilities, warehouses, car and mining vehicle garages, storage yards, and an internal road network, constitutes the external pollution source for the leak waters of the “Franciszek” dipheading. Also, the waters infiltrating from the “Roznos” canal, carrying treated water from the town of Olkusz, and the “Dąbrówka” canal, collecting mine water from the western facility of the “Pomorzany” mine, affect groundwater quality. It is hard to identify the pollution that originates from these sources, but, undoubtedly, the increased chloride and sodium ion concentrations occurring in certain leaks in the “Franciszek” dipheading must be traced to these sources.

The concentration of the influences of both geogenic and anthropogenic sources causes the diversity of the chemical compositions of leak waters in the dipheading. The determination of



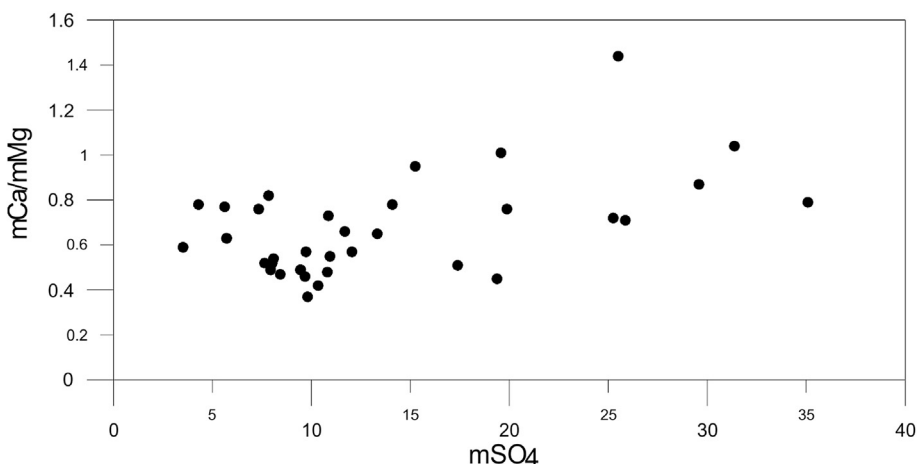
**Fig. 7.** A – An example of melanterite (blue colour) impregnating breccias sulphide of metals (Olkusz mine); B – Examples of metal sulphate weathering products (white colour: magnesium sulphate) among the breccias (Olkusz mine).

the effects of those factors is fairly difficult, owing to the instability of the hydrodynamic field and the high heterogeneity of the geochemical field in the aeration zone above the “Franciszek” dipheading. The instability of the hydrodynamic field is connected with the changing intensity of the meteoric water infiltration stream, depending on the rainfall rate and the pattern of rainfalls over time. The directions of the infiltration water flows depend on the configuration of the hydraulic network and the hydrogeological properties of water conduits (Motyka, 1998; Zuber & Motyka, 1998). The heterogeneity of the geochemical field results from the uneven distribution of metal sulphates in the carbonate rocks that are cut through by the dipheading, as well as various oxidation reaction rates. Nevertheless, a stochastic approach, with a fairly large prediction range, provides us with uncertain interpretational possibilities.

The main natural factor on which the chemical composition of groundwater depends is the mineral composition of the rocks infiltrated by water. In the case of the “Franciszek” dipheading, the rocks primarily include dolomites (Fig. 2). An approximate measure of the influence of the metal sulfide weathering process on the chemical composition of inflows in the particular working under discussion can involve the molar proportion of the magnesium and calcium concentrations (mMg/mCa), when compared to sulphate concentrations. Much higher magnesium sulphate solubility in comparison to that of calcium sulphates provides a premise for such an assumption (Lide, 2001). One can therefore expect that, together with the increase of sulphate concentration, an increase trend of the molar concentration of particular ion proportions will be visible.

