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DELIBERATIONS ON ZINC – A TRACE MINERAL OR A TOXIC ELEMENT?

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Abstract

The paper gives a comprehensive insight into the role of zinc in the biosphere. It reviews numerous functions of this metal at various levels of the organisation of ecosystems. An attempt has ben made to assess its importance as a microelement, while not neglecting its toxicity due to excessive accumulation of zinc in the environment. Zinc is a natural component of the Earth's crust, but in many places it has accumulated in amounts near or above the safe levels. Currently, the use of this metal is very broad, and therefore attention should be drawn to possible consequences arising from elevated levels of zinc in the environment. Dispelling controversies surrounding heavy metals is a necessary step for gaining systematic and wider knowledge on these elements. This in turn will create an opportunity for the development of strategies and subsequent actions undertaken by everyone, from individuals to major international industrial corporations, aimed at achieving homeostasis in an environment polluted with heavy metals. Increased levels of zinc can adversely affect microbiological and biochemical processes occurring in the soil and the development of plants, which has a negative impact on the quantity and quality of crops. Therefore, low bioavailability of heavy metals, including zinc, in agricultural land is a key to the stability of ecosystems and food security.

Keywords: sustainable development, zinc toxicity, plant nutrition, microbiological and biochemical activity.

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INTRODUCTION

Heavy metals are among the most common contaminants in the environment. Their distinguishing feature is the inability to decompose. The total content of heavy metals in the environment does not change, but they can undergo transformations into forms inaccessible to living organisms (Adriano et al. 2004). The stability of trace elements makes them subject to bioaccumulation in living organisms (Herrera-Estrella, Guevara-García 2009). Small amounts of zinc are essential for the normal development and activity of living organisms (Chibuike, Obiora 2014), whereas an increased content of this element can pose a threat to the biological equilibrium. Therefore, a dual role of zinc, as an element necessary for maintaining life on the Earth as well as a potential threat to the stability of ecosystems, should be considered.

CHARACTERISTICS OF ZINC

Zinc occurs in the solid form and belongs to heavy metals, possessing features characteristic for this group of metals. It is a metal in the 12th group of the periodic table of elements, with the atomic number 30, atomic weight 65.38 u, density (at 20°C) of 7.14 g cm^{-3}, melting point at 420°C and boiling point at 908°C (Munn et al. 2010). It is a mixture of five stable isotopes: ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn, ^{70}Zn (Mercik, Mercik 1994). It occurs in 0, +I, +II oxidation states (Ciba et al. 1996) and typically in the form of compounds such as zinc oxide, chloride, sulphide, sulphate, phosphate and borate (Munn et al. 2010). Similarly to other elements in the soil solution, zinc forms 3 types of speciation: complexes with soluble organic matter, complexes with inorganic ligands and individual Zn^{2+} ions (Kabata-Pendias, Pendias 1999). It is obtained from such minerals as zincite, sphalerite, smithsonite, willemite and wurtzite (Kabata-Pendias 2010). It also occurs in the crystal structure of minerals of the amphibole and pyroxene group, as well as of the mica group (Fotyma, Mercik 1995).

This element has been used for thousands of years in the form of brass (an alloy of copper and zinc, naturally occurring together). Originally, it was obtained from zinc ores and used on a large scale in Asia, mainly in China (Aldersey-Williams 2012). Currently, zinc is used broadly in many industries. First of all, it is a component of many alloys, it prevents corrosion of steel and it is used as raw material in the manufacture of rubbers, plastics, pesticides, lubricants and other products. It is also used on a large scale in the production of batteries, tubes, electronic equipment, automotive equipment, as well as in medicine and dentistry (Kabata-Pendias 2010), production of chemicals, paints, varnishes and certain fertilisers and in the pyrotechnic industry (Munn et al. 2010).

SOURCES AND LEVELS OF ZINC POLLUTION

The amount of zinc in the environment is conditioned both by natural processes and anthropogenic activities (Kabata-Pendias 2004). Natural factors affecting the content of zinc in soil include soil pH, particle size distribution, type of bedrock, sorption capacity, amount and type of organic matter, oxidation-reduction potential, plants growing in the soil and its microbial activity (Kabata-Pendias 2010). Moreover, some emission of this metal may be related to volcanic processes (Mather et al. 2012). The main anthropogenic sources of soil pollution with zinc are mining and processing of metal ores, fossil fuel extraction, municipal solid waste, manufacture of dyes and rechargeable batteries, use of crop protection products and fertilisers, including usage of sewage sludge (Gaur, Adholeya 2004). Transportation is another major source of zinc emission and significant amounts of this metal are observed mainly in urban soils in areas with heavy traffic (Luo et al. 2012).

