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Bioavailability of barium to *Trifolium pratense* L. in soils contaminated with drill cuttings**

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Abstract. Barium sulphate is the basic component of drilling fluids. Due to the widespread use of drilling processes there is a fear that barium will appear in the environment and that it may become available to plants in different conditions. In this study the bioavailability of barium in soil with the addition of drill cuttings was examined using red clover (*Trifolium pratense* L.) in a pot experiment. The barium concentration in the examined soils, determined by an inductively coupled plasma mass spectrometry method, was in the range 56-15 800 mg kg^{-1}, depending on the dose of the drill cuttings (2.5-15% of dry weight) added to the mineral soil (control sample). The addition of drilling waste to the soil (pH 4.1, total exchangeable bases 2.1) significantly changed the physicochemical properties of the soil, increasing the pH (up to 7.1) and the concentration of alkaline cations (total exchangeable bases up to 51.2 cmol kg^{-1}). The biomass production in the soil containing drill cuttings was higher compared to the control sample, but the maximum biomass level was found in soil with a 5% dose of the waste. Plant shoot biomass production and the concentration of barium in shoots and roots were closely related to the concentration of barium in the soil. Higher concentrations of barium were found in the roots. Red clover showed a marginal accumulation of barium (transfer factor 0.02-0.08).

Keywords: barium, barite, drilling waste, bioavailability, transfer factor, translocation index

INTRODUCTION

Barium (Ba) is an alkaline earth metal and its biological function has not yet been fully explained. However, in high concentrations it has toxic effects, on both plant and animal life. In the case of humans, it causes cardiac irregularities and disorders of the nervous system, which may even lead to death (Patnaik, 2003). Kuperman *et al*. (2006) found that toxic effects for the animals *Eisena fetida*, *Folsomia candida* and *Enchytaeus crypticus* were observed when the Ba concentration in the soil was in the range 165-2000 mg kg^{-1}. Montereiro *et al*. (2011) stated that the toxic level of free Ba (Ba^{2+}) in the nutrient solution used in a pot experiment with tropical forage grass (*Panicum maximum* Jacq.) was 170 mg l^{-1} (1.24 mmol l^{-1}). However, conducting comparative studies on the critical toxicity concentration of Ba for different species is difficult because its toxicity largely depends on the bioavailability of Ba, which in turn depends on the chemical binding of Ba and the soil conditions (Llugany *et al*., 2000).

Naturally, Ba appears in soils in concentrations from 13-2368 mg kg^{-1} (Kabata-Pendias, 2010; Ong *et al*., 2013). According to Ong *et al*. (2013), a wider range of Ba concentrations were observed in subsoil (13-2 050 mg kg^{-1}) rather than topsoil (30-1 870 mg kg^{-1}). However, the Ba resource contained in the soil is not entirely available to plants. Its availability depends mainly on the chemical form of the element, this factor determines its solubility in the soil solution. Chloride, acetate, perchlorate and nitrate compounds of Ba are soluble in water, but barium sulphate ($BaSO_4$), which is also called barite, is a mineral that is insoluble in water, acids and alkali (Hatipoglu *et al*., 1990). Barium carbonate, called witherite ($BaCO_3$) is practically insoluble in water, however, it is soluble in most acids, with the

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exception of sulphuric acid (PubChem). These latter compounds are the most commonly occurring Ba minerals in nature (Boffito, 1991; Llugany *et al*., 2000).

The solubilization of Ba is encouraged by acidic conditions (Menzie *et al*., 2008), the absence of oxygen and the presence of sulphate-reducing bacteria, *e.g*., *Desulfovibrio desulfuricans* (Baldi *et al*., 1996), while neutral or basic pH conditions favour Ba precipitation in the form of sulphates or carbonates (Abreu *et al*., 2012).

Barium is found in the soil in the form of both soluble and insoluble compounds, both of an organic and inorganic nature. Due to their toxicity, the water-soluble forms of Ba pose a real threat to the environment. Studies have shown that dissolved Ba (free ions Ba^{2+}) is very mobile in soils and can move between the water phase and soil colloids, such as clay minerals and humic compounds (Atun and Bascetin, 2003; Celebi *et al*., 2009). Soil organic matter is able to interact with metal ions via adsorption, ion-exchange and complexation mechanisms (Celebi *et al*., 2009). The stability of the organic matter bound to Ba is similar to the case of complexes with calcium, but lower than copper (Kononova, 1966). Barium can also become bound to the humic acids that are dissolved in soil water. However, according to Hiraide *et al*. (1994) associations of this type are difficult to form. Zhang *et al*. (2001) even claimed that stable complexes of Ba with dissolved organic matter are unknown.