In natural groundwater, the theoretical proportion of mMg/mCa molar concentration is close to 1 (Hem, 1992; Witczak, Kania, & Kmieciak, 2013). Nevertheless, the proportion of magnesium and calcium ion concentrations in the groundwater migrating in dolomites depends on other factors as well. Appelo and Postma (1999) emphasised that dolomite dissolution processes are very complex, while Stumm and Morgan (1996) mentioned that water pH and CO<sub>2</sub> content in water were important factors that influenced the dolomite dissolution processes. Hem (1992) wrote that magnesium concentration would tend to increase along the flowpath of groundwater. One can presume that water residence time is indirectly involved in that process. On the other hand, White (1988) stated, on the basis of experimental research, that the dolomite dissolution process had not been fully recognized in the area close to the solution's saturation boundary. According to Ford and Williams (1989), dolomites dissolve selectively. In the first stage of the dissolution process, CaCO<sub>3</sub> passes to the solution faster than MgCO<sub>3</sub>, which is important in the case of discontinuous water flow through the aeration zone.

The remarks quoted above in relation to the solubility of dolomites led to the authors of this study assuming that the mMg/mCa proportions occurring in natural waters from Triassic dolomites can be treated as background for the consideration of the influence of metal sulphate weathering on the carbonate rock environment. “Natural waters” mean here ones in which the changes of the chemical composition, caused by the metal sulphate weathering process, are unnoticeable. The authors used sulphate concentration as the criterion for respective evaluation.



**Fig. 8.** mMg/mCa to mSO<sub>4</sub> relation diagram.



To estimate the mMg/mCa proportion in the waters in which the influence of the metal sulphate weathering process is noticeable, 15 inflows in the “Olkusz” and “Pomorzany” mine workings were selected. Sulphate concentrations occurring in these water inflows were in the range of 26–73 mg/L. The mMg/mCa proportions for these waters ranged from 0.23 to 0.5, with an average value of 0.32. In the case of the “Franciszek” dipheading water leaks, the mMg/mCa molar proportions ranged from 0.37 to 1.44, with sulphate concentrations ranging from 169 to 1665 mg/L (Table 1). Although the increasing trend of the mMg/mCa proportion, together with the increase of SO<sub>4</sub> ion concentrations, was poorly marked, the proportion established in the majority of inflows far exceeded the range of values which are typical for natural waters (Fig. 8).

This conclusion allowed the authors to state that the waters of the “Franciszek” dipheading displayed the influence of the metal sulphate weathering process on their chemical composition in the majority of the water inflows.

Metal sulphate weathering in the carbonate rock environment is a very complex geochemical process. If we add to that the instability of the hydrodynamic field in the aeration zone, our search for regularity in the changeable micro-element concentration in the

water leaks of the “Franciszek” dipheading is rather complicated. The mobility of metals is supported by low pH; however, in a carbonate rock environment, the acid reactions of the solutions developed in the metal sulphide weathering process are quickly neutralised. We are unable to notice the dependence between the concentration of trace elements and the solution’s pH or sulphate concentration, probably owing to the complexity of the chemical reactions that occur in such an environment. This interdependence is shown here in the example of selected trace elements (Fig. 9A and B).

The effects of external contamination sources are visible in the relatively high concentrations of chloride and nitrate ions in certain leaks occurring in the “Franciszek” dipheading (Fig. 5). According to Adamczyk (1998), the natural hydrochemical background is found for Cl ions in the groundwater of the Triassic formation, with the value of ca. 14 mg/L. The majority of water samples collected from the inflows in the “Franciszek” dipheading represented the chloride concentration much exceeding that background value (Fig. 5).

The previously mentioned surface infrastructure, developed around the “Dąbrówka” shaft, is the source of contamination from which chloride, sodium, potassium, and nitrate ions originate. The

