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Potential influence of drill cuttings landfill on groundwater quality—comparison of leaching tests results and groundwater composition

Justyna Kujawska, Małgorzata Pawłowska*, Wojciech Cel, Artur Pawłowski

Environmental Engineering Faculty, Technical University of Lublin, Nadbystrzycka 40B, 20-618 Lublin, Poland, Tel. +48 81538 4409; email: m.pawlowska@pollub.pl (M. Pawłowska)

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ABSTRACT

Real and potential environmental effects of drill cuttings deposition in open-mining pit were studied. An analysis of selected parameters of deposited drilling waste, groundwater taken from piezometers and eluates obtained during batch leaching tests of drill cuttings was the basis for the estimation. The high concentrations of barium, lead, and zinc in drilling waste (maximum measured values equal to 54; 152; and 438 mg/kg dry weight, respectively) do not allow to classify the examined materials as inert waste from the extractive industries. The groundwater taken from the piezometers located around the drilling waste landfill contained high concentrations of total organic carbon (up to 21.9 mgC/L) boron, calcium, magnesium, manganese, aluminum, and potassium (up to 2.12; 455; 148; 1.75; 5.11; and 25 mg/L, respectively). In contrast to this observation, concentrations of barium and chlorides were the most exceeded in the batch leaching tests. It suggests that pollution of groundwater was not caused by drilling waste deposition.

Keywords: Drill cuttings; Heavy metals; Elution tests; Groundwater quality

1. Introduction

The fuel and energy industry is essential for the development of modern world. The crisis of 1973, when the OPEC countries dramatically elevated oil prices, thus limiting its supply, showed the world how important fossil fuels are. A number of countries commenced actions toward achieving energy independence. The greatest changes were introduced by France, which developed nuclear power to the point where virtually entire energy demand in this country is covered by nuclear power plants. On the other hand, Brazil developed the sugar cane bioethanol production, becoming the top producer of this fuel in the world [1].

Despite decreasing energy consumption of industry, which over the years 1973–2013 dropped by 32%, a global increase in fuel consumption is observed. In 1990, 8,109 billion tons of coal equivalent were consumed, while in 2013, the consumption increased by 65%. A further increase to 16,632 billion tons of coal equivalent is projected to take place in 2030 [2]. At present, 80% of energy comes from the combustion of fossil fuels. The demand for energy till 2035 is forecast to increase by 40%. Therefore, energy supply issue will be one of the greatest challenges facing humanity [3–6].

In recent years, extraction of shale gas underwent rapid development [7–10]. The development of shale gas extraction gives hope for lowering CO_2 emission

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*Corresponding author.

from energy industry, on the one hand, and raises significant concerns regarding environmental pollution during search and exploitation, on the other hand [11]. Ground and surface waters, soil and atmosphere are potentially endangered. Apart from that, large amounts of drilling waste are produced during the search and extraction of shale gas. These wastes include drill cuttings, spent drilling fluid and flow back waters.

Drill cuttings comprise rocks from drilling, which surface along with drilling fluid. During the search for shale gas, oil-based or water-based fluids are used. Drilling fluids contain numerous chemical compounds that are potentially harmful to the environment.

In Poland, management of drill cuttings most often involves dumping it in landfills. Ordinary drilling waste is not considered hazardous and its deposition does not entail employing special protective barriers. However, taking into consideration the composition of drilling fluids, especially the heavy metals, there is the risk of accumulating the pollutants in various environment elements, which may have a negative impact on the quality of water and lands adjacent to the landfill. Heavy metals are elements listed in Annex 4 to the Polish Act on waste [12], meaning that they might be hazardous. Moreover, these metals are capable of accumulating in tissues, which amplifies their detrimental effects. On the other hand, heavy metals are microelements necessary for the proper functioning of plants. Therefore, it is important to determine their concentrations, rather than their presence. In order to assess whether drill cuttings are hazardous to the environment, it is necessary to specify which detrimental substances are found in them and what are their concentrations.

The aim of this study was to assess the impact of the landfill of drill cuttings, created during the search for shale gas in eastern Poland, on groundwaters. The assessment was carried out on the basis of analysis of composition of drill cuttings deposited in the landfill and water collected from piezometers placed in its neighborhood. Laboratory tests regarding leaching of selected chemical pollutants from drill cuttings were also conducted. A comparison of laboratory and field test results was the basis for determining the causes of groundwater pollution.