Industrial activity increases the risk resulting from the presence of Ba in the environment. The element is used, among other functions, for the production of extinguishing agents, insecticides and drilling fluids (Shock *et al*., 2007). The mining industry contributes significantly to the increase of Ba concentration in the surface layer of the Earth's crust. Barite, which is characterized by a high specific gravity, equal to 4.50 g cm^{-3}, is used as a weighting agent for different types of drilling fluids. The waste that is produced from rock drilling contains high amounts of Ba. In places such as drilling sites, heaps and landfills of mining waste the accumulation of this element may be high (Raghu, 2001). However, little is known about the risk that barite poses to the environment, although it is generally thought to be low.

In some countries, limit values for Ba concentrations in different types of environments have been established. For example, Canadian law sets the limit value for: agricultural soil at 750 mg kg^{-1}, residential and parklands zones 500 mg kg^{-1} and commercial and industrial zones 2 000 mg kg^{-1} (Canadian Soil Quality Guidelines for Barium, 2013). Polish law is more restrictive in this respect and sets the acceptable Ba content at a level of 200-600 mg kg^{-1} for agricultural soil (depending on grain size and pH); 400 mg kg^{-1} for residential zones, 1000 mg kg^{-1} for forest sites and 1500 mg kg^{-1} for industrial zones (Regulation of the Polish Minister of the Environment, Journal of Laws 2016, Item 1359). Additionally, Ba is considered a potential environmental risk factor in the case of waste classification. According to the Polish Waste Act, Ba compounds (apart from barite) belong to a group of components which, if present may be considered a reason for including the waste in the hazardous group (Act of Waste, Annex No. 4, Journal of Laws 2013, Item 21, as amended).

The potential for reclaiming soils contaminated by Ba is as yet poorly developed. One of the tested methods is phytoremediation (Ribeiro *et al*., 2018). The special ability of some plants to uptake and accumulate metallic contaminants via the root system and store them in various plant compartments is the basis for this method (Tangahu *et al*., 2011). There are only a limited number of reports concerning Ba accumulation by plants. A significant potential for Ba accumulation, expressed in the form of high bioconcentration factors (ratio of Ba concentration in plant biomass and soil) ranging from 2-20 was reported for tomatoes and soybeans (Choudhury and Carey, 2009). Li *et al*. (2011) found that the common reed (*Phragmites australis)* has a high potential as a plant which may be used in the phytoremediation of Ba contaminated soil. The study also found significant Ba removal capabilities in silvergrass *Miscanthus floridulus*. Barium accumulation was also observed in the biomass of southern cattail (*Typha domingensis*), papyrus sedge (*Cyperus papyrus)* (Ribeiro *et al*., 2018), *Indigofera cordifolia* (Raghu, 2001), Brazil nuts (*Bertholletia excels*), different mushrooms (Harbison *et al*., 2015) and some legumes (Myrvang *et al*., 2016). The latter observed that bird velch (*Vicia cracca* L.) and white clover (*Trifolium repens* L.) examined in a pot experiment carried out on sandy soil accumulated a higher amount of Ba than barley, tall fescue, carrot, radish and spinach. Whelan (1993) showed that an increase in the Ba concentration of the soil due to its fertilization with barium selenate (the source of selenium for plants used as an animal forage) did not cause an increase in Ba concentration in subterranean clover (*Trifolium subterraneum*), even after three years of fertilization.

To the best of our knowledge the potential of red clover (*Trifolium pratense* L.) with regard to the bioconcentration of Ba has not been examined previously. This issue is important because red clover is commonly used as an animal forage plant in Europe and in addition, it is recommended for the reclamation of poor quality or degraded soils (McKenna *et al*., 2018), due to its capacity for the fixation of atmospheric nitrogen.

The aim of this study was to evaluate the migration of Ba from soil containing drilling waste into red clover *Trifolium pratense* L. and the bioaccumulation of this element in the above-ground and underground parts of the plant. The main objective was to indicate whether the increase in the Ba concentration in the soil, caused by the presence of drill cuttings, increases the concentration of Ba in the biomass of plants that are commonly used as animal forage.

MATERIALS AND METHODS

Examined materials: The main component used in the experiment was mineral soil (silt loam), which was taken from an arable field in the vicinity of Lublin, from a depth of 10-20 cm. The soil was acidic (pH 4.1) and poor with regard to organic substances (the content of organic matter was 0.7% of the dry weight). Drilling waste in the form of drill cuttings dewatered in a chamber press was used as the second component of the soil. The waste was obtained at the site of their management, in a facility located in South-eastern Poland. The drill cuttings were characterized by a dry matter content of 62-68% by weight and a strongly alkaline pH (pH 10.8).

Pot experiment: The studies were conducted on four types of mixtures designated as S1-S4, which were prepared based on different combinations of soil and drill cuttings. The share of cuttings in the soil ranged from 2.5-15% by weight, based on the air-dried weight (Table 1). The control sample (S0) test consisted of soil without drill cuttings.

