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The influence of selected soil parameters on the mobility of heavy metals in soils

The activity of zinc-lead industry has a very negative impact on the environment, mainly because of the accumulation of post-mining and metallurgical waste, which in the long term leads to an adverse transformation of natural environment due to migration of dust and metals to soils, surface waters and groundwater. Metals and their compounds present in the soil fractions vary in the degree of mobility. Their bioavailability is regulated by physical, chemical and biological processes and interactions between them. The method of binding heavy metals, and hence their bioavailability, depends on several soil properties, which include: granulometric composition, organic matter content, occurrence and form of cations, pH value, sorption capacity, content of macro and micronutrients, oxidation-reduction potential, activity of microorganisms, bioavailability for plants and animals, resistance of the soil. Mechanical composition of soil is one of the important factors determining the extent of soil contamination with heavy metals and their content in plant tissues. Heavy soils, as compared to light soils, due to large amounts of suspended fraction, have a greater ability to retain metallic elements. On the other hand, light soil does not have such ability of sorption. At a comparable state of heavy metal pollution, it may contain metals in dissolved form, easily available for plants. All soils with high sorption capacity for cations, i.e. land containing a large amount of clay minerals, have the ability to accumulate metallic elements. Increasing the amount of organic matter in the soil, helps to minimize the absorption of heavy metals by plants. Land rich in organic matter actively retains metallic elements. Forms of occurrence of heavy metals in soil significantly affect their mobility. The most mobile elements include the Cd, Zn and Mo, while the least mobile are Cr, Ni and Pb. Soil pH is considered one of the most important factors determining the concentration of metals in the soil solution, their mobility and availability to plants. The increase of hydrogen ion concentration affects the mobilisation intensity of heavy metals. In highly acidic soils, the mobility of metallic elements is much higher than in soils with neutral and alkaline reaction. The potential of oxidation - reduction of soil significantly determines participation in the form of a mobile element, which can enter the biological cycle, in relation to the total element content. Lack of oxygen in the soil causes start-up and increase the mobility of the large part of heavy metals.

Each plant needs for growth and development the appropriate amounts of mineral salts, i.e. macronutrients and micronutrients. Plants draw heavy metals from the soil in a similar way as the macronutrients and micronutrients through the root system. The rate of uptake by the roots of metallic elements depends on the chemical form in which they appear in the soil. Insufficient amount of micronutrients in the soil often results in excessive accumulation of several heavy metals in plants. Properly balanced and well chosen level of nutrients in the soil, ensures high yields with a low content of heavy metals.

Stress caused by an excess of heavy metals is the beginning of disturbances in the metabolism of plants and can lead to disturbances in the collection, transport and assimilation of macro-and micronutrients. Metallic elements accumulated in the soil inhibit the growth of microorganisms that inhabit it, leading to a distortion of their basic life functions, and especially the processes of decomposition and transformation of organic matter. Microorganism activity in ryzosphere is also a major determinant of growth of the plant and its resistance to pathogens.

Soil contamination processes are constant, but compared to other elements of the environment, they are the most capable to defend themselves, acting as a buffer for pollutants. Resistance to contamination, regarding the pressure of degrading factors, land owes to its physical, chemical and biological properties. Resistance of soil is biochemical, because it results from the ability of plants to absorb and neutralize chemically active pollutants.

Keywords: **heavy metal, soil contamination, bioavailability heavy metals, granulometric composition, occurrence and form of cations, pH value, sorption capacity, macronutrients, micronutrients, oxidation-reduction potential, activity of microorganisms, resistance of the soil**

The activity of zinc-lead industry has a very negative impact on the environment, mainly because of the accumulation of post-mining and metallurgical waste, which in the long term leads to an adverse transformation of natural environment due to migration of dust and metals to soils, surface waters and groundwater. Such actions have led to the contamination of large areas by heavy metals, in particular by cadmium, zinc and lead as well as dangerous metalloids. The elements introduced into the environment are subject to biological accumulation. Disruption of the existing balance in the soil usually leads to a reduction in its productivity and the quality of agricultural products [1-4].