2. Materials and methods

2.1. Mining waste deposition site

Examinations were carried out at the facility of mining waste, produced during shale gas searching in eastern Poland. In this facility, drilling waste (drilling fluids with cuttings) are mixed with coagulant—aluminum sulfate (VI) (up to a few percent), dewatered in chamber filter press, mixed with cement (up to 10%) and in such form deposited in open mining pit.

Samples of waste were gathered in 24 randomly chosen measurement points on the landfill. In three of them, placed on a straight line going through the middle of the landfill, samples were taken 5 (Point A), 50 (Point B), and 100 m (Point C) from its edge at the depth of roughly 0.5 and 1.5 m.

Samples of water were taken from piezometers placed in three points around the landfill. Two piezometers collecting water from different depths are found in each point (Table 1). Piezometers marked as PC I are placed in the northmost and highest part of the landfill, adjacent to arable lands. PC II piezometers are 130 m southwest from the highest point and are found in a place with high water accumulation for most of the year. PC III piezometers are 290 m west from the highest part of the landfill and are located in the sawmill area. The location of piezometers in relation to the landfill is presented in Fig. 1.

2.2. Analytical methods

The following parameters were determined in the samples of waste collected from the landfill:

(1) pH value by means of potentiometric method in water solution and in 1 M solution of potassium chloride (PN-ISO 10390: 1997P soil quality. Determination of pH).

(2) Dry matter content by means of loss on drying method in the temperature of 105˚C (PN-ISO 11465:1999P soil quality. Determination of dry matter content of soil and water in soil per dry mass of soil. Gravimetric method).

(3) Volatile solids content by means of loss on ignition method in the temperature of 550˚C.

(4) Specific gravity (ρ_s), Le Chatelier flask method, in the temperature of 22˚C.

(5) Bulk density (ρ_b), Kopecky's cylinder method with standard volume of 100 mL.

(6) Total porosity (n) was calculated on the basis of actual density and volumetric density, according to the following equation:

$$n = \frac{\rho_s - \rho_b}{\rho_s} 100\%$$

(1) Carbonate content was determined with Scheibler's volumetric method.

Table 1
Data pertaining to the groundwater intake points

Name	Altitude [m]	Piezometer depth measured from the surface [m]	Water table depth measured from the surface [m]
PC I Q	237	6.1	4.20
PC I T		17.0	4.40
PC II Q	229	6.2	5.10
PC II T		17.5	4.90
PC III Q	225	6.0	3.40
PC III T		16.5	3.10

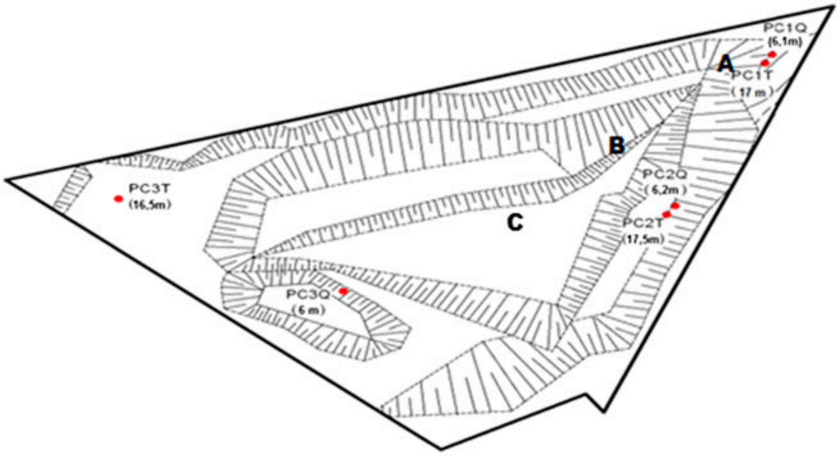

Fig. 1. Location of piezometers on waste deposition landfill. The depth of piezometers is given in brackets.

(2) Saturated hydraulic conductivity *K*sat was determined with California Test Method 220.
(3) Mineralogical composition was determined with X-ray diffraction method (XRD).
(4) Content of selected elements, including heavy metals, was determined with X-ray fluorescence spectroscopy.

Having examined the properties of waste, their water solutions were prepared in the solid to liquid phase ratio of 1 kg: 10 L. Leachability of selected elements, including heavy metals was determined by means of a single batch test (in line with PN-EN 12457-2:2006 standard).