Table 1. Composition of the soil used in the pot experiment

Soil	Drill cuttings	Mineral soil
	% of "air dried" mass	
S0 (control)	0	100
S1	2.5	97.5
S2	5	95
S3	10	90
S4	15	85

The materials were placed in plastic pots with a capacity of 350 ml and each pot was sown with 12 clover seeds (*Trifolium pratense* L). The studies were carried out in three replicates for six weeks. The culture was carried out in accordance with the recommendations given in PN-EN ISO 11269 – 2: 2013-06. After the experiment, the plants were harvested and the roots were gently separated from the soil by repeated rinsing. The collected plants were divided into roots and above-ground (shoots) parts. Next, the plant material was dried at 70°C to a constant weight, then ground in a laboratory ball mill to homogenize the composition. The dried biomass was weighed with an accuracy of 0.01 g.

Additionally, the water extracts of the soil were prepared by shaking the samples taken from particular pots with deionized water, in a ratio of 1:10 by weight at ambient temperature for 24 h, in accordance with the procedure described in PN-EN 12457-2: 2006.

Analytical methods: The scope and nature of the analytical methods used for the determination of the physical and chemical parameters of the mixtures and their components were as follows:

– Granulometric composition with the sieve analysis method (PN-EN ISO 14688-2:2006).

– Organic matter content by means of gravimetric methods, correcting for the loss of weight during calcination at a temperature of 550°C.

– pH value by means of a potentiometric method, in distilled water and in a 1 M solution of potassium chloride (PN-ISO 10390: 1997 P).

– Specific gravity through the use of the Le Chatelier flask method, at a temperature of 22°C.

– Hydrolytic acidity (HAC) and total exchangeable bases (TEB) by means of the Kappen method.

– Cation exchange capacity (CEC) was calculated as the sum of HAC and TEB.

The concentration of Ba in the examined soil, water extracts of the soil and plant biomass were determined with ICP-OES Ultrace 238 (Jobin Yvon Horriba France) using a direct calibration method. The samples of homogenized soil (1 g) and biomass (0.1 g) were digested in an acid mixture of HNO_3:HCl (1:3), and the water samples (15 g) were digested in HNO_3 (3 ml) in a microwave system (Multiwave 3000, Anton Paar). The digestion process lasted for 45 min at 180°C and at a pressure of 18 bars. The Ba concentrations were determined at wavelengths of 455.403 nm. The detection limit for Ba was 10 ppb.

Result elaboration: The percentage of Ba extracted using elution tests with deionized water were calculated according to the equation:

$$\%\text{Ba} = \frac{M_e}{0.1\,M_t}\ \ 100\%, \qquad (1)$$

where: M_e is the Ba concentration in the water extracts of the soil (mg kg^{-1}), M_t is the Ba concentration in the soil (mg kg^{-1}) and 0.1 is the mass conversion ratio.

The Ba transported from the soil to the plant was evaluated using the transfer factor (*TF*) according to the equation:

$$TF = \frac{PC}{SC}, \qquad (2)$$

where: *PC* is the Ba concentration in the biomass of the whole plant (root and shoot) (mg kg^{-1}) and *SC* is the concentration of Ba in the soil (mg kg^{-1}) (Abreu *et al*., 2012; Rahman *et al*., 2013).

The ability of a particular species to translocate Ba from the roots to the shoots was assessed on the basis of the calculation of the following translocation index (T_i, %) according to the equation:

$$T_i = \frac{LC}{RC}\ \ 100\%, \qquad (3)$$

where: *LC* is the Ba concentration in the biomass of the shoots (mg kg^{-1}) and *RC* is the Ba concentration in the biomass of the roots (mg kg^{-1}) (Ociepa *et al*., 2014).

All data were subjected to regression analysis (GLM) conducted using Statistical Application 13.1 (license: Lublin University of Technology), System Software Version 6.08 (SAS 1996).

RESULTS AND DISCUSSION

The physical and chemical properties of the soil used in the experiment are presented in Table 2. The addition of drill cuttings to the soil influenced the granulometric composition of the soil, clearly increasing the proportion of the sand fraction in relation to the silt fraction. The clay fraction content did not change significantly due to waste addition.

Table 2. Physico-chemical properties of the soil used in the experiment

Soil	Granulometric composition (% of weight) Fraction			Organic matter* (% dry weight)	pH	Total exchangeable bases	Hydrolytic acidity	Cation exchange capacity
	Sand	Silt	Clay			cmol kg^{-1}		
S0 control	23	71	6	1.9 ± 0.05	4.01 ± 0.01	2.1	5.9	8.0
S1	27	68	5	2.0 ± 0.05	6.27 ± 0.02	13.3	0.4	13.7
S2	30	65	5	2.2 ± 0.05	6.62 ± 0.1	25.9	0.6	26.5
S3	32	63	5	2.3 ± 0.1	6.85 ± 0.05	46.6	1.2	47.8
S4	52	42	6	2.6 ± 0.01	7.10 ± 0.02	51.2	1.2	52.4

*Including the organic compounds, *e.g.* hydrocarbons, polymers, glycols derived from drilling waste.