A characteristic feature of soil contamination by heavy metals is their slow pace of change, especially of those in the cationic form. In general, these elements are rather insusceptible to leaching, and they stay in soil for a long time [5-9].

Metals and their compounds present in the soil fractions vary in the degree of mobility. Their bioavailability is regulated by physical, chemical and biological processes and interactions between them. The method of binding heavy metals, and hence their bioavailability, depends on several soil properties, which include [5, 10-14]:

- granulometric composition,
- organic matter content,
- occurrence and form of cations,
- pH value,
- sorption capacity,
- content of macro and micronutrients,
- oxidation-reduction potential,
- activity of microorganisms,
- bioavailability for plants and animals,
- resistance of the soil.

All of these factors also determine how many metallic elements will be accumulated in biological material, how many will be subjected to the process of sorption, complexation, or will be immobilized in the soil particles.

Mechanical composition of soil is one of the important factors determining the extent of soil contamination with heavy metals and their content in plant tissues.

Clay fraction, which is mainly composed of clay minerals, stands out because of its high potential to bind heavy metals. Soils having granulometric composition characteristic for clay, silt and dust, and those with a high content of organic matter, have a high sorption capacity and a strong ability to bind metallic elements. However, sandy soils, distinguished by a low sorption capacity and acidity, weakly absorb heavy metals, which leads to their movement to groundwater and surface water [5, 6, 9, 10].

All soils with high sorption capacity for cations, i.e. land containing a large amount of clay minerals, have the ability to accumulate metallic elements [3, 15].

Binding of metal cations increases with increase of their valence, atomic weight and ionic potential. The affinity of metal cations relative of clay minerals is arranged in a series of $Cu^{2+} > Cd^{2+} > Fe^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+}$. This phenomenon, depending on the structure of the mineral, can occur inside or on the surface of the grains [5, 10, 16].

Soluble low-molecular organic compounds, like the highly polymerized humic solids combined with ions, can form stable complexes called metal chelates. In addition, cations of metallic elements undergo a strong specific adsorption, forming partially covalent bonds with ligands, mainly on the surface of iron oxyhydroxide, aluminum and manganese [10, 17].

Hydroxides of Fe, Mn and Al play an important role in the binding of heavy metals by the mineral phase. Mostly hydrous oxides of Fe, Mn and Al contribute to the formation of the coating on crystalline particles in the soil solid phase. Heavy metals together with the compounds of Fe, Mn and Al are easily displaced in suitable conditions [5, 18].

Metals associated with soil sorbents, both organic and mineral, are usually a small part of their total content. This part, however, is readily available for plants, which is advantageous, if the element is an essential nutrient, but disadvantageous if it has toxic properties. Exchangeable metals are the easiest to release, because they can be replaced by other ions present in high concentrations in soil solution, including oxonium ions and they are part of the soil metals that go into solution during the acidification [19-21].

Absorption of heavy metals by plants depends largely on the mechanical composition of soils. Heavy soils, as compared to light soils, due to large amounts of suspended fraction, have a greater ability to retain metallic elements. On the other hand, light soil does not have such ability of sorption. At a comparable state of heavy metal pollution, it may contain metals in dissolved form, easily available for plants. Light soils are also more susceptible to acidification, which is an additional factor causing metallic elements to run in them [6, 21].

Increasing the amount of organic matter in the soil, helps to minimize the absorption of heavy metals by plants. Land rich in organic matter actively retains metallic elements (Fig. 1). The binding of heavy metals by organic matter is a complex process, due to the diversity of its connections with the mineral phase. Sorption capacity of organic matter is well above the mineral sorption capacity of the soil [5, 6, 11, 22].