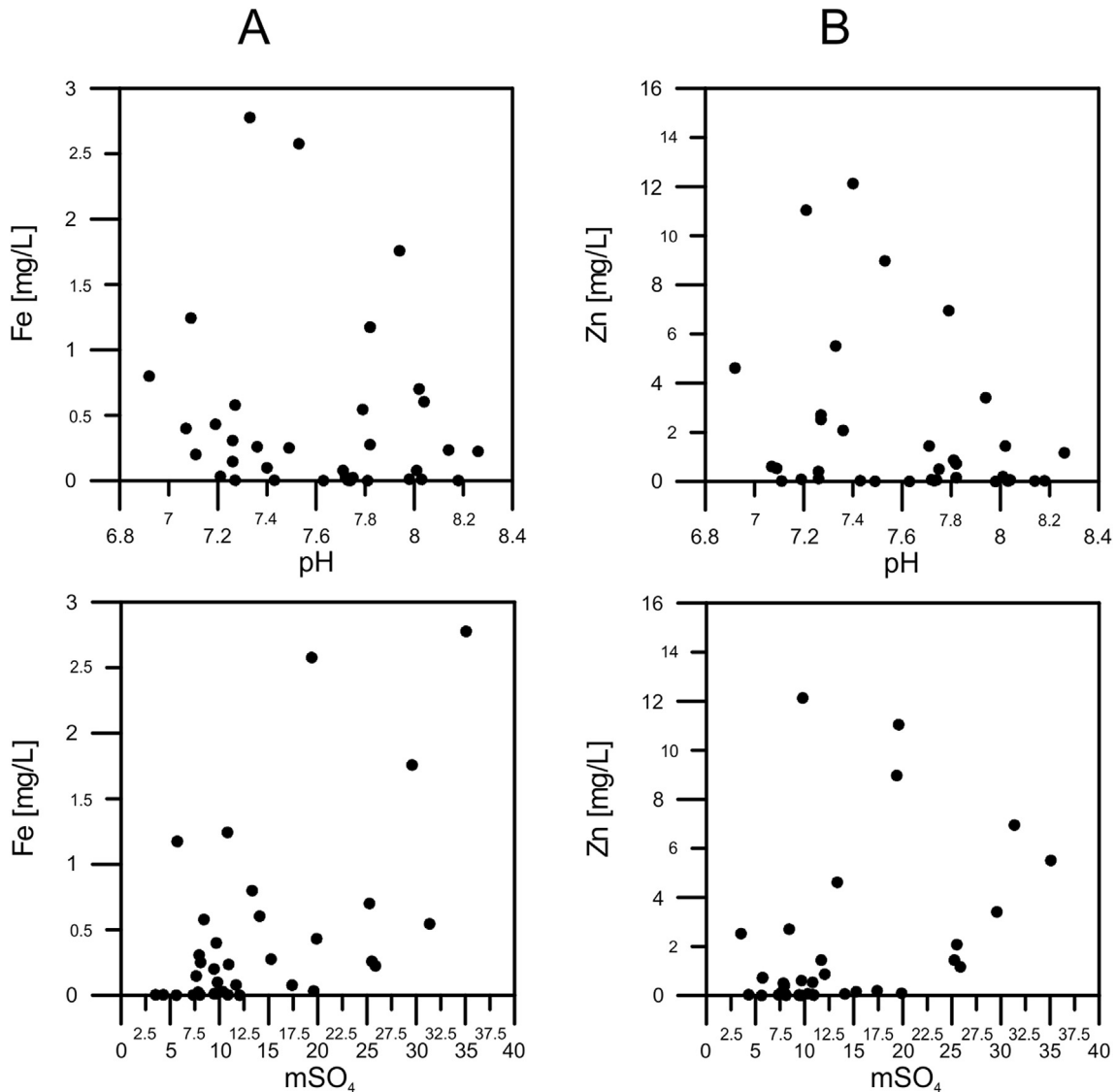


Fig. 9. Selected microelements of pH and rSO<sub>4</sub> relation diagram A – Fe, B – Zn.