The following parameters were determined using eluates acquired from leaching drill cuttings and in water from piezometers:

(1) pH value and electrolytic conductivity with potentiometric method by means of Orion Versa Star multiparameter meter.
(2) Chloride content with Mohr argentometric method.
(3) Content of elements: Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Na, Ni, Pb, Sn, and Zn were determined by ICP-OES Ultrace 238 (Jobin Yvon-Horriba France) using direct calibration method after microwave digestion (Multiwave 3000, Anton Paar). The samples of homogenized soil (1 g) were digested in acid mixture of HNO_3:HCl (5:2) and water samples (15 g) were digested in HNO_3 (3 mL). The digestion process lasted 45 min at 180˚C and at the pressure of 18 bars. Metal concentrations were determined at different wavelengths (213–395 nm). Detection limits for particular metals did not exceed 10 ppb.
(4) Organic carbon content, by means of TOC-5050A analyzer Schimadzu (PN-ISO 4335 standard).
(5) Sulfate ions content was determined using spectrophotometry on the basis of HACH 8051 PBL/CH/28/06 method, issue 02 of 07.11.2011.

3. Results and discussion

3.1. Mineralogical composition of drill cuttings

The main mineral components of examined drill cuttings are clay minerals, amounting to 45.5% of weight on average. Clay minerals are characterized with high specific surface area and low hydraulic conductivity, which allow them to sorb surface pollutions. According to XRD analysis, drill cuttings contain quarts (27.4% of weight), dolomite (10.7%), potassium feldspar (2.6%), sodium–calcium feldspar (3.1%), pyrite (2.4%), and kerogen (1.3%).

Minerals found in the waste, such as quartz, silicates, and alumina silicates; carbonates, such as calcite or dolomite, are considered to be not hazardous to the environment. However, pyrite (FeS_2) can pose a threat to the environment. Oxidization of pyrite occurs with the participation of oxidizing agents such as oxygen and nitrates [13]. The pyrite oxidation products are conducive to the dissolving processes of carbonate minerals in rock material [14]. In the case of supersaturation of water solution with calcium or magnesium sulfates or other cations, secondary materials such as gypsum may be precipitated [15].

3.2. Physical and chemical properties of drill cuttings

According to the data presented in Table 2, a sand fraction (2-0.05 mm) comprising 65–90% of total mass in each examined sample was the dominant in the granulometric composition of drill cuttings examined in the unfragmented (natural) state. Silt fraction (0.05-0.002 mm) constituted 5–30%, while clay fraction (<0.002 mm) only 2–13% of total material mass (Table 2). The considered waste may be classified geotechnically as fine grain mineral material (according to PN-EN ISO 14688-1:2006 standard—classification of soils—Part 1: classification and description). Granulometric composition determines many physical and physicochemical properties of the material, including water and air permeability and sorption properties. Physical properties of waste deposited on landfill are essential considering the evaluation of pollution migration into the layer of waste. Low share of silt and clay fraction increases permeability and lowers the sorption capacity in relation to cations, while the large share of silt increases susceptibility of material to water erosion. Granulometric composition of drilling waste depends not only on the type of drilled rocks but also on the type of tool and drilling technique [16].

Saturated hydraulic conductivity (*Ks*), determined under laboratory conditions ranges from 1.04×10^{-4} to 2.23×10^{-4} m/s (Table 2). This parameter is higher even in comparison with sand materials examined by Widomski et al. [17,18], in which case it amounted to 8.9×10^{-5} m/s. Taking water permeability into consideration, the examined drill cuttings deposited on landfill can be classified as highly permeable. High hydraulic conductivity is connected with granulometric composition, in which sand fraction comprises 70%. Such level of water permeability is conducive to the migration of potential pollutants to groundwater.

Average specific gravity of drill cuttings, amounting to 2.64 ± 0.07 g/mL is lower than the density of mineral formations which have the density comparable or higher than quartz (2.65 g/mL). This phenomenon can be attributed to a high volatile solids content, reaching up to 11.52 of dry weight. Drilling fluid is probably the source of organic substances as it contains base substances or ones altering the drill fluid properties. Organic substances content impacts mechanical and physicochemical parameters of soils. It determines porosity, sorption capacity in relation to water and various components, including heavy

Table 2
Granulometric composition and selected parameters of drilling waste (*n* = 30)

Parameter	Mean value	Standard deviation
Granulometric composition		
Sand fraction [% Weight]	78.33	8.57
Silt fraction [% Weight]	14.56	7.54
Clay fraction [% Weight]	7.11	3.41
Specific gravity [g/mL]	2.64	0.07
Bulk density [g/mL]	0.85	0.07
Total porosity [% obj.]	67.64	2.76
Saturated hydraulic conductivity K_s [m/s]	1.53×10^{-4}	2.1×10^{-5}
Carbonate content [% dry weight]	36.49	8.22
Volatile solids content [% dry weight]	11.52	2.46
pH	9.46	1.23

metals, which may limit their migration to land and aquatic environments. However, binding of cations by organic substance is significantly less durable than in the case of sorption on clay materials.