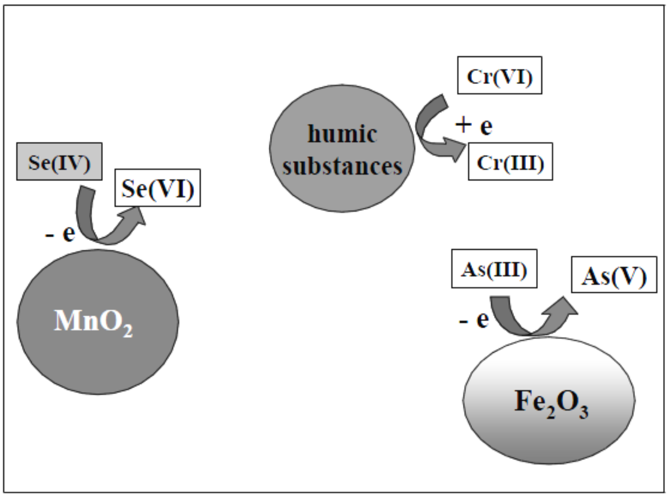

Fig. 1. Possible abiotic redox processes occurring on the surfaces of humic substances and Fe- and Mn-oxides [23]

Low content of organic fraction in soil is responsible for the low cation exchange capacity, low buffering properties of soils, low water capacity and susceptibility to erosion, and it reduces microbial activity [11].

Organic matter can immobilize heavy metals, or work as a factor which causes their release. The solubility of metal compounds which are structural components of organic matter, or form strong complexes with it, is dependent on the solubility of the associated organic matter. Usually its dissolution leads to a distribution of smaller and more soluble products. This is an important factor, which enables the transition of metal elements to the aqueous phase [19, 21, 24].

In the temperate climate, the mineral soil in the forested regions is covered by a layer of organic litter (renewable each year), which decomposes. The result of this process is the creation of small molecules, such as organic acids and stable and insoluble humic substances. Organic acids, acting as ligands for many metal ions, increase their transport of water along the soil profile [16, 19].

Forms of occurrence of heavy metals in soil significantly affect their mobility. The most mobile elements include the Cd, Zn and Mo, while the least mobile are Cr, Ni and Pb [10, 13].

Metallic elements that are present in the form of readily soluble in water and in the form of barter are seen as mobile in the soil profile, and thus readily available to plants. On the other hand, carbonate, oxide and organic forms are usually not very mobile, and therefore less available. However, in case of changes in the soil pH (carbonate form), reduced reduction potential (oxide form) or the creation of conditions conducive to oxidation processes (organic form), they may also become a source of metals available for plants [11, 15].

Metallic elements soluble in water, i.e. present in the soil solution, are collected in the first place. While the metal compounds present in the soil in the so-called exchangeable fraction, therefore adsorbed on the particles of soil, will be charged in the second place, only after entering the soil solution. Among the forms of metals that are present in the soil solution, simple ions are easier to collect (Pb^{2+}, Zn^{2+}), in comparison with the complex ions. A cadmium, however, is an exception, because increase concentration of Cl^{-} in soil solution, also increases the concentration of cadmium, thereby resulting in increased collection of this metal by plants [11, 22, 25].

Anthropogenic factors, which could include acid rain and agrotechnical treatments (e.g. introduction of fertilizers) can significantly affect the lowering of soil pH, or lead to the opposite phenomenon, i.e. raise the pH (e.g. by liming). Soil pH is considered one of the most important factors determining the concentration of metals in the soil solution, their mobility and availability to plants [11, 17].

The increase of hydrogen ion concentration affects the mobilisation intensity of heavy metals. In highly acidic soils, the mobility of metallic elements is much higher than in soils with neutral and alkaline reaction. Mobility of metals in soils with low pH decreases in the order: Cd > Ni > Zn > Mn > Cu > Pb. However, note that the effect of pH on the mobility of metallic elements in the soil is highly variable, depending on the content and type of organic matter [5, 17, 24].

In alkaline soils with a pH range there is the possibility of heavy metal complex anions with the increased mobility and bioavailability. However, usually the intensity of root uptake of metal by plants decreases with increasing soil pH to about pH 6.5÷7.5 [4, 13].