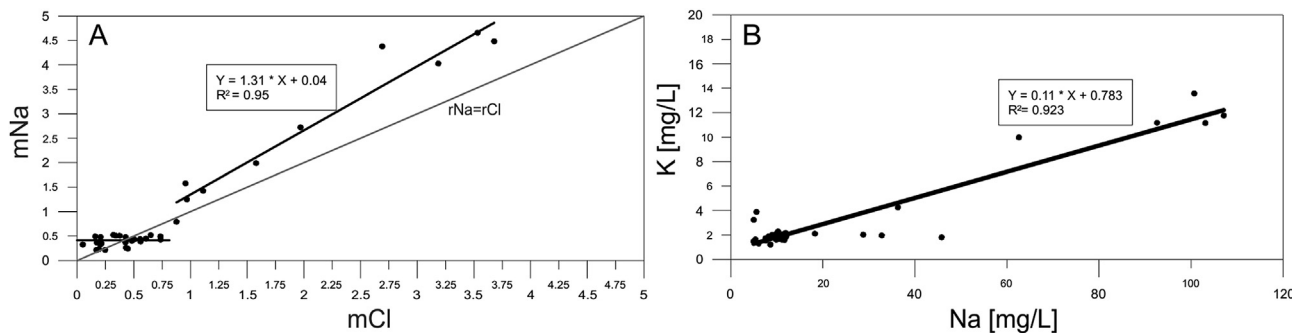


Fig. 10. A. – mNa to mCl relation diagram; B. – K to Na relation diagram.

authors also considered a possible water leakage from the “Roznos” channel that removes treated waste water from the Olkusz waste water treatment plant, as well as from the “Dąbrówka” channel designed for mine waters leaving the “Pomorzany” mine. The “Roznos” channel flows into the “Dąbrówka” channel above the lower section of the “Franciszek” dipheading (Fig. 4). The results of the chemical analysis of the water samples collected from those channels in August 2017 (Table 1) indicated that possible water penetrations might not be the sources of relatively high concentrations of chlorides and sodium found in the dipheading.

It is hard to clearly identify the origin of the Cl, Na, and K ions found in the inflow waters in the “Franciszek” dipheading. The plot of the molar concentrations of Na on Cl (Fig. 10A) does not provide an answer.

If the ions in question originated from the dissolution of sodium chloride, the points shown on the graph should be arranged around the  $mNa = mCl$  line. However, the mCl concentrations are around 0.75 mmol/l (or ca. 27 mg/L), and mNa concentrations are around 0.4 mmol/l (or ca. 10 mg/L). Above these concentrations, the dependence of mNa on mCl is linear, although this is the case above the  $mNa = mCl$  line (Fig. 10A). Most probably, a portion of sodium is associated with bicarbonates and sulphates. The linear dependence of the potassium and sodium concentrations (Fig. 10B) proves that both elements come from the same sources. In the case of the inflows occurring in the “Franciszek” dipheading, one should take into account the municipal liquid waste and the sodium chloride as the sources of the ions under discussion.

To clarify the origin of Cl ions in the inflows of the “Franciszek” dipheading, analysts can consider the proportions between

strontium and calcium (Andreo, Martin-Martin, & Martin-Algarra, 1999; Dogramaci & Herczeg, 2002; Hem, 1992; Hsissou et al., 1996). The mSr/mCa proportion above 1‰ indicates the influence of evaporite dissolution on the chemical composition of water. In the case of the waters occurring in the “Franciszek” dipheading, one can clearly see that, up to the concentration boundary of Cl ions of ca. 40 mg/L, the mSr/mCa proportion is changing within a small range around a value equal to ca. 0.4‰. With higher concentrations of chlorides, the linear dependence of the mSr/mCa proportion on Cl ion concentrations is visible. For higher Cl concentrations, equal to ca. 130 mg/L, the proportion reaches the value of ca. 2‰ (Fig. 11).

Municipal liquid waste, leaking from unsealed sewers, and/or sodium chloride, used for example for winter road de-icing and yard maintenance in the households and facilities surrounding the “Dąbrówka” shaft, could be the sources of chloride ions found in the inflows in the “Franciszek” dipheading. It seems that at lower concentrations of chlorides and when molar proportions of strontium to calcium are much below 1‰, liquid waste is the source of increased chloride concentrations. This premise is additionally supported by the increased concentrations of nitrates, which are essential components of municipal liquid waste, found in the leak samples in which the concentrations of chlorides reaches 1.76–130.6 mg/L were recorded. As to the leak waters in which the chloride concentrations exceeded 40 mg/L, while the molar proportion of strontium to calcium amounted to 1‰, one can assume that Cl ions, as well as those of Na and K, mostly originated from sodium chloride dissolution.