Drill cuttings taken from the landfill were characterized by low bulk density, equaling 0.85 g/mL as well as high porosity amounting to 67.64% of volume on average. While assessing soil compaction on the basis of criteria for soils, it was noted that these materials are medium compacted.

The examined drill cuttings are characterized by alkaline pH, ranging from 8 to 11. Such pH potentially eliminates the migration of heavy metals to the soil solution and also to the groundwaters. The high content of alkaline cations, i.e. Ca^{2+}, Na^{+}, and Mg^{2+} determines the alkalinity of waste. Some of these ions may be bound as carbonates.

3.3. Content of selected elements in drill cuttings deposited on landfill

The content of such elements as As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, V, and Zn is one of the five criteria for the evaluation of mining waste in terms of their classification to the category of neutral waste [19]. Waste can be regarded as neutral only when all the criteria are met in both short-term and long-term perspectives. In regard to the content of compounds of afore-mentioned elements, waste can be considered inert if soil quality standards for group B are met (according to [20]). This group includes, among others, agricultural area and forestland. Vanadium is not included in the case of soil and earth quality assessment, and therefore its permissible content in the waste from extractive industries was specified in the relevant regulation [19] and cannot exceed 500 mg/kg dry weight.

According to McFarland et al. [21], heavy metals usually found in drill cuttings in high concentrations include arsenic, barium, chromium, copper, lead, nickel, and zinc. Elevated concentrations of barium, lead, and zinc were found in the examined waste. Average barium concentrations and maximum Pb and Zn values in waste exceeded the standards for quality of soil and earth of group B (Table 3). Hence, the considered extractive industries' waste cannot be regarded as inert. The concentration of Zn reached 438 mg/kg d.m, while the concentration of lead—152 mg/kg dry weight. Kabata-Pendias [22] stated that the content of Zn ranging from 100 to 400 mg/kg dry weight and Pb from 30 to 300 is considered harmful to plants, with zinc being the more common element than lead. Mobility of zinc increases when pH drops below 6–6.5, while mobility of lead rises significantly when pH drops below 5 [23]. Drill cuttings are characterized by high pH; therefore, it can be assumed that the bioavailability of metals to plants planted on the landfill surface during its remediation phase will be low.

The considered material also did not met the quality standards for group C according to the regulation of the Polish Minister of Environment [20], which includes industrial lands, mining grounds, and transportation areas, due to exceeded barium levels. The content of this element in drill cuttings on landfill is several dozen times higher than the permissible level for materials belonging to this group. The content of barium in rocks and soils from different parts of the world range from 20 to 2,000 mg/kg, while higher values were noted in materials with a large share of silt or clay [22]. Drilling fluids are a source of barium, where it increases density. Toxicity of this element for animals mainly depends on solubility of the compound including it in water.

In the case of drill cuttings, barium is present predominantly in the form of sulfates (barite), which are insoluble in water, and therefore constitutes insignificant hazard to the environment. Barium sulfate (VI) is excluded from the list of compounds causing waste to become harmful to the environment (Annex 4 [18]).

High concentrations of Fe, amounting to 10,690.6 mg/kg dry weight on average, were found in drill cuttings. However, the concentration of this element is not limited by the relevant regulation [20]. Iron is a natural component of numerous soil-forming minerals; therefore, it is found there in large quantities. The content of iron in drill cuttings is comparable to the one found in urban environment, reaching up to 16,790 mg/kg dry weight. Most of the chemical forms of iron in soils are difficult to access by plants [24]. Bioavailability of iron for plants drops as pH and carbonate content increases in the base [25]. Taking both these parameters into consideration, it can be stated that availability of iron is low.