The addition of drill cuttings to the soil, which was strongly acidic (pH 4), significantly increased the pH value of the resulting soil. The soil-waste mixtures were characterized by weakly acidic or neutral pH (pH 6.3-7.1). Such a reaction may limit the bioavailability of Ba occurring in the form of sparingly soluble compounds, *e.g.*, carbonates. It was confirmed that Ba mobility in soil decreases with increasing pH, which is determined by the reduced solubility of carbonate minerals (ATSDR, 2007).

The examined soil-waste mixtures were characterized by a low value of hydrolytic acidity, ranging from 0.4-1.2 cmol kg^{-1} and a high content of exchangeable basic cations, ranging from 13.3-51.2 cmol kg^{-1} (Table 2). The S4 mixture reached a level of total exchangeable bases (TEB) almost three times higher than the average value of this parameter measured in Polish soils, at 18.2 cmol kg^{-1} (CIEP, 2012).

The TEB values indicate the high cation exchange capacity (CEC) of the soils. The CEC value was strongly positively correlated with soil pH ($R^2 = 0.78$), organic matter ($R^2 = 0.95$) and total barium concentrations ($R^2 = 0.97$). Usually, in soils with high CEC values (*e.g.*, fine textured mineral soils or soils rich in organic matter), Ba mobility is limited by adsorption (Bates, 1988; Kabata-Pendias 2010). On the other hand, its absorption is influenced by the composition of basic cations that compete with Ba for sorption sites.

There are studies confirming that a high content of organic matter is the most effective way to limit the bioavailability of heavy metals and Ba in soil (Karczewska, 2008). Organic matter has the ability to form complexes with some metals. The greater the amount of organic matter, the greater the retention of metals in the surface layers of the soil and the greater the extent to which the mobility of such elements as Ba, Cd, Cr and Pb in the soil profile is reduced (Merlino *et al*., 2010). Unfortunately, in the examined mixtures the organic matter content was low. The addition of drilling waste slightly increased the organic matter value compared to the control soil, but the organic substances introduced with the cuttings did not contain humus compounds, which have the potential to increase the sorption capacity of the soil, this was found in the case of the adsorption of hydrocarbons.

The addition of drilling waste significantly increased the Ba content in the examined soil (Table 3). The highest value, which exceeded 10 000 mg kg^{-1}, was measured in the S3 and S4 mixtures. The Ba concentrations in the soil mixtures were much higher than the average content of this element in Polish soils, which is 43.9 mg kg^{-1} (Kabata-Pendias, 2010). However, the Ba content in the control sample (56 mg kg^{-1}) was also higher (approximately 26% higher) than the average value for Polish soils. According to the Regulation of the Minister of the Environment of 1st September 2016 regarding the assessment of contamination on the surface of the earth (Journal of Laws, 2016, Item 1395), the acceptable content of Ba in the surface layer (0-25 cm) of arable soils (Group II) varies from 200-600 mg kg^{-1}, depending on grain size and pH, while for industrial zones (Group IV) it is 1500 mg kg^{-1}. As such, the value measured in the control soil did not exceed the permissible limits, while in the soil-waste mixtures it exceeded the limits for industrial zones, by 2.7 to over 10 times the limit.

The concentrations of Ba eluted from the soil to the water extracts were at a very low level (0.03-0.05 mg kg^{-1} of soil), despite the high total barium concentration in the solid phase of the soil (Table 3). The percentage of Ba extracted from the solid phase of all soil mixtures (S1-S4) during elution in deionized water was low (≤0.012%) and did not change significantly with the increase in the drill cuttings content within the mixture. The highest Ba

Table 3. Concentrations of barium in the soils and the results of its elution

Soil	Ba concentration in soil	Eluted Ba concentration	Percentage of Ba elution (%)
	mg kg^{-1}		
S0 (control)	55.96 ± 7.92	0.06 ± 0.001	0.110
S1	2657.43 ± 11.9	0.03 ± 0.03	0.001
S2	4180.25 ± 11.1	0.05 ± 0.05	0.001
S3	10781.62 ± 51.3	0.05 ± 0.05	0.0005
S4	15787.79 ± 17.7	0.05 ± 0.05	0.0003

elution value (1.07%) was found in the case of the control sample, which indicates another type of Ba chemical form contained in the soil as opposed to the drill cuttings. The low elution of Ba from the soil containing drilling wastes indicates that this element was permanently bound in the form of water-insoluble compounds. As a consequence, Ba should not be available to living organisms, because the main threat to the environment is related to the easily soluble and the most mobile Ba compounds (Seguin *et al*., 2004). Low Ba mobility in soil containing drilling waste may also be promoted by an elevated pH which is close to neutral. According to Abreu *et al*. (2012), the mobility of Ba is negligible under neutral or basic pH conditions, reducing the risks of leaching.

