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Review

Ecotoxicology of Aluminium

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Abstract

Aluminium is an element commonly occurring in nature, the third most abundant in the earth's crust after oxygen and silicon. It forms numerous mineral and organic complexes, characterised by different degrees of hydration. Its easy transition from solid to liquid phase and high solubility in acid environment are decisive factors for its important function in the environment. Until recently, aluminium was considered harmless for the human organism as it is readily excreted through urine.

However, studies of environmental toxicology conducted in recent years indicated that aluminium could be a cause of many diseases in humans, animals and plants. Acid rains and increasing acidification of the environment induced water and soil pH changes which resulted in the mobilisation of toxic aluminium ions which in turn evoked many unfavourable alterations, such as plant poisoning, forest drying, crop reduction, vanishing of water fauna, and numerous disturbances in the function of human and animal organisms.

Aluminium can be found in many food products and feed for animals. In this way it enters the organism and accumulates in various tissues. Although the mechanism of toxic aluminium actions on humans has not been elucidated yet, prophylactic action should be undertaken aimed at limiting the contact of humans with aluminium. Most of all, it should be eliminated from food, food additives and medicines. We should avoid tools, kitchen utensils and appliances made of aluminium as well as aluminium wrappings and containers.

Keywords: ecotoxicology, aluminiumin in soil and foods, effect on various plants, animals and humans, toxicity of aluminium

Introduction

Studies of environmental toxicology in recent years have revealed that aluminium can be a cause of many diseases in humans and animals. It can also exert harmful effects on plant roots [17, 22, 24, 25]. Although aluminium has not hitherto evoked significant interest of toxicologists, increasing acidification of the environment and investigations of the effects of acid rains on water chemistry indicated that water pH change into more acid was accompanied by a rise in aluminium concentration in water. It has also been shown that high concentrations of this metal has detrimental effects on all water organisms [9,10]. Moreover, soil acidification, resulting from abrupt aggravation of air pollution by acidic nitrogen and sulphur oxides, caused the mobilisation of toxic aluminium ions, which evoked numerous harmful changes in soil environment such as plant poisoning, forest drying or a dramatic decrease in cereal crops cultivated on acidified soils [12].

Widespread use of aluminium in everyday life is based on the conviction that this element is harmless for humans, and that it is quickly excreted from the organism with urine. It should be emphasised that aluminium has been widely used for manufacturing, e.g. kitchen utensils, parts of medical and scientific equipment, various wrap-

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pings and containers. Aluminium salts have been used as food additives (leavens, pH stabilisers, preservatives against caking). Different aluminium compounds are used in clinics (dialysing fluids) and also in the manufacturing of cosmetics. Furthermore, aluminium sulphate is often used in drinking water treatment to remove organic pollutants which are a potential source of aluminium pollution for people and farm animals [8, 21, 23, 35].

Many studies indicate that aluminium can exert a negative effect on many metabolic pathways in the organism, particularly on calcium, phosphorus, fluorine and iron metabolism. Aluminium ions show affinity for DNA and RNA, and inhibit such enzymes as hexokinase, acid and alkalic phosphatase, phosphodiesterase and phosphoxidase. It has been demonstrated that aluminium is harmful mainly for the nervous, osseous and haemopoietic systems [6, 7, 11, 16, 27, 37].

Bielariski [5] and Kabata-Pendias and Pendias [14] reported that aluminium is a very common element in the natural environment, and its content in the earth's crust amounts to about 8%, which makes it the third most abundant element after oxygen and silicon. In the earth's crust, aluminium occurs in the form of compounds with oxygen, fluorine, silicon and other elements. Its easy transition from solid to liquid phase and high solubility in acid environments are decisive factors for its important function in the environment. It forms numerous mineral and organic complexes characterised by different degrees of hydration. *Its* highest mobility in soil is observed at pH 4.0-4.5, and the presence of sulphate and nitrate ions and organic substance increase dissolution of aluminium compounds and minerals in soil.

Aluminium Distribution in Soil, Water and Air

Aluminium content in soil depends on a parent rock and soil type. Most commonly, its total content falls into the range 1-25%. The highest aluminium amounts occur in numerous ahuninosihcates such as orthoclase, albite, anorithe, nepheline, leucite and micas: muscovite, biotite, lepidolite. Moreover, aluminium occurs in clay minerals such as kaolinite, montrnorylonite and illite [13].