Content of strontium is also not limited by the regulations regarding waste. However, it was noted that the considered waste contains elevated amounts of this element in relation to soils, equaling 1451.78 mg/kg dry weight of waste on average. Concentrations of strontium in Polish arable lands measured in 2010 usually ranged from 1.7 to 58 mg/kg [26]. Strontium salts are widely used in drilling fluids [27], which explains its increased concentrations in drill cuttings. Moreover, strontium is relatively common in the surface layers of Earth's crust. It is a natural component of rocks, found in minerals such as strontium sulfate (celestine) and strontium carbonate (strontianite). The geochemical characteristic of

Table 3
Concentration of selected metals [mg/kg dry weight] in samples of drilling waste taken from the landfill

	Cu	Pb	Zn	Ni	As	Sn	Cd	Cr	Ba	Fe	Sr
Point A–from surface	56	71	201	38	10	<d.l	<d.l	9.80	53,750	10,380	1,566
Point A–from the depth of approximately 0.5 m	56	<d.l	200	0	8	<d.l	<d.l	7.43	44,261	10,058	970
Point A–from the depth of approximately 1.5 m	49	<d.l	194	41	<d.l	<d.l	<d.l	8.23	41,878	12,941	1,068
Point B–from surface	52	73	233	<d.l	12	<d.l	<d.l	6.30	53,178	11,279	1,567
Point B–from the depth of approximately 0.5 m	68	<d.l	438	46	9	<d.l	<d.l	6.25	56,410	7,494	1,594
Point B–from the depth of approximately 1.5 m	40	63	271	<d.l	<d.l	<dl	<d.l	5.78	55,019	8,906	1,577
Point C–from surface	45	152	163	<d.l	11	<d.l	<d.l	4.70	28,641	15,911	1,058
Point C–from the depth of approximately 0.5 m	52	51	257	<d.l	9	<d.l	<d.l	5.30	71,777	9,167	1,838
Point C–from the depth of approximately 1.5 m	66	<d.l	235	48	<d.l	<d.l	<d.l	1.1	87,007	10,079	1,828
Mean value from all measurements	53.78	45.56	243.56	19.22	6.56	–	–	6.09	54,657.9	10,690.6	1,451.78
Standard deviations	9.77	55.97	92.83	22.18	5.02	–	–	2.44	19,102.7	2,802.40	339.51
Minimum value	40	<d.l	163	<d.l	<d.l	–	–	1.1	28,641	7,494	970
Maximum value	68	152	438	48	12	–	–	9.80	87,007	15,911	1,838
Mean value for the samples gathered from surface	71.29	116.50	197.57	23.64	12.57	4.14	<1	5.02	65,494.79	7,866.86	1,223.07
Minimum value	<d.l	<d.l	149	<d.l	<d.l	<d.l	<d.l	1.0	17,245	305	947
Maximum value	256	240	261	45	51	33	-	8.98	345,743	12,180	1,719
Standard deviation	56.27	71.43	37.24	17.63	16.48	10.65	-	2.22	84,899.15	3,132.89	233.85
Permissible concentration in soils for group B$^{(a)}$, depth 0.3–15 m, $Ks \geq 1 \times 10^{-7}$	100	100	350	50	20	30	5	150	250	–	–
Permissible concentration in soils for group C$^{(a)}$, depth 0 −2 m	600	600	1,000	300	60	350	15	500	1,000	–	–

[a] Notes: Limit values given in regulation on soil quality standards [20].

Ks– saturated hydraulic conductivity [m/s].

strontium is similar to the one of calcium, which is why these elements are often found together in soil [22]. Strontium compounds are soluble in water and may infiltrate into groundwaters or be absorbed by plants. However, the presence of calcium and magnesium in soil solution limits strontium uptake [26].

3.4. Examination of water taken from piezometers around the landfill

Groundwaters were taken from six piezometers (PCIT, PCIIT, PCIIIT, PCIQ, PCIIQ, and PCIIIQ), placed around the landfill. The research results of selected parameters were presented in Table 4. The assessment of groundwater quality around the considered object was carried out on the basis of Polish regulation regarding groundwater quality [28].

Values of pH of considered waters did not change significantly during the examinations and were neutral or mildly alkaline (ranging from 6.2 to 7.7). These values did not exceed the permissible levels. The electrolytic conductivity varied from 665 to 2,804 µs/cm. These values are within the acceptable ranges for waters of classes II–V of groundwater quality. Increased electrolytic conductivity means that significant amounts of mineral compounds are dissolved in the considered waters. Total organic carbon (TOC), which informs about organic compounds content ranges from 6.03 to 21.80 mg C/L. Therefore, waters can be included into class II (PCIIQ and PCIIT), class IV (PCIQ, PCIT, PCIIIQ), or class V (PCIIIT) of water quality. Drill cuttings can be a source of organic compounds, but the elevated TOC values are also observed in swamps [29]. Wetlands are found in the vicinity of the examined area.