Zinc is a natural component of the Earth's crust. The average content of this element in bedrock and soil formations is approximately 70 mg kg^{-1}. Zinc is very mobile in well-aerated and acidic (pH below 6.5) soils, but it becomes more stable and does not undergo leaching at an increase of pH to neutral, about 7.0 (Kabata-Pendias 2004, 2010). The activity of zinc decreases hundredfold with a rise of pH by one unit in the range from 5 to 8 (Fotyma, Mercik 1995). Immobilisation of zinc in alkaline and limestone soils is due to the formation of zinc hydroxide and the precipitation of carbonates or insoluble forms of zinc compounds. Concentrations of zinc in ferruginous and manganese soil concretions equal 2,500 mg kg^{-1} and 5,500 mg kg^{-1}, respectively (Kabata-Pendias, Pendias 1999). Furthermore, loamy minerals such as montmorillonite and illite bind the ions of this metal more efficiently than kaolinite (Bradl 2004). Globally, the content of zinc in soils varies from 30 to 235 mg kg^{-1}, and more specifcally up to 30 mg in podzolic soils, up to 60 mg in soils formed from light clays and up to 80 mg of Zn kg^{-1} in soils formed from heavy clays. Soils formed from compacted clay formations, dusts, loess and carbonate and sulphate rocks belong to the group of soils rich in zinc (Kabata-Pendias, Pendias 1999). The concentration of zinc as an active metal in the soil solution varies from $3 \cdot 10^{-3}$ to $3 \cdot 10^{-1}$ mol dm^{-3} (Fotyma, Mercik 1995). The position of zinc in the series of elements present in soil according to biological activity indicates that its ability to form stable complexes with organic compounds is smaller in comparison to other metals. According to Barabasz et al. (1998), the sequence is as follows: U > Hg > Pb > Cu > Ni > Co > Cd > Zn > Mn > Cr.

An elevated content of zinc is observed above all in mining areas (of both active and closed mines), in areas associated with the processing of extracted zinc ores and industrial processes of electrogalvanisation (Verma, Dwivedi 2013). Transportation of zinc from mining areas is closely associated with characteristics of the mining sites and climatic conditions, and specifically depends on such parameters as the soil type, consistency of mining output, topography, as well as regional and microclimatic features (Navarro et al. 2008). In 2012, the load of zinc deposition in Silesia, Poland, was 428 g ha^{-1} $year^{-1}$ (Wrześniak, Kopyczok 2013). Another example of the impact of mining on the environment is the surroundings of Aznalcóllar (Seville, Spain), where the zinc content in the soil is over 3,000 mg kg^{-1} (García-Sánchez et al. 1999).

Industry is the largest emitter of zinc to the environment. According to Kabata-Pendias, Mukherjee (2007), the contamination of soil with zinc in the industrial areas of the United States may be as high as 80,000 mg kg^{-1} of soil. In the surroundings of zinc ore processing plants (Huludao, China), high concentrations of zinc and its accompanying elements are detected. The content of heavy metals in the particulates subjected to the pressure of such plants is significantly higher than in areas with less anthropogenic activity. The average zinc content in the particulates of an industrial area was 5,271 mg kg^{-1} but its range was from 517.8 to 79,869 mg Zn kg^{-1} (Zheng et al. 2010). An increased content of zinc in soil (above 1,000 mg kg^{-1}) is a common problem of Chinese cities, including Changchun, Fuzhou, Hangzhou and Shanghai. These values are significantly higher than those naturally occurring in these places, what indicates strong intensification of human activity (Luo et al. 2012). This is a serious problem, mainly because the emission of this metal into the environment is often correlated with the release of other elements, such as copper and lead (Sun et al. 2010). Diversity of sources and the emission scale leads to large variations of the zinc content in soil. A study on the urban area of Wolverhampton (the United Kingdom) demonstrated that the content of Zn in the soil ranged from 54.2 to 6,740 mg kg^{-1}. The analysed city was subjected to long-term impact associated with the local industry (mining and processing of metal ores). The lowest values of the zinc content were observed in rural areas situated far from industrial facilities (in the range of 80.8 - 200 mg kg^{-1}). Significantly higher values were observed in industrial (66 - 3,040 mg kg^{-1}), recreational (54.2 - 2,950 mg kg^{-1}), and developed (54.6 - 6,740 mg kg^{-1}) areas. For comparison, the authors determined the Zn content in the area of one of London's boroughs (Richmond upon Thames), which, despite the impact of its population, is not affected by the problem of intensive emissions of industrial pollutants. In the study area, the amount of zinc in the soil was from 11.4 to 1,810 mg kg^{-1} while in recreational areas the highest determined content was 657 mg kg^{-1} (Kelly et al. 1996).