For agriculture the most important forms are active aluminium. These include mobile and exchangeable aluminium, assimilable aluminium and aluminium contained in water-soluble compounds occurring in solution as Al^{3+} cations. The increased concentration of these ions and augmented activity of aluminium fraction is connected with soil acidification (pH < 5.5), which is damaging for physico-chemical and biological soil properties and exerts a toxic influence on plants. Aluminium released in acidified soils is the main cause of crop decreases [1, 2].

Due to the exceptionally slight solubility of aluminium in water, its content in waters is very low, ranging from 60 to 300 µg/l at pH 5-9. In river water, it averages 64 µg/l in sea water it is about 1-5 µg/l, while in water of open oceans it amounts to only 0.5 µg/l. Increased acid rainfalls have caused acidification of surface waters in many areas, which in turn have resulted in mobile aluminium release from metastable compounds in bottom sediments and their transition into water. A pH drop to 6.0 leads to dying out of snails and bivalves; a further decrease to pH 5.5 brings death to more sensitive insects, e.g. mayfly pupas and caddis-fly larvae; pH below 5.0 kills trout and below 4.0 exterminates eels. Lowering pH to 4.0 causes dying out of less sensitive insects and plankton, while at pH 3.0 some water plants disappear. It is evident that a disturbance of ecological balance in the ecosystem is conveyed through food chain to terrestrial organisms (birds), which elicits further disadvantageous changes in the whole biocenosis [15, 19].

In Poland, high concentrations of monomeric, inorganic aluminium in water have been observed mainly in the Tatra, Karkonosze and Lysogory Mountains, and on the slopes of Barania Mountain. Water of montane streams and creeks flow on granite bedrock and cannot neutralise excessive amounts of acids, entering water. It should be mentioned that the content of aluminium ions is positively correlated with the concentration of hydrogen ions. The highest aluminium concentrations were observed during snow melting and after heavier rainfalls [36].

The presence of aluminium in the air is dependent on human activities. It is injected into the atmosphere mainly by carbon combustion, motor vehicle exhaust, waste incineration and exhaust gases of metallurgical and cement industry. Aluminium can also be released into the air as a result of weathering of rocks, e.g. aluminosilicates. This is so-called natural dust formation (continental dust). Average aluminium concentration in the air falls into the range 50-5000 ng/m^3 [30].

Aluminium Influence on Plants

Numerous studies conducted for many years have shown that aluminium can be both beneficial and harmful for plants, causing even death. The beneficial effect of aluminium on plants consists of the stimulation of iron absorption by root system, increased absorption of phosphorus, prevention of toxic effects of copper and manganese and plant protection against phytopathogenic fungi. Furthermore, aluminium increases plant resistance to unfavourable environmental conditions, such as drought, high and low temperatures, soil salinity [4].

On the other hand, detrimental aluminium effect on plants manifests itself as crop decrease which is caused by changes in the morphology of root system, inhibition of its elongative growth, root callosity, reduced number of rootlets, and dying away of growth cone. Moreover, aluminium phytotoxicity is expressed as disturbances in the absorption of mineral substances (changes in plasma membrane structure and function), inhibition of cell divisions and elongation, and disturbances of important processes determining normal growth of the root system [9,32].

Aluminium influence on symbiotic relationships between plants and *Rhizobium* and *Bradyrhizobium* bacteria is also very damaging. Studies of Strzelec [31] have indicated that bacteria are more sensitive to aluminium than leguminous plants. A similarly disadvantageous effect has aluminium on plant-fungus symbiotic cooperation called mycorrhiza [34], which participates in nutrient supply. Furthermore, we observed disturbances in plant growth leading to a decrease in increments, weakening of immunity from diseases and resistance to pests, which resulted in premature physiological aging.

Many years' studies of Filipek [9], Barszczak and Bilski [4], and Kotowski et al. [15] allow us to divide plants into three groups differing in sensitivity to aluminium:

Table 1. Sensitivity of plants to aluminium.

Very sensitive species	Medium-sensitive species	Less sensitive species
Beet	Pea	Lupine
Lettuce	Sunflower	Buckwheat
Mustard	Potato	Turnip
Cucumber	Triticale	Currant
Tomato	Oat	Cranberry
Alfalfa		Tea
Cotton		Peanut
Sorghum		Datura
Timothy grass		Corn
Barley		Rye
Wheat		

Wide variability of plant tolerance to aluminium action results from the fact that there are two mechanisms of resistance:

a) extracellular - blocking the aluminium entrance into the cell,

b) intracellular - consisting of changes in metabolism of the cells which were polluted by aluminium, leading to Al immobilisation and detoxification.