The concentration of heavy metals: Cd, Zn, Cr, Pb, Cu, and Ni in groundwaters taken from six piezometers placed near the landfill does not exceed class I

Table 4
Chemical parameters of groundwater taken from the piezometers located around the drilling waste landfill

Piezo-meter	Sample collection time	pH	Conductivity μS/cm	TOC mgC/L	Al	B	**Ba**	Ca	**Fe**	K	Mg	Mn	**Na**	Ni	Chlorides
					mg/L										mgCl/L
PC I T	III	7.7	665	17.02	<d.l	0.82	0.038	17.67	0.12	5.46	3.98	0.01	128.90	<d.l	9.50
	VII	7.8	639	16.19	<d.l	0.99	0.042	17.92	0.04	5.87	4.38	0.025	132.8	<d.l	5.10
	X	7.7	647	17.00	<d.l	0.89	0.04	22.23	<d.l	6.57	4.90	0.03	119.12	<d.l	8.60
PC I Q	III	7.4	781	18.50	<d.l	<d.l	0.04	128.61	0.13	2.38	10.80	0.02	25.02	<d.l	54.0
	VII	7.5	733	16.30	<d.l	<d.l	0.05	126.05	0.15	2.45	11.80	0.05	20.08	<d.l	53.09
	X	7.3	794	15.59	<d.l	<d.l	0.04	121.40	<d.l	2.72	11.70	0.01	17.47	<d.l	59.10
PC II T	III	7.7	665	8.77	<d.l	<d.l	0.104	105.19	<d.l	17.03	7.92	0.24	96.09	<d.l	70.80
	VII	8.0	694	8.79	<d.l	0.46	0.13	121.18	0.06	21.08	11.73	0.35	127.11	<d.l	80.45
	X	7.6	654	8.46	<d.l	0.40	0.13	147.12	<d.l	25.07	12.57	<d.l	129.99	0.003	78.21
PC II Q	III	6.7	1112	6.16	<d.l	<d.l	0.06	298.75	0.26	3.36	45.46	0.10	92.32	<d.l	133.0
	VII	6.2	1065	6.49	<d.l	0.13	0.074	294.6	0.24	3.70	51.93	0.17	91.83	<d.l	106.5
	X	6.5	1108	6.03	1.01	0.17	0.08	215.42	0.36	2.81	41.15	0.19	98.79	0.005	121.2
PC III T	III	6.7	2050	21.90	<d.l	1.86	0.01	424.86	0	3.30	90.3	<d.l	36.99	<d.l	50.1
	VII	6.5	2065	21.60	4.19	2.12	0.016	424.54	0.16	4.40	96.17	0.02	34.94	<d.l	56.1
	X	6.9	2050	21.80	0.04	2.08	0.02	404.8	0.28	3.85	88.0	<d.l	33.38	<d.l	52.77
PC III Q	III	6.2	2710	16.49	5.11	1.74	0.02	426.62	0	10.24	130.01	1.75	25.73	0.10	10.5
	VII	6.1	2804	17.51	<d.l.	1.86	0.023	454.62	0.02	11.98	127.83	1.41	23.01	0.09	10.65
	X	6.1	2669	16.99	<d.l.	1.10	0.06	376.65	0	14.73	148.42	1.71	27.66	0.08	7.1
Limit values for ground water[1)]		6.5-9.5	2500	10	0.2	1	0.7	200	5	15	100	1	200	0.02	250

░ parameters within class IV water quality standards (unsatisfactory quality) [28],

▓ parameters within class V water quality standards (low quality) [28],

[1)] to be considered as having good chemical status, corresponding to border values of physicochemical parameters specified for class III of ground water quality [28]
n.l. - no limited
<d.l -below detection limit

groundwater purity laid out in the relevant regulation [28]. The content of sodium and chloride in water from piezometers was low as well. Only in three piezometers the concentration of sodium (PCIT, PCIIT, and PCIIQ) and chlorides (PCIIT, PCIIQ, and PCIIIT) exceeded 60 mg/L, which sets these waters in the II class of quality. However, elevated concentrations of boron, manganese, potassium, and calcium were found in waters from some piezometers. Due to boron concentration, the quality of water in PCIT piezometer corresponded to class II standards, in PCIIIQ—to class IV, and in PCIIIT—to class V (exceeded 2 mg/L). Sources of boron in groundwaters might include boranes found in soils and rocks, as well as boron compounds which migrated from sewage and waste, as they are often used in households [29].