The results of the Ba content measurement in the water extracts could form the basis for assessing the potential impact of the soil on the aquatic environment, in the case of their release into the environment. Because there are no standards specifying the limit values for pollutants leaching from the ground into the groundwater, the limit values for the wastewater introduced into the environment could be used as a potential reference for assessing the impact of water solutions leached from the solid phase of the soil. These limit values refer to the concentrations of selected pollutants specified by the regulation of the Minister of the Environment of 18th November 2014 on the conditions to be met when introducing sewage into waters or into the ground, in addition to the substances particularly harmful to the aquatic environment (Journal of Laws 2014, Item 1800). The Ba concentration in the obtained aqueous extracts from the tested soil is many times lower than the permissible value determined for wastewater introduced into the environment of 2 mg Ba dm^{-3}.

The addition of drilling waste to acidic soil increased the biomass production of the test plants in the experiment (Fig. 1).

The drill cuttings dose had an influence on the growth of plants. The 5% (S2) dose, which resulted in a 2.4-fold higher biomass than the control, was the most favourable. As such, a high Ba concentration in the soil did not inhibit the growth of red clover completely. Even with the Ba concentration in the biomass exceeding 450 mg kg^{-1} (S4) the total weight of the biomass was over 1.5-fold higher compared to the control soil. The lack of a highly toxic influence may be explained by the low solubility of Ba in the water, which suggests that the Ba in the cuttings was bound in sulphates. The lack of any toxic effects of the Ba compounds on the tested plant is in accordance with the results of the study carried out by Menzie *et al*. (2008), who assessed the impact of Ba on soil organisms. The study compared the influence of barite and soluble Ba salts, which are used to determine the levels of ecological soil screening (Eco-SSL) for Ba (U.S. EPA, 2005). No effects for invertebrates were observed with regard to the barite concentration in the tested soil, in the range of 17 000-1 000 000 mg kg^{-1}. It was several orders of magnitude higher than the Eco-SSL (determined for soluble Ba salts) for soil invertebrates, at 330 mg Ba kg^{-1} of soil. In contrast to this observation,

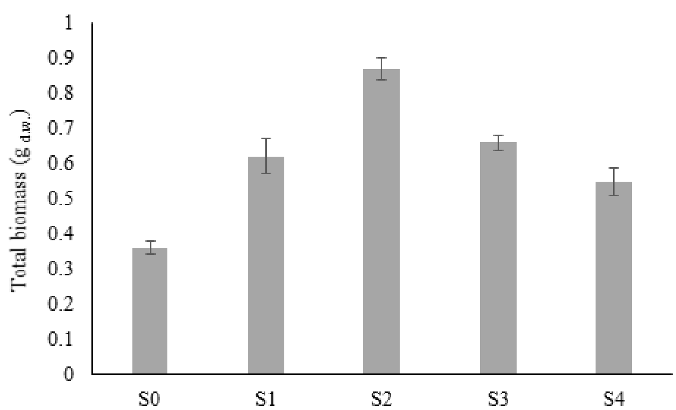

Fig. 1. Average values of the total dry biomass of red clover obtained in the pot experiment.

barite contaminated soils in which the Ba concentrations were in the range 1,300-292,000 mg kg^{-1} had a negative impact both on the tested plant *Lactuca sativa* L. and on the soil invertebrate *Eisenia fetida,* relative to the control soil (Lamb *et al*., 2013), causing a decrease in shoot biomass production in the case of lettuce, and body weight loss in the case of earthworms. In their experiment, the biomass of plants cultivated in soil with a Ba concentration of 500 mg kg^{-1} was 50% lower than in the control soil; while an increase in the Ba content ranging from 1 833-3 667 mg kg^{-1} caused a further drop in biomass production, at a dose of 21 670 mg kg^{-1} the growth of plants was inhibited. Different barite effects on plants may be explained by differences in the control soil properties, which was strongly acidic in our study (pH 4) and deprived of organic matter, as well as alkaline elements. In the studies of Lamb *et al*. (2013) it had properties that are beneficial to plants which the addition of drill cuttings was found to inhibit. Therefore, the effect of the addition of drill cuttings was conditioned by the initial soil properties.

