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The concentration of molybdenum and copper in rocks, soils and plants in the area of Jabłonki (Eastern Beskids Mts.)

Zawartość molibdenu i miedzi w skałach, glebach i roślinach w okolicy Jabłonek (Beskidy Wschodnie)

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Abstract

Molybdenum is one of the major trace elements for plants, but its excess and the deficiency of copper in soils can lead to the production of feed that may be toxic to animals and cause molybdenosis. Menilite shales that occur in the Eastern Beskids Mts. are characterised by an elevated content of this element. The concentration of molybdenum and copper has been determined in samples of bedrock, soils and plants (*Trifolium hybridum* L. and *Plantago major* L. plants), taken in the area of occurrence of menilite shales and the Otryt Sandstones. The molybdenum concentration in rocks varies from 0.80 to 40 mg/kg, in soils – from 1.97 to 19.58 mg/kg, and in plant material – from 0.54 to 11.76 mg/kg. The copper concentration in rocks ranges from 11 to 111 mg/kg, in soils – from 23 to 76 mg/kg, and in plants – up to 20 mg/kg. The average Mo concentration in all kinds of plants is significantly higher in the area of occurrence of menilite shales than in the area where the Otryt Sandstones are dominant. The higher content of Mo in the samples collected from clover was accompanied by the lower Cu/Mo ratio, which may cause a molybdenosis disease in animals in the study area.

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Streszczenie

Molibden jest jednym z podstawowych mikroelementów dla roślin, ale jego nadmiar w glebach przy niedoborze miedzi może prowadzić do produkcji pasz, które mogą być toksyczne dla zwierząt i powodować molibdenozę. Łupki menilitowe występujące na obszarze Beskidów Wschodnich charakteryzują się podwyższoną zawartością tego pierwiastka. W próbkach skał podłoża, gleb oraz roślin (rośliny *Trifolium hybridum* L. i *Plantago major* L.) pobranych na terenie występowania łupków menilitowych oraz piaskowców z Otrytu oznaczono zawartości molibdenu i miedzi. Zawartość molibdenu w skałach wynosi od 0,80 mg/kg do 40 mg/kg, w glebach jest w zakresie 1,97–19,58 mg/kg, a w materiale roślinnym jest w przedziale od 0,54 do 11,76 mg/kg. Zawartość miedzi zmieniała się w skałach od 11 mg/kg do 111 mg/kg, w glebach od 23 do 76 mg/kg i badanych roślinach do 20 mg/kg. Średnia zawartość Mo we wszystkich rodzajach roślin jest zdecydowanie wyższa na terenie występowania łupków menilitowych niż na obszarze gdzie dominują piaskowce z Otrytu. Z wyższą zawartością Mo w próbkach koniczyny wiąże się niższa wartość stosunku Cu/Mo, co może skutkować występowaniem molibdenozy u zwierząt w badanym rejonie.

1. INTRODUCTION

Molybdenum is the 54th most common element in the Earth's crust (1.2 mg/kg). This is a strongly chalcophile element forming several minerals, of which the most important are molybdenite (MoS_2), wulfenite (PbMoO_4) and powellite (CaMoO_4). In igneous and metamorphic rocks, Mo is most common in feldspars and biotite. In sedimentary rocks, it is strongly complexed by organic matter and absorbed by iron compounds [de Vos et al. 2006]. In the hypergenic zone, molybdenum mobilised due to weathering processes is readily bound by organic matter, clay minerals and Al-Fe-Mn hydroxides [Kabata-Pendias 1996]. Its average contents in igneous rocks, depending on the rock type, are in the range of 0.2–2 mg/kg, in clayey rocks – 2–2.5 mg/kg, in carbonates – 0.2–0.4 mg/kg and in sandstones – 0.2–0.8 mg/kg [Kabata-Pendias, Mukherjee 2007]. Higher molybdenum concentrations are found in copper-bearing and bituminous shales, ranging up to 200 mg/kg, and in caustobolites – up to 2% [Pasiieczna 2012]. The average molybdenum concentration in soils of the world has been determined at 1.8 mg/kg, although, depending on its concentration in the parent rocks, it ranges from 1.3 in sandy soils to 2.8 mg/kg in calcareous soils [Kabata-Pendias, Mukherjee 2007]. In Europe, the subsoil layer contains from <0.1 to 17.2 mg/kg of molybdenum [de Vos et al. 2006]. In the territory of Poland, the value of molybdenum geochemical background is variable. The