Low soil pH value in addition to the mobilization of heavy metals, also contributes to reducing the value of the exchangeable cations and the capacity to intensify the development of affected populations of microorganisms. pH factor also determines the activity of many metal ions in the water contained in the pores of the soil, affecting their bioavailability. The contents of some metallic elements (i.e. cadmium) in crops is inversely proportional to pH value. Usage of the liming in acidic soils can reduce the intake of heavy metals by plants [6, 21].

The relationship between pH and the bioavailability of many elements exists, apart from plants, in many aquatic organisms, i.e. fish in acidic lakes contained higher concentrations of Al, Cd, Hg and Pb than in neighboring lakes with higher pH [21].

The potential of oxidation-reduction of soil significantly determines participation in the form of a mobile element, which can enter the biological cycle, in relation to the total element content. Lack of oxygen in the soil causes start-up and increase the mobility of the large part of heavy metals [5, 15].

The release of metallic elements in the soil occurs when the land located in an oxidizing environment, i.e. in conditions of good aeration, is flooded with water.

Transportation of oxygen is then reduced, and oxygen is consumed in the aerobic microbial reactions. The consequence of this phenomenon is the reduction of hydrated metal oxides, which makes them mobile [14, 19].

Each plant needs for growth and development the appropriate amounts of mineral salts, i.e. macronutrients and micronutrients. The vast majority of mineral salts contained in soil is bound to the solid phase and rather unavailable to plants. Only their small portion is dissolved in the aqueous phase, which is contained in the soil solution. Plants absorb minerals from the soil through the root system. Taking into account the fact that the roots can download the macro- and microelements only in dissolved forms, soil solution is the basis, and sometimes the only source of plant mineral salt. Plants uptake heavy metals from the soil in a similar way as the macronutrients and micronutrients through the root system (Fig. 2). The rate of uptake by the roots of metallic elements depends on the chemical form in which they appear in the soil [11, 26]. Strong influence on biogeochemical processes in the soil has calcium oxalate, associated with the occurence of fungi, both pathogenic and symbiotic. Precipitated oxalate compounds (Cd, Co, Cu, Mn, Sr and Zn), constitute a reservoir of calcium for plants, and the changes affect the bioavailability of phosphorus for plants [14]. Properly balanced and well chosen level of nutrients in the soil, ensures high yields with a low content of heavy metals. Therefore, fertilization should be adapted to soil and climate conditions prevailing in the area of crop cultivation and to its purpose [25, 27].

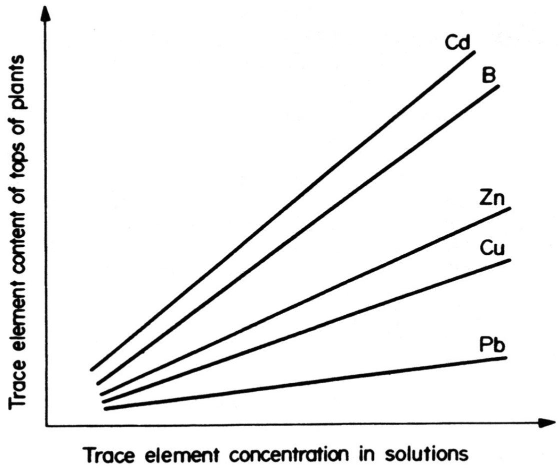

Fig. 2. Trace element uptake by plants as a function of their concentrations in nutrient solutions [28]

Insufficient amount of micronutrients in the soil often results in excessive accumulation of several heavy metals in plants. For trace elements we include elements such as Fe, J, F, Cu, Zn, Co, and to macronutrients inter alia: N, P, S, Ca, Mg, Na, K, Cl. These elements may be introduced in the soil with organic and mineral fertilizers. Land can also be enriched with the necessary components using compound fertilizers, which in addition to high chemical purity are characterized by slow operation, so to a lesser extent alter the physicochemical properties of the soil, and thus the collection of cadmium by plants is limited [9, 24, 25, 27].