In urban areas, huge amounts of zinc are introduced into soil as a result of traffic. Some estimations indicate that the emission of zinc may be as high as 179 Mg per year worldwide (Ajmone-Marsan, Biasioli 2010). Increased emission of heavy metals related to traffic arises from their penetration into the environment along with exhaust fumes and as a result of the wearing of surfaces, tyres, brake pads and motor vehicle bodies. Significantly lower amounts are observed in residential areas and the lowest ones in green recreational areas (Luo et al. 2012). The second major source of this element in soil is agricultural practice, including fertilisation with sewage sludge. In this case, the application of sludge causes an increase in the content of bioavailable zinc (Kabata-Pendias 2010). Furthermore, significant pollution of the environment with zinc is a result of waste disposal, especially of post-consumer electronic equipment (Dagan et al. 2007).

The degree of soil contamination with zinc is very high. The content of zinc in Oslo (Norway), Wrocław (Poland) and Kolkata (India) is 173 - 576 mg kg^{-1}, 23 - 1,150 mg kg^{-1}, 213 - 1,640 mg kg^{-1} and 90 - 10,300 mg kg^{-1}, respectively. High contents of zinc in urban soils were recorded for the following cities: Avilés (Spain) – 1,959 mg kg^{-1}; Jakobstad (Finland) – 2,368 mg kg^{-1}; Naples (Italy) – 2,550 mg kg^{-1}; Newcastle upon Tyne (the United Kingdom) – 4,625 mg kg^{-1}; Berlin (Germany) – 25,210 mg kg^{-1}; Gibraltar (the United Kingdom) – 44,900 mg kg^{-1} (Ajmone-Marsan, Biasioli 2010).

It should be noted that the threat created by heavy metals present in soil results mainly from their mobility, bioavailability and assimilability as well as ecotoxicity (Luo et al. 2012).

BIOLOGICAL ACTIVITY OF SOILS SUBJECTED TO ZINC IMPACT

Soil is an extremely important resource due to its environmental, economic and social role, and this resource is non-renewable in the time scale of human life. The quality of soil can be assessed based on its natural properties resulting from the soil's ability to retain and detoxify pollutants and to purify water, as well as properties related to productivity (measured as the volume of the biomass obtained) and health issues associated with the incorporation of elements into the food chain (Wyszkowska et al. 2013*c*).

The role of microorganisms in soil is crucial for the circulation of matter and flow of energy in the environment (Kabata-Pendias 2010). Heavy metal contamination is destructive to natural processes occurring in the soil. Presence of these elements distorts the structure of microorganisms and their activity associated with the circulation of key macronutrients, such as carbon, nitrogen, phosphorus and sulphur, in the environment (Kandeler et al. 1996). The size of a crop yield greatly depends on the biological activity of soil microorganisms, which shapes the fertility of the soil. Pollutants decrease the microbial activity and lead to an increased content of heavy metals in plant tissues (Yang et al. 2006).

Interactions between heavy metals and microorganisms in the soil environment are extremely complex. Microorganisms can affect both the mobilisation and immobilisation of metal. Toxicity associated with the degree of oxidation may be reduced or stimulated by oxidation and reduction processes. Metals such as zinc can be statically adsorbed on the surface of microbial cells or undergo either passive accumulation or active transport into the cells. Moreover, the substances secreted by microorganisms can reduce the mobility of metals by forming complexes, while their biodegradation leads to the release of zinc back into the environment. An indirect impact of microorganisms on the bioavailability of the metal involves processes which result in a change of the pH of the environment (Ledin 2000).