Concentration of manganese in PCIIQ and PCIIT waters corresponded to class II, while in PCIIIQ—to III class of water quality. The presence of manganese in groundwaters might be caused by its migration from igneous and sedimentary rocks in the examined area. Due to a strong relation of manganese concentration to water pH, its high concentrations might be found in groundwaters in acidic environments, created naturally or through human pressure [29].

The concentration of potassium found in the water from PCIIIQ piezometer exceeded the border value for class III of water quality, while in PCIIT piezometer—for class V. Drill cuttings contain significant amounts of potassium. However, laboratory tests did not prove that it is easily released into water. Organic substance decay might be a source of potassium in groundwaters; it may also flow from arable lands where mineral or organic fertilizers are used [29].

Examined waters contained high concentrations of calcium. In PCIQ and PCIIT piezometers, they exceeded permissible Polish regulation [28] values for class III of water quality, in PCIIQ—for class IV, while in PCIIIQ and PCIIIT—for class V. Sources of calcium in groundwaters might include limestones, as well as municipal and industrial waste landfills.

According to the guidelines found in the regulation [28], the chemical status of groundwaters can be considered good, as the parameters do not exceed the border values determined for class III of water quality. The comparison of experimental results of water samples taken from piezometers with permissible values shows that none of them meets the requirements for waters of good quality. The water from PCIIIQ piezometers (6 m deep) located on the western side of the landfill in the sawmill area was characterized with the lowest quality. As many as eight parameters exceeded permissible levels: conductivity, TOC, concentrations of B, Ca, Mg, Mn, Ni (in all measurements), and Al (only in March). In the adjacent, 16.5 m-deep PCIIIT piezometer, four parameters exceeded: TOC, B, Ca (in all measurements), and Al (in July). In the remaining piezometers, only a single parameter exceeded; TOC in PCIT and PCIQ piezometers, K concentration in the case of PCIIT and Ca concentration in PCIIQ.

Out of the 14 considered parameters, only pH value and Ba, Na, Fe, and chloride concentrations did not exceed the permissible levels for class III water quality in any test.

3.5. Leachability of soluble components from drill cuttings under laboratory conditions

The results of leaching test, presented in Table 5, were compared with the highest permissible value of pollutant indices in treated industrial sewage introduced to waters or ground, specified in Polish legal regulations [30]. Drill cuttings eluates do not meet the criteria for sewage in many respects. It is characterized with a highly alkaline pH (10.5–12.01), which exceeds the permissible levels ranging from 6.5 to 9.0. The concentration of barium is also higher than allowed, with the mean value measured in extracts reaching 2.98 mg/L, while 2 mg/L is the limit. Despite exceeding border values, barium is unlikely to be absorbed by plants. According to Kabata-Pendias and Mukherjee, acidic pH is conducive to barium uptake from the ground. Barium might accumulate in animal tissues, thus hindering bone mineralization process, causing muscle weakness and difficulty in breathing [31].

Concentrations of chlorides and sulfates also exceeded in water extracts. In several cases, the sum of these compounds exceeded the permissible level, which equals 1,500 mg/L. According to Bojarska and Bzowski [32], chloride concentrations above 70 mg/L may have a negative impact on the growth of plants and cause pollution of surface, or even ground waters. Concentration of such elements as calcium, magnesium, and manganese is not limited by legal regulations concerning wastewater discharged into environment; therefore, these values were correlated with the regulations on groundwater quality [28].

The comparison shows that Mg and Mn concentration was very low in relation to standards. Mean Mg concentration amounted to 0.45 mg/L, while in the case of Mn—0.002 mg/L (Table 5). The border values for I class of water quality are 30 and 0.05 mg/L, respectively. On the other hand, the concentration of calcium ranging from 125.3 to 302 mg/L classified the water as class III—V.