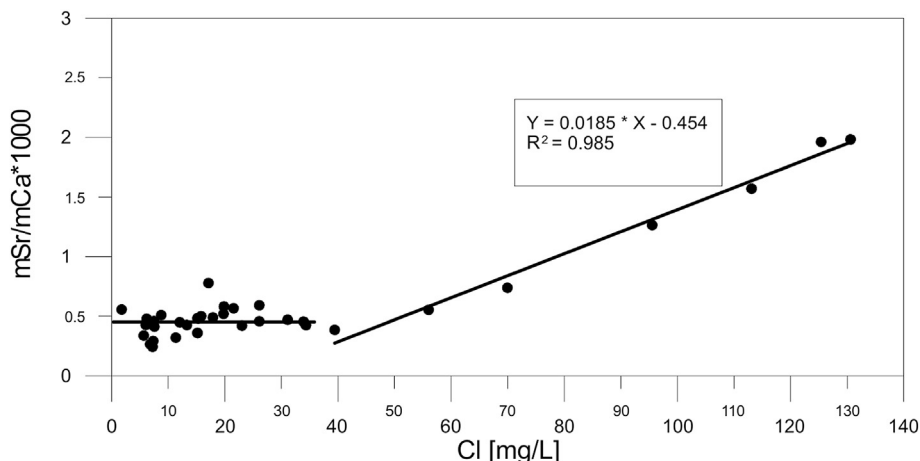


Fig. 11. mSr/mCa × 1000 to Cl relation diagram.

## 5. Conclusions

The “Franciszek” dipheading is one of the main transportation routes cut out in the “Pomorzany” zinc and lead ore mine (situated in the Olkusz Zn-Pb Ore District). The dipheading cuts through dolomites and limestones of the Middle and Lower Triassic, which are host rocks for Zn-Pb ores. The overburden of these rocks contains Quaternary sands, with a thickness reaching 55 m. The rocks which exist above the dipheading were dewatered as a result of mine drainage and, for that reason, the facility is situated in a relatively young aeration zone.

The aeration zone situated above the “Franciszek” dipheading, composed of Quaternary sands (porous rocks), and Triassic dolomites limestones (fissured-karstic type of rocks), being lithologically diverse, creates very complex conditions for the flow of infiltrating meteoric waters.

The majority of the water inflows occurring in the “Franciszek” dipheading appears temporarily after copious rainfalls or thaws. A considerable diversity of streams of the infiltrating meteoric water recharge, supplemented by complex geochemical processes that occur in the aeration zone above the dipheading, essentially influence the chemical composition of leak waters found in the working. Finally, the chemical composition of a specific water sample collected at a particular time is an effect of the mineral composition complex consisting of the rocks infiltrated by meteoric waters, dissolution of the products of sulphide mineral weathering, and the influences of external contamination sources originating from the land surface above the “Franciszek” dipheading.

Meteoric waters infiltrating the rock mass migrate through Quaternary sands and Triassic dolomites and limestones that are cut through by the dipheading. The dissolution of carbonate rocks by the migrating meteoric waters produces water of the Ca-Mg-HCO<sub>3</sub> type. Oxidation of metal sulphides in the environment of dolomites and limestones causes the development of acid mine drainage (AMD) solutions, with their concurrent neutralization. This process results in the occurrence of very easily soluble hydroxysulphates, mainly of calcium, magnesium, and iron. Dissolution of these minerals increases the concentration of, primarily, calcium and magnesium, as well as iron, zinc, and other metals which occur within zinc and lead ores (arsenic, nickel, cobalt, cadmium, and thallium). Owing to a large difference in the solubility of calcium and magnesium sulphates, the molar proportion of magnesium to calcium concentrations is increasing, together with the increase of sulphate concentrations. Above the value of 0.5 in water inflows originating from the above described process, magnesium concentration is increasing more than that of calcium. Consequently, one can observe an increasing trend of the molar concentration proportions of magnesium to calcium, especially at higher concentrations of sulphates (above 800 mg/L). Metal concentrations found in the tested waters did not correlate with pH values or sulphate concentrations.