Conclusions on the condition of soil should be based on a multi-parameter analysis because individual indicators are insufficient for demonstrating the whole complexity of interactions between the impact of a heavy metal and the microbial consortium in soil (Castaldi et al. 2004, Wyszkowska et al. 2013b).

An optimal dose of zinc may stimulate microbial growth in soil, as reported by Kucharski et al. (2011c). Zinc applied at an amount of 300 mg kg^{-1} of soil d.m. positively affected the growth of organotrophic bacteria, actinomycetes and fungi. However, with a prolonged retention time of the metal, a decrease in counts of these microorganisms was observed. Zinc exerted the strongest negative impact on bacteria of the *Azotobacter* sp. After 120 days of incubation of soil samples contaminated with 300 mg Zn kg^{-1}, the resistance of microorganisms can be ranked as follows: oligotrophic bacteria > fungi > organotrophic bacteria > actinomycetes > *Azotobacter* sp. Many authors emphasise that zinc at doses higher than optimal inhibits the microbial activity of soil (Wyszkowska et al. 2008). In a study by Wyszkowska et al. (2008), the pollution of soil with zinc in doses of 500 and 1,000 mg kg^{-1} of soil d.m. resulted in decreased numbers of soil microorganisms. The negative impact of zinc on the counts of oligotrophic, copiotrophic, ammonifying and nitrogen-fixing bacteria, bacteria of the *Arthrobacter* sp.*, Azotobacter* sp. and *Pseudomonas* sp., as well as actinomycetes and fungi, has been proven. Soil pollution with 1,000 mg of Zn kg^{-1} inhibited the development of microorganisms according to the following series: *Azotobacter* sp. > copiotrophic bacteria > *Arthrobacter* sp. > ammonifying bacteria > *Pseudomonas* sp. > oligotrophic bacteria > nitrogen-fixing bacteria > fungi > actinomycetes. An excess of zinc in soil interferes with the nitrification process, which mainly results from the negative impact of this metal on nitrifying bacteria (Borowik et al. 2014*a*).

Despite the great variation in susceptibility to the presence of individual trace elements, microorganisms are adaptable to environmental conditions modified by high pollution. Typically, fungi are more tolerant to the presence of heavy metals than bacteria (Kabata-Pendias 2010). Moffett et al. (2003) indicated that the impact of zinc caused changes in the microbial structure of soil. The investigation of the tolerance to zinc showed that a dose of 200 mg of Zn kg^{-1} increased the resistance of bacteria in the soil environment (Bååth et al. 1998). Adaptation to an increased content of zinc in soil may result from the elimination of microbial species sensitive to the metal along with the simultaneous acquisition of resistance and adaptation of microorganisms to varying environmental conditions through physiological or genetic changes. This leads to some loss of diversity, which is unfavourable for the quality of the environment (Lock, Janssen 2005).

Evaluation of the ratio of microbial biomass to the organic matter content and the relationship between microbial biomass and the biological activity of soil provides very useful indications for a comprehensive determination of the effect of heavy metals on soil (Kunito et al. 2001). Other studies have shown a reduction of microbial biomass under zinc pollution (Castaldi et al. 2004) and a disturbance in the ratio of enzymatic activity to microbial biomass (Kunito et al. 2001). Microbial mass reduction results from the stress caused by the high pressure of zinc. Microorganisms in adverse environmental conditions consume more energy in order to survive. This is due to an increase in cellular respiration and thus organic carbon consumed in dissimilation processes is not used for the development of microbial biomass (Mikanova 2006). The extent, frequency and specificity of cellular respiration changes as well as the degree and specificity of nitrogen mineralisation increase as the pollution of soil with zinc becomes more severe. An increasing C:N ratio suggests that the share of fungal biomass increases with the growth of zinc toxicity, hence its value can serve a specific indicator of the soil contamination degree (Dai et al. 2004).