Stress caused by an excess of heavy metals is the beginning of disturbances in the metabolism of plants and can lead to disturbances in the collection, transport and assimilation of macro- and micronutrients. Effects of heavy metals on the uptake and movement of other cations and anions is the result of competition for a place for sorption on the surface of roots or creation of non-assimilable complexes [7, 27]. Correlation between metallic elements and macroelements is individual. For example, levels of nitrogen fertilization has no direct effect on the accumulation of heavy metals in the plant, the only form of the element which decreases the pH is ammonium, also increasing the availability of heavy metals to plants. In the ground systematically lime treated, with a regulated reaction, there is no threat of mobilising the metallic elements. On the other hand, the physiologically based nitrogen fertilizers reduce bioavailability of metals [25, 27, 29].

The presence of phosphorus in the soil is an important factor limiting the collection of metallic elements by plants, because the higher content of readily soluble forms may precipitate sparingly soluble phosphates of zinc, cadmium, lead and copper. However, phosphate fertilizers, depending on the origin of phosphorites and apatites used in their production, may contain significant amounts of heavy metals and thus contribute to increased pollution of the soil [17, 27, 29].

After application of nitrogen fertilizers, however, especially the chloride form, the availability of heavy metals for plants may increase. Mobility of cadmium, and thus its availability to plants, as demonstrated by tests, is higher at fertilization with the potassium chloride than potassium sulfate [17, 27, 29].

Organisms, especially fungi, bacteria and higher plants can strongly modify the physical and chemical conditions and processes that affect the bioavailability of metals. An important factor responsible for metal mobility or their immobilization in contaminated soils is microbial activity (Fig. 3). The advantage of the process is, inter alia, the type of microorganisms involved in the process, as well as environmental factors and the physico-chemical properties. Mobilisation of metals may occur as a result of leaching, complexation by metabolites and siderophores and methylation processes. The process of immobilization of metals in soil is related to their sorption in / on microbial biomass and exopolymers, transport, and intracellular sequestration and precipitation in the form of organic and inorganic compounds such as oxalates and sulfates [14, 17]. Microorganisms by its heterotrophic metabolism can lead to acidification of soils due to the release of protons across the cell membrane and the secretion of organic acids, such as oxalic acid may form with Al and Fe soluble complexes. Additionally, the valence changes can affect the mobility of metals, and as such changes in the oxidation of Mn(IV) to Mn(II) increase the mobility of a metal, and changes in the oxidation of Cr(V) to Cr(III) results in its immobilization. Chemolithotrophic and acidophilic bacteria can affect the acidity of the soil and increase the solubility of metals or cause precipitation in the form of metal sulfides. Microbes may cause the change in the number of organic substances in soil and modify the redox potential and pH of the substrate. Human activity that causes an increase in the soil environment due to changes in the mobility of redox potential and pH, in an indirect way influence the activity of microorganisms in the soil [11, 15]. Higher plants during their growth affect the concentration of metal and their speciation in contaminated soils by:

– Uptake of metal ions and protons in secretion due to an antiport uptake causes acidification of ryzosphere and increase the mobility of metals in weakly buffered soils.
– Secretion of simple phenolics and other organic acids also changes the mobility of metals [17].

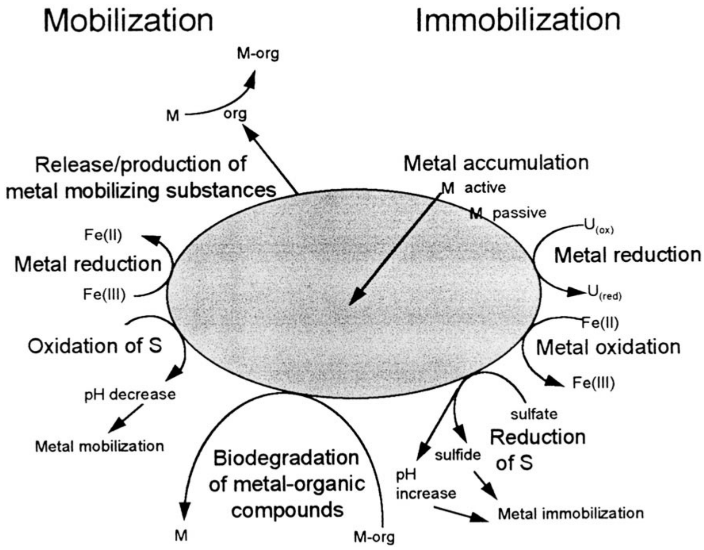

Fig. 3. Interactions between metals and microorganisms [30]