The chemical composition of inflows sampled in the “Franciszek” dipheading was also influenced by anthropogenic contamination sources identified on land surface. Such contamination was visible primarily in the increased concentrations of chlorides, sodium, and potassium in certain leaks, and also of nitrates in a few cases. Based on the analysis of molar proportions of sodium and chlorides,  $mNa = f(mCl)$ , it was recognized that, up to the Cl ion concentration value equal to ca. 40 mg/L, those ions originated from the admixtures of municipal liquid waste leaks, entering the infiltrating meteoric waters. Liquid waste flew out of unsealed sewers located within the households and industrial facilities around the “Dąbrówka” shaft. Cl, Na, and K ions, occurred in higher

concentrations than background values, most probably due to sodium chloride because of waters flowing from the land surface and infiltrating the “Franciszek” dipheading. It is also probable that sodium chloride originated from winter road maintenance operations carried out above the dipheading.

## References

- Adamczyk, A. F. (1998). Hydrogeologiczne i hydrochemiczne warunki udostępnienia złożeń rud Zn-Pb Olkusz-Podpoziom [Hydrogeological and hydrochemical conditions of the development of Zn-Pb ore deposit Olkusz-Sub-level]. *Gospodarka Surowcami Mineralnymi*, 14(1), 51–67.
- Andreo, B., Martin-Martín, M., & Martín-Algarra, A. (1999). Hydrochemistry of spring water associated with travertines. Example of the Sierra de la Alifanera (Granada, southern Spain). *Comptes Rendus de l'Académie des Sciences-Series IIA-Earth and Planetary Science*, 328(11), 745–750.
- Appelo, C. A. J., & Postma, D. (1999). *Geochemistry, groundwater and pollution*. Rotterdam: A.A. Balkema.
- Bethke, C. M. (2008). *Geochemical and biogeochemical reaction modeling* (2<sup>nd</sup> ed.). Cambridge: Cambridge University Press.
- Clark, I. (2015). *Groundwater geochemistry and isotopes*. Boca Raton: CRC Press.
- Dogramaci, S. S., & Herczeg, A. L. (2002). Strontium and carbon isotope constraints on carbon-solution interactions and inter-aquifer mixing in groundwater of the semi-arid Murray Basin, Australia. *Journal of Hydrology*, 262(1–4), 50–67.
- Dold, B. (2017). Acid rock drainage prediction: A critical review. *Journal of Geochemical Exploration*, 172, 120–132.
- Ekiert, F. (1970). Występowanie utworów mezozoicznych w Polsce. Obszar pozakarpaccy. Rudy cynku i ołowiu [Occurrence of Mesozoic works in Poland. Extra-Carpathian area. Zinc and lead ore]. In R. Osika (Ed.), *Geologia i surowce mineralne Polski* (pp. 408–418). Biuletyn Instytutu. Geologii, 251. Warszawa: Wydawnictwo Geologiczne.
- Fernandez-Rubio, R., Fernandez Lorca, S., & Estaban Arlequi, J. (1986). *Abandono de minas. Impacto hidrológico [Abandonment of mines. Hydrological impact]*. Madrid: Imprenta IDEAL.
- Ford, D., & Williams, P. (1989). *Karst geomorphology and hydrology*. London: Chapman & Hall.
- Hem, J. D. (1992). *Study and interpretation of the chemical characteristics of natural water*. Alexandria: US Government Printing Office.
- Hsissou, Y., Chauve, P., Mania, J., Mangin, A., Bakalowicz, M., & Gaiz, A. (1996). Caractérisation des eaux de l'aquifère turonien du bassin du Tadla (Maroc) par le rapport des concentrations molaires Sr<sup>2+</sup>/Ca<sup>2+</sup> [Characterization of the waters of the Turon aquifer of the Tadla basin (Morocco) by the ratio of the molar concentrations Sr<sup>2+</sup>/Ca<sup>2+</sup>]. *Journal of Hydrology*, 183(3–4), 445–451.