Biochemical activity is a good indicator of the condition of soil. Assays of soil enzyme activity are quick and inexpensive; moreover, they generate representative indices of the integrity of soil metabolism processes and reflect the nature of the changes occurring under the influence of toxic substances (Kizilkaya et al. 2004, Chaperon, Sauvé 2007, Wyszkowska et al. 2013*b*). Enzymes may react diversely to the presence of zinc ions in soil. There are reports supporting the stimulating effect of zinc ions on enzyme activity, including phosphatase and invertase, whose activities were positively correlated with the metal dose. With a growing amount of zinc ions (in the range of 100 to 400 mg kg^{-1}) an increase in the activity of these enzymes, as compared to the control soil, was observed (Yang et al. 2006). The factor which may explain it is the soil's organic matter (Badora 2011). In soils with a higher organic matter content, a weaker toxic effect of zinc on the biochemical properties of soil is observed (Bååth 1989, Moreno et al. 2009, Badora 2011, Boros et al. 2011, Wyszkowska et al. 2013*a*). However, studies on the activity of acid and alkaline phosphatases, enzymes involved in the cycling of phosphorus, have demonstrated that they can be inhibited by soil pollution with zinc (Castaldi et al. 2004, Hinojosa et al. 2004, Moreno et al. 2009, Kabata-Pendias 2010).

Dehydrogenases, intracellular enzymes which catalyse oxidation-reduction reactions involving organic matter, are the most sensitive enzymes to soil pollution with zinc (Chaperon, Sauvé 2007, Kucharski et al. 2011*a*, Borowik et al. 2014*b*, *c*). Because they are bound to living microbial cells, they are considered to be good indicators of heavy metal toxic effects on microorganisms (Kizilkaya et al. 2004, Oliveira, Pampulha 2006, Zaborowska et al. 2015*a*). The negative influence of zinc on the activity of these enzymes is widely documented in literature (Kunito et al. 2001, Castaldi et al. 2004, Mikanova 2006, Chaperon Sauvé 2007, Moreno et al. 2009). According to Chaperon, Sauvé (2007), even a dose as low as 11.5 mM of Zn kg^{-1} halves dehydrogenase activity. Mikanova (2006) observed an inhibitory effect of zinc on the activity of these enzymes in soil polluted with 407 mg of Zn kg^{-1}. Moreno et al. (2009) reported that soil contamination with 300 mg of Zn resulted in a decrease of dehydrogenase activity by 49%, while an application of 1,300 mg of Zn kg^{-1} led to an an inhibition by 69% compared with the control.

In turn, the impact of zinc on extracellular enzymes can be modified by the immobilisation or complexation of these proteins with organic matter, which may result in a protective effect (Kizilkaya et al. 2004). Moreover, plants growing on soils contaminated with zinc affect the microbiological properties of the soil by stimulating the growth of heterotrophic bacteria and fungi and enhancing the activity of dehydrogenases, urease and β-glucosidase, the enzymes related to the cycling of the most important nutrients. This is reflected by higher values of total organic carbon and total nitrogen in agricultural soils. The phenomenon may be related to root exudates, which stimulate the biological properties of soil (Castaldi et al. 2009). Urease is an extracellular enzyme which is responsible for the circulation of nitrogen in the soil. The inhibition of this enzyme under the influence of soil pollution with zinc has been reported (Kunito et al. 2001, Castaldi et al. 2004, Hinojosa et al. 2004, Yang et al. 2006, Chaperon, Sauvé 2007, Moreno et al. 2009). The availability of carbon is associated with the decomposition of cellulose accumulated in the soil. This depends on the activity of cellulases, which are therefore an important measure of the soil quality. Deng and Tabatabai (1995) found that the activity of this enzyme complex is sensitive to the effect of zinc ions (in an amount of 5 mM kg^{-1}), causing a reduction in cellulose activity. Contamination of soils with zinc results in reducing the activity of other enzymes, including arylsulphatase (Hinojosa et al. 2004, Mikanova 2006), β-glusosidase (Kunito et al. 2001, Castaldi et al. 2004, Hinojosa et al. 2004, Moreno et al. 2009), sulphatase (Castaldi et al. 2004), protease (Castaldi et al. 2004, Moreno et al. 2009) and catalase (Yang et al. 2006).

Soils subjected to anthropogenic pressures are typically characterised by both diverse composition and a diverse content of toxic substances. Therefore, analysis of individual metals in environmental samples is often very difficult to perform (Chaperon, Sauvé 2007). The toxicity of zinc measured by different parameters and under the influence of other elements may vary (Table 1). This results from the fact that the response of microorganisms to heavy metals is also affected by environmental conditions, which modify the availability of metals to organisms. Thus, different soil properties often lead to discrepancies in data concerning the effect of heavy metals on biological processes (Bååth 1989).