Metallic elements accumulated in the soil inhibit the growth of microorganisms that inhabit it, leading to a distortion of their basic life functions, and especially the processes of decomposition and transformation of organic matter. Effects of heavy metals on microorganisms is revealed in the limitation of their activity, reduction of their size, disappearance of susceptible species and expansion of microorganism species resistant to these changes [10, 14]. Immobilization of heavy metals by microorganisms can be caused by different mechanisms, such as adsorption, precipitation, ion exchange, complexation, or active transport into the cell. Metallic elements are mainly bound by soil bacteria and fungi [10, 13, 14]. Microorganism activity in ryzosphere is also a major determinant of growth of the plant and its resistance to pathogens [14].

Soil contamination processes are constant, but compared to other elements of the environment, they are the most capable to defend themselves, acting as a buffer for pollutants. Resistance to contamination, regarding the pressure of degrading factors, land owes to its physical, chemical and biological properties. A special role is played by phytosphere. Resistance of soil is biochemical, because it results from the ability of plants to absorb and neutralize chemically active pollutants [1, 10]. The lowest resistivity is shown by a loose sandy soil, strongly acidic, poor in nutrients and water. In these soils the degradation processes are occurring particularly quickly. Soil resistance increases proportionally to the content of colloids. Soils rich in colloids and calcium carbonate neutralizes acid substances, and excessive concentrations of metallic elements. A very good indicator of the ground destruction is also the plant cover [1, 7, 10, 24]. The content of clay and humus fraction in the soil composes so-called buffering capacity of the soil, the sorption capacity of soils which despite the increase in concentrations of pollutants do not cause adverse biological effects. Buffer capacity is large, but this does not mean that it is unlimited. Long-term contamination results in irreversible changes in the chemical composition of soil and its biological degradation [1, 10, 20].

Information on the forms of heavy metals occurrence in soils and the mechanisms of their binding to organic and inorganic components of soil are very important, and the same knowledge of only the total content of metallic elements in the soil is insufficient. By examining the concentration of heavy metals and their chemical form the conditions prevailing in the soil needs to be taken into account, especially the physical and chemical properties, which significantly affect the mobility of trace elements and their absorption by plants.

Acknowledgements

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Wpływ wybranych parametrów gleby na mobilność metali ciężkich