topsoil layer in most areas of the country contains <0.45 mg/kg of molybdenum [Pasiieczna 2012]. In the Carpathians, the molybdenum concentration is much higher and can attain 144 mg/kg, with an average of 35 mg/kg. The most likely source of molybdenum is the silica-clay-marl menilite layers that have an elevated content of this element [Gucwa, Wieser 1980]. In soils, molybdenum is present predominantly in anionic forms. The MoO_4^{2-} anion predominates in neutral and moderately alkaline soils, and is the most easily available form to plants. The HMoO_4^- ion is present in soils with lower pH values. These anions are easily co-precipitated by iron hydroxides and absorbed by organic matter. In the literature, it is most frequently reported that the molybdenum concentration in soil solutions is in the range of 0.8–8 mg/l and is higher in the cambic and accumulation horizons. In the case of Cu, the most common values of its concentrations in the soils of Poland vary from 3 to 15 mg/kg [Kabata-Pendias, Pendias 1993]. Molybdenum is an essential element required for the normal development and growth of both plants and animals. Terrestrial plants collect metals mainly from the soil solution through the root system [Eapen, d 'Souza 2004]. The availability of Mo to plants is closely related to the pH value of the soil and to the amount of iron oxides and organic constituents. In acidic soils (pH <5.5) that contain much iron, the availability of Mo to plants is very low

[Kabata-Pendias, Pendias 1993]. Some plants have a specific potential for the bioaccumulation of molybdenum above their physiological needs, e.g. legumes. They can accumulate up to about 350 ppm Mo without any signs of toxicity [Kabata-Pendias 2011]. The occurrence of Mo toxicity in plants is sparse; however, high molybdenum concentrations in animal feed may cause copper deficiency in ruminants and induce the so-called molybdenosis, especially in animals that graze in dry areas, where there are soils with high organic matter content [He et al. 2005]. Molybdenum may affect the availability of copper to animals only in the presence of sulphur due to the formation of an insoluble compound representing sulphosalts – CuMoS_4 [Fisher George 2008]. Demand for Mo in ruminants varies between 0.1 and 3.5 mg/kg; for Cu – between 5 and 25 mg/kg DM feed [Kubiński 1996]. Animal feed containing 10–20 ppm Mo can cause molybdenosis in ruminants. The greatest susceptibility to molybdenosis is observed in cattle, sheep, horses and pigs [Singh 2005]. Average molybdenum contents in plants, depending on their type, are in the range of 0.04 mg/kg (carrot root) to 1.0 mg/kg (wheat). In the grass of meadows, where cattle graze and no toxicity effects are observed in animals, the molybdenum content is below 1 mg/kg. In the

grass of grasslands, where negative impact on the health of grazing animals is observed, the content is higher and amounts to a few and locally even tens of mg/kg.

The aim of this study was to trace the migration of molybdenum from the bedrock through the soil to the plant. Previous geochemical studies on molybdenum content in the area of the Dukla Folds in the Bieszczady Mts. showed a relationship between the occurrence of areas with high molybdenum content in modern alluvial sediments and the occurrence of menilite beds. Increased contents were observed in sediments, e.g. in the river systems of Wetlinka, Dołżyczka, Solinka and Jabłonka. The highest molybdenum contents were found to the north of the village of Cisna (10.6 mg/kg) and to the west of the village of Przysłop (10.8 mg/kg) [Bojakowska, Borucki 1994].

2. MATERIAL AND METHODS

The working area is located south of Jablonki in the district of Lesko, Poodkarpacie Voivodeship. Geochemical studies were carried out in the border zone with the northeastward located tectonic unit of the Bystre Slice (Fig. 1).

Fig. 1. Location of sampled sites.

The samples of rocks, soils and plants were collected at two locations: W1 – in the area of menilite shales and W2 – in the area of the Otryt Sandstones. A total of 80 samples of four plant species were taken at location W1: from alsike clover, red clover, greater plantain and ribwort plantain. Soil samples were collected from four holes spaced 0.5 m, and then averaged (mixed). At location W1, soil samples were collected from two depth levels: from the interval down to 30 cm and from the 30 cm – 1.0 m interval. At this site, five rock samples were also collected. A total of 40 samples of two different species of plants were collected at location W2: from alsike clover and greater plantain. Soil samples were taken from three holes spaced 0.5 m, and then averaged (mixed). Due to the very shallow soil profile and the high proportion of rock fragments, the soil was taken from one level down to a depth of 30 cm. At this site, two rock samples were also taken.