Aluminium Influence on Animals and Humans

Considerable acidification of water environment in the middle of the fifties and mobilisation of toxic aluminium ions by acid rains caused a decrease in fish populations in many countries. This compelled governments to support multidirectional and extensive studies on toxic durninium influence on water organisms. The surveys have shown that ahiminium M acidified waters is particularly harmful for invertebrates such as snails, bivalves and crustaceans because it replaces calcium cation in their bodies. In fish, aluminium accumulates in gills which causes the blockade of ion exchange and respiration, while in frogs, reproductive processes are disturbed [18, 33].

In other animals, e.g. birds and mammals, aluminium is usually taken in with food and evokes diversified toxic actions. In birds, aluminium most frequently affects egg shells and the metabolism of calcium and phosphorus, causing diminished efficacy of Ca absorption and decreased metabolic rates of its transformations, resulting in aluminium incorporation into bones. In mammals, aluminium evokes many disturbances in blood function (erythropoiesis, leucocytosis, lymphopenia), gastrointestinal systems (absorption of nutrients, active transport, digestive enzymes), and osseous systems (changes in mineral bone structure, worsening mechanical strength parameters of long bones), [3].

Aluminium in human diet derives from food, water, drugs, cosmetics, aluminium utensils and containers.

Table 2. Potential aluminium sources for humans [19].

Aluminium source	Daily dose [mg/kg]
Food products	2-5
Food additives	10-20
Aluminium utensils	< 0.1
Regularly taken antacids	1000-4000
Buffered aspirin	4000

Aluminium toxicity for humans results from replacing Mg^{+2} and Fe^{+3} by Al^{+3}, which induces numerous disturbances in the organism, connected with intercellular communication, secretory functions, and cellular growth. The severest danger of toxic aluminium action lies in its neurotoxicity (neuronal atrophy, mainly in substantia nigra, striatum and locus ceruleus, and the decreased nucleoli size). Aluminium-evoked changes in neurones are similar to degenerative lesions observed in patients suffering from Alzheimer's disease [24]. Neurotoxic aluminium action probably consists in the displacement of magnesium ions in ATP by aluminium, which induces changes in the function of all enzymes utilising ATP as a substrate, and in the inhibition by aliuninium of tubuhn polymerase activity in the brain.

Aluminium toxicity for the osseous system is reflected, among other ways, by excessive bone softness and proneness for bone fractures. Increased aluminium concentration diminishes collagen synthesis by osteoblasts, and slows mineralisation processes, which is a direct cause of a drop in the normal amount of bone tissue [26].

Aluminium also exerts substantial effects on blood and haemopoietic systems. Anaemia produced by erythropoietin deficit was observed most frequently. High aluminium concentrations inhibit the enzymes participating in heme synthesis and disturb iron metabolism by binding to transferrin.

Notwithstanding many studies, the mechanisms of aluminiums toxic effects on humans have not been fully elucidated. Carcinogenic action of aluminium has not been confirmed or explained yet, although a considerable rise in the content of this element has been detected in human neoplastic cells. The aforementioned data indicate that preventive actions should be undertaken to limit the contact of humans with aluminium. Aluminium utensils should be avoided, and most of all, aluminium should be eliminated from food.

Aluminium Occurrence in Food

Aluminium, as a common element in the natural environment, occurs in almost all food products. Its quantities in different products show wide variations, depending on the food source, method of preparation and storage conditions. The main products supplying aluminium to the organism are cereals, ripened cheese and salt. Also herbs, spices and tea are characterised by natural high content of aluminium [30].

Aluminium contents in such plant food products as fruits and vegetables, and animal products: meat, poultry, eggs do not exceed 10 mg/kg. Among plant products, cereal grams naturally contain higher quantities of aluminium than fruits and vegetables, but products manufactured from them bear less duminium than full grain. Spices and herbs accumulate very high amounts of aluminium, reaching sometimes 2000 mg/kg, while tea even up to 5000 nig/kg of dry leaves. Among milk products, the highest aluminium contents are observed in ripened cheese and cheese spreads [21].

FAO/WHO committee established maximum weekly aluminium intake at 7 mg/kg of body weight, whereas the results of many studies indicate that we often ingest even 10-100 mg of aluminium a day. Estimations of daily aluminium consumption differ considerably, depending not only on soil type and environmental conditions in certain countries, but also on the methods of food processing and storage [23].