The results of a regression analysis showed that the pH value was a factor that influenced red clover growth in our experiment ($p = 0.0004$, $R^2 = 0.48$), but the total concentration of Ba ($p = 0.0004$, $R^2 = 0.071$), organic substance content ($p = 0.0004$, $R^2 = 0.11$), and TEB value ($p = 0.0004$, $R^2 = 0.25$) do not explain the variability in biomass quantity to any significant extent. The best fitted trend lines (determined using the least squares method) indicate a polynominal character with regard to Ba concentration ($R^2 = 0.870$), TEB ($R^2 = 0.973$) and organic matter ($R^2 = 0.777$) in the soil. When these parameters were increased to a certain level, a decrease in biomass production was observed. This suggests that the factors limiting plant growth on the control soil included an inappropriate pH and a lack of alkaline elements in the sorption complex. However, the addition of excessive drill cuttings (>5%) inhibited plant growth. The lack of a linear relationship with organic matter contentmay be explained by the nature of the organic compounds contained in the drill cuttings, which may include aliphatic and aromatic hydrocarbons, phenols and organic polymers that can have a toxic effect on soil organisms (Jamrozik *et al*., 2016). Figure 2 presents the content of Ba in the biomass of the tested plant. The results indicate the visible influence of the presence of drill cuttings in the soil on the concentration of the analysed element in the plant biomass. The mean concentration of Ba in the biomass ranged from the lowest value obtained in the control sample of 10.5 mg kg^{-1}, to the highest value of 459.9 mg kg^{-1} obtained in sample S4 with the highest drill cuttings content. On the other hand, the content of Ba in the biomass of red clover, which grew in S2 and S3 soil, exceeded 100 mg kg^{-1}. In general, Ba concentrations increased along with the share of drill cuttings in the soil (Pearson's R = 0.785). Taking into account that the concentration of Ba in the biomass of the majority of plant species ranges from 4-50 mg kg^{-1} (Kabata-Pendias and Mukherjee, 2007) it may be stated that the values measured for the samples with a drill cuttings content of 5-15% considerably exceed the typical values. However, the same authors state that for some plants, these values may be several times higher, *e.g*., for Brazil nut, they may range from 3000-4000 mg kg^{-1}.

The content of Ba in plant tissues depends on numerous factors, including the plant species and the concentration of Ba in the soil, as well as the physicochemical properties of Ba and the condition of the soil, *e.g*., its humidity or aeration. The dependency of Ba accumulation on plant species is confirmed by the results obtained by Myrvang *et al*. (2016). They demonstrated that legumes exhibit a higher accumulation of Ba from soil than grasses, vegetables or herbs. Apart from legumes, other plants that are characterized by a high affinity to Ba include red ash (*Fraxinus pennsylvanica*), black walnut (*Juglans nigra*), hickory (*Carya* sp.) and Brazil nut (*Bertholletia excels*) (CICAD, 2001).

The diversified affinity of various plant species to Ba was also reported by Coscione and Berton (2009) in research conducted on soils containing $BaSO_4$ in concentrations of 0, 150 and 300 mg kg^{-1}. The concentrations of Ba in the shoots of the plants cultivated in soils with the highest analysed $BaSO_4$ content were 21.3, 19.4 and 10.6 mg kg^{-1} for sunflowers, mustard plants and castor oil plants,

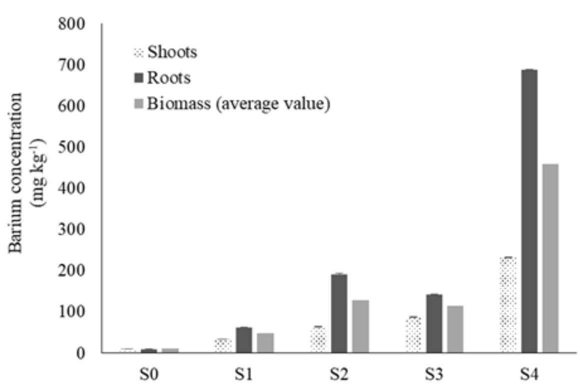

Fig. 2. Barium concentration in the clover biomass obtained in the experiment.

respectively. On the other hand, the concentration of Ba in the biomass of mustard cultivated by Kwiatkowski (2016) in soil containing 20% drilling waste was 130 mg kg^{-1}. This value was many times higher than in the tests carried out by Coscione and Berton (2009). This may be related to the concentration of Ba in the soil, which was several times higher and amounted to 2 700 mg kg^{-1}.

Mrvang *et al*. (2016) theorized that Ba accumulation depends on the soil properties, such as graining, which is connected with the sorption capacity of soil. They investigated the accumulation of Ba by white clover (*Trifolium repens* L.), grey pea (*Pisum sativum* ssp. *arvénse* L.) and barley (*Hordeum vulgare* L.) on sandy soils with the addition of lime, with a total Ba concentration of 500 mg kg^{-1}. The researchers observed that all plant species used in the experiment acquired Ba from the soil in substantial amounts. They explained this phenomenon by citing the low Ba adsorption potential of the sandy soil. Additionally, the study showed that Ba uptake by the tested plants, particularly legumes, seems to be enhanced by a high uptake of Ca.

In our study CEC was positively correlated with Ba concentration in the plant tissues (Pearson's R = 0.784, for the average Ba concentration in the biomass), refuting the theory that increased CEC leads to a decrease in Ba uptake from the soil. This phenomenon may be explained by the simultaneous increase in both the Ba concentration in the soil and its CEC value, since both parameters increase with the dose of drilling waste (Tables 2 and 3). A stable Ba concentration in soils with different CEC values should be maintained to assess the CEC influence on Ba uptake.