To properly prepare the samples for testing, plant samples were purified and then dried in dryers at a temperature not exceeding

38°C. Dried material was ground and digested in a Multiwave 3000 microwave oven (70–71% HNO_3 + 30% H_2O_2). Soil and rock samples were air-dried at room temperature. Thereafter, soil samples were digested in aqua regia (65% HNO_3 + 37–38% HCl) and the rocks were subjected to complete acid degradation (65% HNO_3 + 37–38% HCl + 70% HClO_4 + 38% HF). After digestion, the contents of molybdenum and copper were determined in all samples using the ICP-MS method and a Perkin Elmer Elan DRC II mass spectrometer with inductively coupled plasma. The determination limit for Mo and Cu is 0.05 mg/kg. In addition, the soil samples were analysed for pH in the aqueous extract using the potentiometry method. All tests were performed at the Central Chemical Laboratory of the PGI in Warsaw, accredited for the analyses. As the reference materials, RGM-1 – rhyolite and TB – clay shale were used for the study. Reference materials, used for interlaboratory comparisons (921 Riverclay from ISE comparison; grass from IPE comparison) and organised by the University of Wageningen, were also employed.

3. RESULTS AND DISCUSSION

3.1 Plants

The average molybdenum concentration in plants of four species from location W1: alsike clover, red clover, greater plantain and ribwort plantain, range from 1.3 to 12 mg/kg (Table 1). The maximum concentration of 12 mg/kg was found in *Trifolium hybridum* L. The copper content of the above-mentioned plant species varies from 12 to 20 mg/kg, the highest Cu concentration was measured in *Trifolium pratense* L. In the case of plants taken from location W2, the average Mo concentrations are 0.80 mg/kg in *Trifolium hybridum* L. and 0.54 mg/kg in *Plantago major* L., and the Cu concentrations are 11 and 16 mg/kg, respectively. A comparison of the average Mo concentrations in plants

growing on various substrates is presented in Fig. 2.

Tested plants are characterised by Mo contents significantly higher than the average. Molybdenum concentrations in plants are usually 0.2–2.0 mg/kg DM [Ruszkowska, Wojcieszka-Wykupajtys 1996]. The most common Mo content in red clover is 0.50 mg/kg, and in grass (orchard grass) – 0.33 mg/kg. In areas with molybdenum toxicity in cattle, grass species contained an average of about 3 mg/kg, and clover specimens about 25 mg/kg DM of this metal [Kabata-Pendias, Pendias 1993; Kabata-Pendias 1996]. Tested plants are characterised by copper contents similar to the average values. The copper concentration in red clover commonly varies from 4 to 21 mg/kg, and in grasses (orchard grass) – from 2 to 20 mg/kg [Kabata-Pendias 1996].

Fig. 2. The average molybdenum concentrations in plants growing on the substrate composed of menilite shales and sandstones.

Table 1. Average concentrations of molybdenum and copper in plants growing in areas composed of menilite shales and sandstones

Species	Cu mg/kg	Mo mg/kg	Cu/Mo ratio
Location W1			
<i>Trifolium hybridum</i> L.	11.76	11.76	1:1
<i>Trifolium pratense</i> L.	19.19	9.76	2:1
<i>Plantago major</i> L.	19.09	1.31	15:1
<i>Plantago lanceolata</i> L.	17.88	1.58	11:1
Location W2			
<i>Trifolium hybridum</i> L.	11.04	0.80	14:1
<i>Plantago major</i> L.	15.55	0.54	29:1

Explanation: W1, menilite shales area; W2, Otryt Sandstones area.