THE EFFECT OF ZINC ON PLANTS

The toxicity of heavy metals and their compounds is related to their bioavailability, which results from their biological and physicochemical properties (Duffus 2002, Zaborowska et al. 2015b). However, their content in the biosphere has significantly increased since the industrial revolution, and now their presence is often perceived as a threat to the natural environment (Jing et al. 2007).

Zinc is an essential micronutrient necessary for the proper development

Table 1

Ranks of heavy metals according to their toxicity with respect to selected biological parameters of soil

Parameter	Impact	Reference
Development of microorganisms	Cd > Cu > Zn > Pb	Bååth (1989)
Development of microorganisms	Ag > Cu > Cd > Ni > Zn > Pb > Mn	Kabata-Pendias (2010)
Development of microorganisms	Cr > Pb > As > Co > Zn > Cd > Cu	Wang et al. (2010)
Oligotrophic bacteria	Ni > Pb > Cr(III) > Cu > Zn > Cd	Wyszkowska, Kucharski (2003*b*)
Oligotrophic bacteria	Cd > Zn > Pb > Cu	Wyszkowska et al. (2007)
Copiotrophic bacteria	Cd > Ni > Cr(III) > Zn > Cu	Wyszkowska, Kucharski 2003b
Ammonifying bacteria	Ni > Pb > Cr(III) > Cd > Zn > Hg	Wyszkowska, Kucharski (2003*b*)
Nitrogen-fixing bacteria	Zn > Cr(III) > Hg > Cu	Wyszkowska, Kucharski (2003*b*)
Actinomycetes	Cu > Cr(III) > Ni > Zn > Pb	Wyszkowska, Kucharski (2003*b*)
Actinomycetes	Cd > Zn > Ni >Cr(VI)	Wyszkowska et al. (2007)
Dehydrogenases	Cu > Zn > Cr(VI) > Hg > Ni > Cd > Cr(III)	Wyszkowska, Kucharski (2003*a*)
Dehydrogenases	Cr(VI) > Cd > Zn > Pb > Cu >Ni	Wyszkowska et al. (2006)
Dehydrogenases	Zn > Cu > Ni > Cd	Kucharski et al. (2011*b*)
Acid phosphatase	Cu > Al > Cd > Zn > Fe(III) > Ni > Pb > Sn > Fe(II) > Co	Nowak et al. (2003)
Acid phosphatase	Cu > Ni > Zn > Cd > Cr(III) > Cr(VI) > Hg	Wyszkowska, Kucharski (2003*a*)
Acid phosphatase	Cr(VI) > Ni > Cu = Cd> Pb > Zn	Wyszkowska et al. (2006)
Alkaline phosphatase	Cd > Al > Zn > Fe(III) > Cu > Pb > Ni > Fe(II) > Se > Co	Nowak et al. (2003)
Alkaline phosphatase	Zn > Cu > Ni > Hg > Cr(VI)	Wyszkowska, Kucharski (2003*a*)
Alkaline phosphatase	Cd > Ni > Cu > Zn >Cr(VI) >Pb	Wyszkowska et al. (2006)

of plants. It occurs in amounts of 25 - 30 mg kg^{-1} of leaf d.m. (Kabata-Pendias, Pendias 1999), or 20 - 50 mg kg^{-1} of leaf d.m. (Wiśniewska 2001), which cover the nutritional demand for this element. Zinc content in plants is highly variable and dependent on plant species. More mobile metals, such as zinc, are not only accumulated in the roots of plants, but are also transported to aerial parts, such as stems, leaves and flowers (Sadecka 2008). In the study of Kozłowska-Strawska (2009), the zinc content (mg kg^{-1}) in the aerial parts was 24.2 in *Sinapis alba*; 50.4 in spring wheat; 264.0 in canola; 72.5 - 131.0 in spring barley; and 122.0 in *Dactylis glomerata*. The role of zinc is primarily associated with biochemical processes, because it is a component of certain enzymes (proteases, dehydrogenases, peptidases and phosphohydrolases). It is also suggested that zinc contributes to the formation of plant resistance to adverse weather conditions and plant pathogens (Kabata-Pendias 2010). In both animals and plants, zinc participates in the regulation of DNA and RNA, as well as the chromatin structure (Broadley et al. 2007).