An additional source of aluminium are aluminium salts, used in many countries to improve taste of food products or to facilitate food processing. In Poland, food supplementing by aluminium is not allowed (Decree of The Minister of Health and Social Security dated 31.03.1993 regarding the listing of permissible additives and technical pollutants in food products). Further extra source of aluininium in diet is aluminium used for production of installations for food industry, kitchen utensils and appliances. It has been shown tlat aluminium can migrate to many sour foods. The extent of this migration is determined by aluminium type, food pH and contact duration [28]. Although fats, proteins and sugars present in food inhibit aluminium release, this is a problem which should be taken into consideration. Some data on aluminium migration from utensils to food are presented in Table. 3

Table 3. Migration of aluminium from aluminium utensils to food [28],

Food product	Aluminium content (mg/kg) in a product		
	Uncooked	Cooked in a pot made of	
		aluminium	steel
Tomatoes	0.10	75.1	0.16
Cabbage	0.13	36.1	0.20
Apple juice	0.13	7.1	0.12
Chicken	0.47	1.0	0.66
Ham	0.85	1.2	1.2
Beef	0.19	0.85	0.21
Cod	0.35	0.47	0.40
Cereals	0.62	0.60	0.17
Peas	1.9	1.9	1.9
Rice	1.5	1.7	1.7
Pudding	–	4.2	4.2

Wrappings and containers used in the food industry also contribute, to some extent, to food pollution with aluminium as it is widely used for manufacturing cans, tubes, and foils due to its resistance to corrosion, neutrality for many food products and some bactericidal properties. In spite of aluminium neutrality for a broad variety of food products, it cannot be stated without any doubts that the migration of this element from containers to food does not constitute an additional source of this metal in food products with low pH.

Table 4. Storage time-dependent migration of aluminium to food [281.

Product	Storage time	Aluminium content
Beer	12 months	10 - 20 mg/l
Orange juice	12 months	46 mg/l
Beef stew	5 months	62 mg/kg
Beans, peas, spinach, tomatoes, braised meat	18 months	< 200 mg/kg
Red currant puree	18 months	680 mg/kg

Drinking water can also be an aluminium source for humans. It should be mentioned that in EU member states, permissible aluminium content in drinking water is 0.2 mg/l while in Poland permissible aluminium content in drinking water and water used for domestic purposes is 0.3 mg/l, [13].

Biochemical Basis of Aluminium Toxicity

Aluminium occurs in the natural environment at third oxidation state. Its ionic radius is small at 0.41 A. Besides, aluminium has one empty orbital *p* in valence shell, and therefore it has a strong positive charge and electron acceptor properties. In water solutions it forms complexes with water. In such complexes, aluminium forms bonds principally with oxygen atoms but it can also bind to other electron donors, such as nitrogen and halogens. The Al-O and Al-N bonds are partially covalent and partially chelate complexes, and this is a reason of slow ligand exchange in aluminium complexes. Such slow exchange can explain the fact that it is difficult to confirm and evaluate duminium toxicity in short time intervals. Toxic effect can be intensified and accelerated if environmental conditions increase Al^{+3} concentration, e.g. acidification of the environment [11].

Detailed biochemical studies have indicated that aluminium exerts strong influence the activity of many enzymes. Aluminium fonns tight complexes with ATP so it is a strong inhibitor of numerous enzymes utilising ATP as a substrate, such as Na^+ K^+ ATP-ase. The following enzymes are also inhibited by aluminium: hexokinase, alkalic phosphatase, choline acetyltransferase, ferrooxidase [37].

Sedrowicz et al. [27] observed that in the cells, aluminium is located mainly in the nucleus, where it binds to chromatin, and in lysosomes in equimolar combinations with phosphate groups. Moreover, aluminium was shown to inhibit important neurotransmitters, isolated from synapses (γ-aminobutyric acid, 1-glutamate, choline, noradrenaline and serotonin) which play a role in the transmission of nervous impulses. Aluminium is also responsible for nerve fibre degeneration, leading to a decreased number of microchannels in the damaged neurones, dendrites and the cells implicated in memory processes.

Conclusion

Although the mechanisms underlying aluminium toxicity have not been fully elucidated yet, we are already aware that environmental pollution and acidification of large amonts of soil and surface waters, and also drinking water, can be compared to the opening of "Pandora's box" and releasing a poison, which slow can be harmful for the whole population of humans, animals and plants.

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