3.2 Soils

The average Mo content in soil at location W1 from a depth down to 30 cm is 10 mg/kg, and in soil from a depth >30 cm to 20 mg/kg. The Cu contents are 42 and 76 mg/kg, respectively. The soil pH is acidic and the pH value is 5.46 in the topsoil layer and 6.14 in the subsoil layer (>30 cm). The average Mo content in soil from location W2 is 1.97 mg/kg, and the Cu content is 23 mg/kg. The soil pH is basic – 7.45. Soils from location W1 are characterised by a significantly higher Cu content when compared with the average copper content in soils of the Polish Lowlands (the average content in sandy podsol is 6 mg/kg, in alluvial soil – 24 mg/kg). The Cu concentration in soils from location W2 is comparable with the most commonly observed Cu contents [Kabata-Pendias, Pendias 1993].

3.3 Rocks

The investigations have revealed that the molybdenum concentration in rocks at location W1 ranges from 2.58 to 40 mg/kg, and the average content is 17.91 mg/kg. This is due to the presence of

brown shales (characteristic of the menilite bed) as well as grey calcareous shales and thin- to medium-bedded sandstones. The Cu concentration varies from 31 to 111 mg/kg. The average Mo content at location W2 is 0.80 mg/kg, and the average Cu content – 11 mg/kg. Compared with the commonly found average molybdenum contents in clay deposits (2–2.5 mg/kg) [Kabata-Pendias 2011], the examined rocks are characterised by much higher Mo contents. Sandstones that occur in this area are also characterised by higher molybdenum content when compared with limestones (0.4 mg/kg) and sandstones (0.2 mg/kg) [He et al. 2005]. The average copper concentration in rocks from location W1 is 74 mg/kg. It is greater than the Cu content in clay rocks, ranging between 40 and 60 mg/kg. At location W2, the Cu concentration is 11 mg/kg, and the figure is similar to the most commonly encountered Cu contents in sandstones – 5 to 30 mg/kg [Kabata-Pendias 1996]. The results of the work indicate that there is a correlation between the molybdenum concentration in the substrate and the concentration of this element in clover. The increased Mo contents and thus

the demand of legumes are due to participation of this metal in the processes of assimilation of atmospheric nitrogen and protein metabolism [Kabata-Pendias, Pendias 1996]. In the area of occurrence of menilite shales, the average Mo content is elevated in rocks (18 mg/kg), soil <30 cm (10 mg/kg), soil >30 cm (20 mg/kg) and leguminous plants (12 mg/kg; Fig. 3), in contrast to the samples taken from the Otryt Sandstone layer where the Mo contents are 0.80 mg/kg in rocks, 2 mg/kg in soils and 0.80 mg/kg in clover

(Fig. 4). The concentration of molybdenum in soils generally reflects its occurrence in parent rocks [Kabata-Pendias 1996]. In Poland, there are two clearly marked geochemical provinces: northern and southern, related to the geological structure of the country. Soils of the Northern Province, which developed on Quaternary sandy glaciofluvial and fluvial deposits, contain small amounts of Mo, whereas the Carpathian soils are characterised by enrichment in this element [Pasieczna 2012].

Fig. 3. Average molybdenum concentration in rocks, soil and plants in the area of menilite shales.

Fig. 4. Average molybdenum concentration in rocks, soil and plants in the area of the Otryt Sandstone.

The elevated molybdenum concentrations in clover correlate with the lower ratio of Cu/Mo (Table 1). In the case of both *Trifolium hybridum* L. and *Trifolium pratense* L., the Cu/Mo ratio is below 4–5, which may indicate the potential for the occurrence of Mo toxicity in those areas. In plants that do not exhibit excessive accumulation of Mo, the Cu/Mo ratio is 15:1 for *Plantago major* L. and 11:1 for *Plantago lanceolata* L. In the case of plants collected from location W2, the Cu/Mo ratio is 14:1 for *Trifolium hybridum* L. and 29:1 for *Plantago major* L. The Cu:Mo ratio in the food ratio is a very important factor. The optimal ratio is 6:1, the limit ratio is 2–3:1 and the toxic ratio is lower than 2:1 [Kubiński 1996].

4. CONCLUSIONS

1. The Mo concentration determined in rocks, soils and plants is significantly higher in the area of occurrence of menilite shales than in the area where the dominant rock is the Otryt Sandstone.

2. Mo accumulation by plants of the Fabaceae family (alsike clover) is greater than by plants of the Plantaginaceae family (greater plantain).
3. In areas with naturally elevated Mo concentration in soils and rocks, forage crops, such as alsike clover, show high accumulation of this element (12 mg/kg). It can cause molybdenosis in both farmed and wild animals.

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