Anomalously for natural soils, a positive correlation between the CEC value and sand fraction content (Pearson's R = 0.822) was observed in our study. It should be taken into account that in the case of drilling waste the sand fraction does not refer to quartz grains with a small specific surface area (SSA), but to fragmented rock in the size range 0.05-2.0 mm which may include minerals with large SSA values, thereby increasing CEC.

Pais and Jones (1998) report that high concentrations of Ba in plant tissues may negatively impact living organisms. Lamb *et al*. (2013) observed a negative linear relationship between shoot Ba content and shoot weight, which indicates that Ba accumulation is likely to cause phytotoxicity. A Ba content of 200 mg kg^{-1} in plant tissues is considered to be moderately toxic and values exceeding 500 mg kg^{-1} are considered highly toxic (Pais and Jones, 1998). However, for some plants these values may be lower, as evidenced by the results of the research conducted by Smith (1971). He stated that the critical tissue Ba concentration in *Panicum maximum* was in the range 156-383 mg kg^{-1}.

In our study, the visible effects of the toxic influence of Ba accumulation in red clover biomass were not observed. There were no morphological changes, such as interveinal chlorosis of the leaves, which was observed by Monteiro *et al*. (2011) in the case of guineagrass (*Panicum maximum* Jacq.) although the Ba concentration in the shoots of red clover that was harvested from soil with the highest dose of drilling waste (231 mg kg^{-1}) exceeded the Ba concentration in the biomass of Tanzania guineagrass which was found to be toxic (225 mg kg^{-1}). Morphological changes were also not observed by Brandt and Rickard (1996) in their investigation of Ba accumulation in plants growing in the vicinity of landfills. However, in the case of the plants considered by the study, the concentration of Ba in their biomass was low at 22 mg kg^{-1}.

In this study, the concentration of Ba in the biomass of plants cultivated on soil containing drill cuttings was much greater than in their shoots. In the roots of clover cultivated on soils S2 and S3, the Ba content exceeded 100 mg kg^{-1} and was almost twice as high as it was in the shoots. The highest Ba concentration, reaching over 600 mg kg^{-1} was observed in the roots of the plants grown on S4 soil. It was over three times higher than it was in the shoots. In the case of the plants grown on the control soil, in which Ba was present in lower concentrations, but was more mobile than in other soil (Table 3), the concentration of Ba in the total biomass was similar. Higher Ba concentrations in the biomass of shoots rather than roots were also observed by Lamb *et al*. (2013) in a study conducted on *Lactuca sativa* L. cultivated in soils with added $BaSO_4$. Myrvang *et al*. (2016), who studied Ba intake from sandy soil containing a Ba total of 500 mg kg^{-1} observed a comparable Ba content in the biomass of the roots and shoots of different vascular plant species. They stated that the concentration of Ba in the shoot tissue of a legume (*Trifolium repens* L. – white clover), achieved values of up to 600 mg Ba kg^{-1}, while in the root tissue it reached concentrations of up to 700 mg kg^{-1}. In contrast to these observations, there were lower concentrations of Ba in the roots (*ca*. 6 000 mg kg^{-1}) than in the leaves (*ca*. 9 000 mg kg^{-1}) of other legumes, *i.e*., bean plants (*Phaseolus vulgaris*) were analysed by Llugany *et al*. (2000) during an experiment in which the test plants were watered with agar containing free Ba (Ba^{2+}) at a concentration of 5 000 μM.

These differences may stem from different Ca concentrations in the soil. Myrvang *et al*. (2016) in their studies on various plant species, such as *Trifolium repens* L. (white clover), *Pisum sativum* ssp. *arvénse* L. (grey pea) and *Hordeum vulgare* L. (barley) indicated that the liming of the soil reduces the concentration of Ba in the shoots of plants, particularly in species with a low affinity for Ca. In the drill cuttings used in this study, the concentration of Ca was high and reached over 7% (Chomczyńska *et al*., 2016), which may explain the lower content of Ba in the shoots of the test plants.