- Kubisz, J. (1964). *Studium siarczanowych minerałów hipergeniczných polski [Study of the sulfuric minerals of Poland]*. Prace Geologiczne PAN. 26. Warszawa: Wydawnictwo Geologiczne.
- Lide, D. R. (2001). *CRC handbook of chemistry and physics*. Boca Raton: CRC Press.
- Motyka, J. (1998). A conceptual model of hydraulic networks in carbonate rocks, illustrated by examples from Poland. *Hydrogeology Journal*, 6(4), 469–482.
- Motyka, J., Adamczyk, Z., & Juško, K. (2016). Dopywy wody do olkuskich kopaliń rud cynku i ołowiu w ujęciu historycznym [The historical view of the water inflows to the Olkusz zinc and lead mines (SW Poland)]. *Polish Mining Review*, 72(6), 49–58.
- Motyka, J., & Wilk, Z. (1976). Pionowe zróżnicowanie wodoprzepuszczalności węglanowych skał triasowych w świetle statystycznej analizy wyników próbnych pompowań (monoklina śląsko-krakowska) [Vertical differentiation in the water permeability of carbonate triassic rocks in the light of a statistical analysis of the results of pumping tests (Silesia-Cracow monocline)]. *Geological Quarterly*, 20(2), 381–399.
- Motyka, J., & Witkowski, A. J. (2002). Groundwater contamination in the area of Zn-Pb ore mines situated in the southern part of the Olkusz-Zawiercie Triassic aquifer (Poland). In B. J. Merkel, B. Planer-Friedrich, & C. Wolkerdorfer (Eds.), *Uranium in the aquatic environment. Proceedings of the International Conference Uranium Mining and Hydrogeology III and the IMWA Symposium*. Freiberg, Germany, 15-21.09.2002 (pp. 993–1001). Berlin, Heidelberg: Springer-Verlag.
- Singer, P. C., & Stumm, W. (1970). Acid mine drainage: The rate-determining step. *Science*, 167, 1121–1123.
- Stumm, W., & Morgan, J. J. (1996). *Aquatic chemistry: Chemical equilibria and rates in natural waters*. New York: John Wiley & Sons Inc.
- Torres, M. A., West, A. J., & Li, G. (2014). Sulphide oxidation and carbonate dissolution as a source of CO<sub>2</sub> over geological timescale. *Nature*, 507, 346–349.
- White, W. B. (1988). *Geomorphology and hydrology of karst terrains*. Oxford: Oxford University Press.
- Wirth, L., Motyka, J., Leach, D., Sass-Gustkiewicz, M., Szuwarzyński, M., Adamczyk, Z., et al. (2003). *Water-quality data at selected sites in the Mississippi valley type Zn-Pb ore district of upper Silesia, Poland*. USGS Open-File Report. 283. Reston, Virginia: U.S. Geological Survey.
- Witczak, S., Kania, J., & Kmiecik, E. (2013). *Biblioteka Monitoringu Środowiska. Katalog wybranych fizycznych i chemicznych wskaźników zanieczyszczeń wód podziemnych i metod ich oznaczania. T. 2 [Catalog of selected physical and*

- chemical indicators of groundwater pollution and their methods of determination. Vol. 2]. Warszawa: Oikos.
- Younger, P. L., Banwart, S. A., & Hedin, R. S. (2002). *Mine water. Hydrology, pollution, remediation*. Dordrecht, Boston, London: Kluwer Academic Publisher.
- Żabiński, W. (1963). Z badań geochemicznych strefy utlenienia śląsko-krakowskich złóż kruszców cynku i ołowiu [From the geochemical studies of the oxidation zone of Silesian-Cracow Zinc and Lead Ore Deposits]. *Prace Geologiczne PAN*, 19, 49–84.
- Zuber, A., & Motyka, J. (1998). Hydraulic and solute velocities in triple-porosity karstic-fissured-porous carbonate aquifers: Case studies in southern Poland. *Environmental Geology*, 34(2–3), 243–250.