Cultivation of plants on soil highly polluted with zinc (400 mg of Zn kg^{-1} of soil d.m.) generates huge economic losses, as the yield of pea and spring barley grains obtained in such areas may be lower by as much as 2 Mg ha^{-1} than the yield obtained in unpolluted areas (pea: 4 Mg ha^{-1}, spring barley: 5 Mg ha^{-1}) (Moffett et al. 2003). Interactions between various elements absorbed by plants should also be considered. Antagonistic and synergistic interaction of elements is an interesting phenomenon, which is of high importance for the assimilability of zinc by plants (Ciećko et al. 2006). In facilities where zinc was processed together with two heavy metals, the toxicity of metal mixtures decreased as follows: CuZnNi > CuZnPb > CuZnCd > CuZnCr; while in the case of three metals, it decreased as follows: CuZnNiCr > CuZnNiPb > CuZnNiCr (Wyszkowska et al. 2006). Wyszkowska et al. (2007) found a significant decrease in the yield of oats cultivated in soil polluted with a mixture of metals (NiZnCuPbCdCr). The antagonistic interaction between zinc and iron, copper, cadmium, phosphorus, calcium and magnesium leads to disturbances in their uptake, and thus to changes in plants' chemical composition (Kabata-Pendias 2010). In the study of Jasiewicz (1991), the content of zinc in sunflower was determined by the presence of manganese and copper and in canola it was affected by the presence of iron and manganese. Badora (2002) observed an inhibitory effect of zinc on cadmium accumulation in pea and a high importance of aluminium for the process of zinc immobilization in soil. On the other hand, in the study of Wyszkowski et al. (2006), pollution of soil in a range of 4 to 400 mg of Zn kg^{-1} resulted in an increase in the content of nitrogen, calcium, magnesium and potassium in the aerial parts of spring barley, while a dose of 400 mg kg^{-1} reduced the content of sodium and phosphorus.

The uptake of heavy metals by plants depends on several factors, such as soil characteristics, climatic conditions, crop management and plant type, including genotypic determinants (McLaughlin et al. 1999). Zinc is relatively easily absorbed by plants, but at such concentrations which, despite having a toxic effect on plants, do not constitute a health risk to humans (Clemens 2006). It is best absorbed in the form of Zn-EDTA, zinc sulphate and, to a lesser extent, in the form of zinc chloride and oxide (Karczewska 2000). Where the zinc content in plant tissue is less than 20 mg kg^{-1}, a deficiency of this element is recognised. In turn, the tolerance of plants to high concentrations of zinc is in the range of 300 to 400 mg kg^{-1} (Ociepa-Kubicka, Ociepa 2012). Li et al. (2009) indicates that there is a close correlation between the content of zinc in the soil and the amount in roots and aerial parts of plants.

Zinc deficiency in plants is manifested by chlorosis of intravenous spaces in leaves, the appearance of red and brown spots and a reduction of internodes and leaf size (Broadley et al. 2007). Cereals, legumes, hop and flax are the plants most sensitive to zinc deficiencies (Kabata-Pendias, Pendias 1999). However, an excess of zinc is unfavourable for many plants and is manifested by chlorosis of leaves and inhibition of the growth. According to Tukendorf (1989), disorders of plant metabolism associated with excessive accumulation of zinc are the result of a direct interaction of cations with -SH groups of metabolites and enzymes. The intensification of lipid peroxidation processes, associated with impaired calcium homeostasis, is also significant.

Therefore, it is extremely important to maintain good soil conditions by reducing the content of undesirable substances, thereby eliminating the negative pressure exerted by heavy metals (including zinc). The experiment conducted by Shute, Macfie (2006) demonstrated that an increase of zinc in soil caused a significant reduction in soybean biomass and pollution of soil with this metal at a sufficiently high dose (2,000 mg of Zn kg^{-1} of soil) exerted a toxic effect on plants. Plants have developed different defence mechanisms against heavy metals, for example the synthesis of phytochelatins, which maintain metal homeostasis in the cell. These proteins transfer zinc ions to a vacuole, where they are bound by oxalates. These, in turn, together with malic acid, are chelating agents for zinc ions (Tukendorf 1989).

SUMMARY

It is extremely difficult to draw firm conclusions on the toxicity of zinc. Zinc performs a number of functions in living organisms and is widely used in everyday life. Its excess may have a negative impact, but the actual consequences depend on many factors. The doubts whether zinc is a nutrient or a toxic element can be dispelled by recalling the words of Paracelsus, which are fundamental to modern toxicology: “All things are poison and nothing is without poison. Only the dose makes a thing not a poison”.

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