On the basis of the linear correlation results, it was observed that the concentrations of Ba in the roots (Pearson's R = 0.863) and shoots (Pearson's R = 0.937) depends to a significant extent on the concentration of Ba

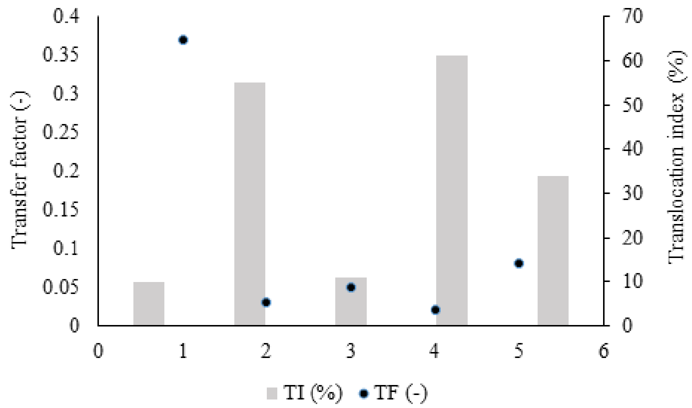

Fig. 3. Transfer factor (*TF*) and translocation index (T_i) calculated on the basis of the results obtained in the experiment.

in the soil. At a Ba concentration of 56 mg kg^{-1} in the soil, its content in the biomass of clover shoots reached 10.9 mg kg^{-1}; when the Ba concentration in the soil increased to approximately 2650 mg kg^{-1}, the concentration of this element in the shoots increased to 34 mg kg^{-1}, while at a concentration in the soil of approximately 11 000 mg kg^{-1} it increased to 230 mg kg^{-1}. On the other hand, no dependencies were identified between the Ba concentration in the water extracts and its concentration in the red clover biomass (Pearson's R = 0.08).

The key parameters for the assessment of the availability of the elements in soil and their accumulation are the transfer factor (*TF*) and translocation index (T_i) (Nan *et al*., 2002). The values of these indicators calculated for the examined plants are presented in Fig. 3.

The *TF* for plants cultivated in soil containing drilling waste was very low, ranging from 0.02-0.08. These values indicate that the clover did not exhibit the capacity for Ba accumulation, despite its high concentration in the soil (Table 3). Only higher *TF* values indicate that a particular plant accumulates the given element (Ogunkunle *et al*., 2014). The highest *TF* value was observed for plants growing on the control soil, which contained low Ba concentrations, but with higher mobility than in other soils, which is evident from the highest leaching level of 0.11% observed in the experiment (Table 3). The *TF* value observed for the control soil was similar to the mean for various species estimated by Hope *et al*. (1996) and cited by CICAD (2001), amounting to 0.4 ± 0.02, assuming a mean Ba concentration in the soil and biomass equal to 104.2 ± 9.5 and 29.8 ± 13.7 mg kg^{-1}, respectively.

Similarly, low values of *TF* for plants cultivated on soil containing drilling waste were obtained by Kwiatkowski (2016). In his studies, the *TF* of Ba for mustard plants grown on soil with a 20% addition of drilling waste and a total Ba concentration in the soil of 2 700 mg kg^{-1} reached 0.02. On the other hand, Coscione and Berton (2009) obtained a higher *TF* of 0.113 for mustard plants grown on soil containing 150 mg kg^{-1} of $BaSO_4$. This plant was characterized by a higher content of the considered compound than castor oil plants, for which the *TF* reached 0.071 and 0.075. Abreau *et al*. (2012) obtained significantly higher *TF* values of 0.29, 0.47 and 0.70 for castor oil, sunflower and oilseed radish, respectively, the plants were cultivated on soil polluted by scrap metal residues, with a total Ba concentration of 105 mg kg^{-1}. These values are still below one, which indicates a lack of Ba accumulation capacity by these plants, despite its probable higher mobility in the soil.

The translocation indices indicate the migration capacity of metals from roots to shoots. The translocation of Ba in red clover may be considered low or moderate, as it ranged from 10-61%. The lowest T_i value was observed in the case of plants cultivated on the control soil, while the highest was observed for plants grown on S1 and S3 mixtures. Higher translocation indices of Ba for oilseed radish, sunflower and castor oil, cultivated on soils with an elevated Ba content (105 mg kg^{-1}) were found by Abreu *et al*. (2012). These indices reached 89, 74 and 59%, respectively. Andrade *et al*. (2014) investigated soil with a mixture of waste from an oil prospecting well, in which the concentr ation of Ba was 6700 mg kg^{-1}. The translocation index of *Brachiaria decumbens* grass reached 77%. Ba mobility in the root-surface part of the plant in the soil under consideration is low. Research indicates that the transport of Ba in a plant may be influenced by the concentration of Ca in the soil.

CONCLUSIONS

1. The addition of drilling waste significantly raised the Ba content in the soil.

2. The Ba introduced to the soils was insoluble, which is evidenced by its low concentration in the water extracts obtained from soil mixtures containing drilling waste.

3. Significant dependencies were observed between the concentration of Ba in plant roots and shoots and the total concentrations of Ba in the soil.

4. The migration of Ba from the soil to the biomass of red clover (*Trifolium pratense* L.) was limited. The transfer factor of Ba from the soil to the plants was very low (<0.1), which indicates that red clover did not exhibit any significant capacity for Ba bioaccumulation.

5. Studies show that Ba is accumulated in higher concentrations in the roots of red clover than in the aboveground parts. This observation is of practical importance, because clover is commonly used as animal forage.

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