Działalność zakładów przemysłu cynkowo-ołowiowego bardzo negatywnie wpływa na środowisko przyrodnicze, co prowadzi do jego niekorzystnego przekształcenia na skutek pylenia i migracji metali do gleb oraz wód powierzchniowych i gruntowych. Metale oraz ich związki obecne we frakcjach glebowych charakteryzują się różnym stopniem mobilności. Sposób wiązania metali ciężkich, a tym samym ich biodostępność zależy od wielu właściwości gleby, do których zaliczyć można: skład granulometryczny, zawartość materii organicznej, formę występowania kationów, wartość pH, pojemność sorpcyjną, zawartość makro- i mikroelementów, potencjał oksydacyjno-redukcyjny, działalność mikroorganizmów, biodostępność dla roślin i zwierząt, oporność gleby. Skład mechaniczny gleby jest jednym z istotnych czynników decydujących o stopniu zanieczyszczenia gruntu metalami ciężkimi oraz ich zawartości w tkankach roślin. Gleby ciężkie, w porównaniu do gleb lekkich, za sprawą dużych ilości części spławianych posiadają większe zdolności zatrzymywania pierwiastków metalicznych. Natomiast gleby lekkie, nie posiadając takich zdolności do sorbowania metali ciężkich, przy porównywalnym stanie zanieczyszczeń mogą zawierać metale w formie rozpuszczonej, czyli łatwo dostępnej dla roślin. Wszystkie gleby charakteryzujące się wysoką pojemnością sorpcyjną w stosunku do kationów, czyli grunty zawierające dużą ilość minerałów ilastych, wykazują zdolność akumulacji pierwiastków metalicznych. Zwiększenie ilości materii organicznej w glebie sprzyja zminimalizowaniu pobierania metali ciężkich przez rośliny. Grunt bogaty w substancję organiczną aktywnie zatrzymuje pierwiastki metaliczne. Formy występowania metali ciężkich w glebie w znacznym stopniu wpływają na ich mobilność. Do najbardziej mobilnych pierwiastków zaliczyć można Cd, Zn i Mo, natomiast do najmniej ruchliwych należą Cr, Ni i Pb. Wartość pH gleby uważana jest za jeden z najważniejszych czynników decydujących o stężeniu metali w roztworze glebowym, ich ruchliwości oraz dostępności dla roślin. Wzrost stężenia jonów wodorowych ma wpływ na intensywność uruchamiania metali ciężkich. W glebach silnie zakwaszonych mobilność pierwiastków metalicznych jest znacznie wyższa niż w glebach o odczynie obojętnym i zasadowym. Potencjał oksydacyjno-redukcyjny gleby w istotny sposób warunkuje udział danego pierwiastka w formie mobilnej, w której może wejść w obieg biologiczny, w stosunku do całkowitej zawartości pierwiastka. Niedostatek tlenu w gruncie wywołuje uruchomienie oraz wzrost mobilności znacznej ilości metali ciężkich.

Każda roślina potrzebuje do wzrostu i rozwoju odpowiednich ilości soli mineralnych, czyli makroelementów i mikroelementów. Rośliny pobierają z gruntu metale ciężkie w podobny sposób jak makroskładniki i mikroskładniki za pomocą systemu korzeniowego. Szybkość pobierania przez korzenie pierwiastków metalicznych uzależniona jest od postaci chemicznej, w jakiej występują w glebie. Niedostateczna ilość mikroelementów w gruncie powoduje często nadmierną akumulację wielu metali ciężkich w roślinach. Zrównoważony oraz właściwie dobrany poziom składników pokarmowych w glebie zapewnia uzyskanie wysokich plonów o niskiej zawartości metali ciężkich.

Stres spowodowany nadmiarem metali ciężkich jest początkiem zakłóceń w metabolizmie roślin i może prowadzić do zaburzeń w pobieraniu, transporcie i asymilacji makro- i mikroskładników. Pierwiastki metaliczne nagromadzone w glebie hamują rozwój mikroorganizmów, które ją zasiedlają, prowadząc do zakłócenia ich podstawowych funkcji życiowych, a zwłaszcza procesów związanych z rozkładem i przemianą substancji organicznej. Aktywność mikroorganizmów ryzosfery stanowi także główny czynnik warunkujący wzrost samej rośliny oraz jej odporność na patogeny.

Gleby stale ulegają procesom zanieczyszczenia, jednak ze wszystkich elementów środowiska są w stanie najskuteczniej bronić się, stanowiąc pewien bufor dla zanieczyszczeń. Odpor-

ność na skażenie, wobec presji czynników degradujących, grunt zawdzięcza swoim właściwościom fizycznym, chemicznym i biologicznym. Odporność gleb ma charakter biochemiczny, gdyż wynika ze zdolności roślin do pochłaniania i neutralizacji ładunków zanieczyszczeń chemicznie aktywnych.

Słowa kluczowe: **metale ciężkie, zanieczyszczenie gleby, biodostępność metali ciężkich, skład granulometryczny, forma występowania kationów, wartość pH, pojemność sorpcyjna, makroelementy, mikroelementy, potencjał oksydacyjno-redukcyjny, działalność mikroorganizmów, oporność gleby**