Table 5
Concentration of selected metals, chlorides, and sulfates in eluates from drilling waste taken from landfill. Results of laboratory batch study

Concentration	Unit	Mean value (n = 30)	Minimum value	Maximum value	Standard deviation	Maximum permissible value 1)	Limit value for ground water 2)
Al	mg/L	2.78	<d.l	10.6	3.31	3.0	0.2
As		0.01	<d.l	0.08	0.03	0.1	0.02
B		0.02	<d.l	0.03	0.02	1.0	1.0
Ba		2.98	0.04	13.5	5.00	2.0	0.7
Cu		0.07	<d.l	0.19	0.07	0.5	0.2
Pb		<d.l	<d.l	0.01	<d/l	0.5	0.1
Ni		0.02	<d.l	0.07	0.02	0.5	0.02
Mn		0.002	<d.l	0.02	0.005	n.l	1.0
Fe		0.06	0.02	0.09	0.02	0.5	0.5
Na		344.1	136.9	708.7	198.4	800	200
Ca		219.2	125.3	302,0	74.1	n.l	200
Mg		0.45	<d.l	3.36	1.06	n.l	100
K		61.1	78.5	64.0	62.9	80	15
Chlorides	mgCl/L	845.6	357.87	1925.5	446.14	1000	250
Sulphates	mgSO_4/L	479.65	386.21	386.21	285.7	500	250

1) specified in the Regulation [30]

2) to be considered as having good chemical status, corresponding to border values of physicochemical parameters specified for class III of ground water quality [28]

<d.l. – below detection limit

n.l. - no limited,

▭ - exceeded limit value [30]

3.6. Comparison of field and laboratory test results

The results for eluates obtained in laboratory leaching tests do not correlate with the results of water tests taken from piezometers around the landfill. Different parameters exceeded in both types of water. In groundwaters, only pH value and Ba, Na, Fe, and chloride concentrations did not surpass the permissible levels for class III water quality in any test, whereas in drill cuttings leaching tests conducted in laboratory, as many as four parameters (pH value, concentration of Ba, Na, and chlorides) exceeded (Table 5). This may mean that the low water quality around the landfill was not due to the migration of pollutants from the deposited drill cuttings. The greatest accumulation of pollutants in piezometers placed in sawmill area, especially in those at a more shallow level (PC IIIQ) suggests that the reason should probably be sought in the area of that object.

This assumption is supported by significant differences in concentrations and their ratios for selected elements in the water from piezometers and water extracts from drill cuttings. Noticeably higher Ca and Mg concentrations, in comparison to the ones in water extracts, were observed in water from piezometers. Moreover, the concentration ratio of Ca/Mg in water ranged from 4.4 to 13, which does not exceed typical values for groundwater in Poland, while in water extracts, this proportion was many times higher and ranged from 89.9 to 125. Taking into account the similarity of chemical properties, it can be expected that in case drill cuttings leachate infiltrated to ground, the proportions between these elements would be similar. High concentrations of calcium ions may stem from chemical composition of rocks in that area. Calcium concentrations may increase due to calcium carbonate leaching reaction. Concentrations of Ba and Al differ significantly as well in both considered media. They were multiple times higher in drill cuttings extracts than in piezometer waters. It can be easily explained, as both these elements are drill fluid component ingredients. The concentration ratio of Ba and Al in water extracts revolved around one; while in piezometer waters it was significantly lower. A low barium share in groundwater is explained by its rarity as a rock component, in contrast to aluminum which is a common one.

4. Conclusions

The conducted research which aimed at the assessment of the properties of drill cuttings deposited on landfill in regard to their potential and actual impact on environment shows that due to exceeding the permissible barium, lead, and zinc concentrations, the waste cannot be considered inert, in accordance with the requirements of extractive industries' waste regulations. The concentrations of metals, such as strontium and iron, which are not limited by relevant law regulations, were many times higher in drilling waste than in natural soils.

Waters from piezometers located around drill cuttings landfill do not meet the criteria for waters of good quality. Out of 14 analyzed parameters, as many as nine of them exceeded: conductivity, TOC, concentrations of B, Ca, Mg, Mn, Ni, Al, or K. The most exceeded parameters (8) were found in the piezometer placed 6 m deep in the sawmill area. Low concentrations of barium, chlorides, and low pH in the waters taken from piezometers in comparison for the laboratory test results of drill cuttings leaching suggest that pollution of groundwater was not caused by deposition of drilling waste. On the other hand, leaching tests show that drill cuttings constitute a potential hazard for land and aquatic environments due to the ease with which chloride, aluminum, and barium leach. Inappropriately, secured drill cuttings landfill may contribute to the elevated concentrations of these substances in soils or groundwaters.

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