DRINKING WATER QUALITY IN THE ASPECT OF THE PRESENCE OF POTENTIALLY TOXIC TRACE ELEMENTS

Jacek Cybulski, Kamila Pokorska-Niewiada, Agata Witczak
West Pomeranian University of Technology in Szczecin, Faculty of Food Sciences and Fisheries

Summary. Sources of drinking water include surface water (lakes, rivers, retention reservoirs) and groundwater. The quality requirements for drinking water result directly from the Polish Regulation of the Minister of Health of 2017, which specifies the maximum allowable concentrations of selected elements in drinking water. Drinking water is used for consumption purposes and is also the basis of the food industry. Quality of drinking water for economic and hygienic purposes is one of the elements ensuring health safety of food and nutrition. A decrease in the quality of surface and underground waters collected for consumption purposes is mainly related to human economic activity. This results from intensive development of industry, especially metallurgy, electrotechnical, chemical and mining industries, and such activities often result in contamination of surface waters and, consequently, drinking water. Due to the degree of hazard, we can distinguish elements with a very high degree of potential threat (cadmium, mercury, lead, copper, zinc, arsenic), a high degree of potential threat (manganese, iron, molybdenum) and a medium degree of potential threat (nickel, cobalt). Accumulation of these elements in the environment varies and depends primarily on the type of element, the dose taken and its chemical form. Concentration of trace elements in water mainly results from their physicochemical properties, water solubility, pH and oxidation-reducing potential, as well as the ability to form soluble complexes. The movement of elements to the human body through subsequent links in the food chain is limited by the protective effect of biological barriers. Heavy metals move in the soil–plant–animal–human trophic chain, with the potential for accumulation at any stage. Heavy metals most often reach the human body through the digestive tract. The health consequences of regular consumption of food products containing even small amounts of these elements can become apparent after many years. The literature analysis performed shows that the problem of the presence of these elements in surface waters as well as in drinking water is still valid and occurs in many regions of Europe. Water contamination with trace elements is one of the most important threats to human health.

Key words: drinking water, consumers safety, trace elements

Agata Witczak https://orcid.org/0000-0002-7705-2138; Kamila Pokorska-Niewiada https://orcid.org/0000-0002-4835-8517
jacek.cybulski@zut.edu.pl
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INTRODUCTION

Sources of drinking water include surface water (lakes, rivers, retention reservoirs) and groundwater. Quality requirements for drinking water are directly derived from the Polish Regulation of the Minister of Health of 2017, which specifies the maximum allowable concentrations of selected trace elements in drinking water, as follows [mg·dm⁻³]: arsenic 0.01, chrome 0.05, cadmium 0.005, copper 2, nickel 0.02, lead 0.01, mercury 0.001, aluminium 0.2, manganese 0.05, iron 0.2, antimony 0.005.

Drinking water is used for consumption purposes and it constitutes the basis of the food industry. Quality of drinking water for economic and hygienic purposes is one of the elements ensuring health safety of food and nutrition [Mulik 2017].

A decrease in the quality of surface and underground waters for consumption purposes is mainly related to human economic activity. This results from intensive development of industry, especially metallurgy, electrotechnical, chemical and mining industries, and the effect of such activities often involves contamination of surface waters and, consequently, drinking water [Herasimowicz-Bąk and Brzeski 2009]. Due to the degree of hazard, we can distinguish elements with a very high degree of potential threat (cadmium, mercury, lead, copper, zinc, arsenic), a high degree of potential threat (manganese, iron, molybdenum) and a medium degree of potential threat (nickel, cobalt). That is why preventive measures involving creation of an integrated system of environmental protection at every stage of production, from raw material extraction to post-production waste management, are important. Water, air and soil pollution as a result of combustion processes (dusts, gases), poor management of sewage water and waste is correlated with pollution by heavy metals. Accumulation of these elements in the environment varies and depends primarily on the type of element, the dose taken and its chemical form. Concentration of trace elements in water mainly results from their physicochemical properties, water solubility, pH and oxidation-reducing potential as well as the ability to form soluble complexes [Khlifi and Hamza-Chaffai 2010, Romanowska-Duda 2015, Michalski et al. 2018].

Negative effects of many trace elements on the human body can become apparent after many years. The movement of elements to the human body through subsequent links in the food chain is limited by the protective effect of biological barriers. However, it should be remembered that with a high concentration of trace elements as a result of their accumulation in the body, the effect of barriers may be limited [Matache et al. 2018].

IMPACT OF THE TREATMENT PROCESS ON THE CONTENT OF HEAVY METALS IN WATER

Excessive concentration of heavy metals in water bodies is a threat to humans, animals and plants. Improvement of the state of water purity can be achieved as a result of limiting pollutant emissions and remediation of polluted environments. Chemical, physicochemical and biological mechanisms are used in water purification processes. Choosing the right method is key to the effectiveness of water purification. For better results, two or more techniques are used simultaneously [Koźmińska et al. 2014].
The presence of heavy metals in treated water is primarily influenced by the filtration process on the filter bed. As indicated by Leszczyńska et al. [2009], heavy metals can get into the water from contaminated aggregates and filter beds. Heavy metals are retained on the bed but are not permanently bound in it [Pruss et al. 2012, Nowak and Imperowicz 2016]. Post-coagulation sediment contains most of the impurities removed from raw water, including heavy metals. Concentration of individual elements varies depending on the characteristics of the reservoir and season, as well as the degree of raw water contamination in the area. The type and dose of coagulant used also have an impact on the content of heavy metals in the sediments. The presence of such metals as chromium 50–130 mg·kg\(^{-1}\) of dry matter, copper 16–168 mg·kg\(^{-1}\) of dry matter, arsenic 9.2–32 mg·kg\(^{-1}\) of dry matter, zinc 91.7–781 mg·kg\(^{-1}\) of dry matter, and also lead, nickel and mercury is observed [Plonka et al. 2012]. Waste in the form of sediment constitutes a real threat to the environment, especially when it is characterized by the presence of trace elements [Nowak and Imperowicz 2016].

**IMPACT OF POTENTIALLY TOXIC TRACE ELEMENTS ON THE HUMAN BODY**

Heavy metals move in the soil–plant–animal–human trophic chain, with the potential for accumulation at any stage. Heavy metals most often reach the human body through the digestive tract. The health consequences of regular consumption of food products containing even small amounts of these elements can become apparent after many years. Inhalation of heavy metals through the respiratory system enables their easiest collection and distribution through the circulatory system. This process is most effective when the element is present in the form of particles with dimensions smaller than 100 μm, e.g. as a vapour or an organometallic compound. Elements can also be absorbed directly through the skin by transfollicular transport. The main role in this process is played by skin appendages, hair follicles and sebaceous glands, and to a lesser extent – sweat glands. The most important effects of potentially toxic trace elements in the body include changes in protein synthesis and abnormal ATP production, which can cause many negative health effects, including cancer. It mainly depends on the amount of a toxic substance taken up, the chemical form of the element, solubility in lipids and body fluids, exposure time, as well as individual resistance of the body [Manahan 2006, Li et al. 2018].

Forms of inorganic cation metals have been shown to be more strongly associated with proteins and other tissues. This relationship causes increased bioaccumulation and inhibits the process of excretion from the body. Metal ions are most often coupled to amino acids. Amino and carboxy groups are the most readily available electron donor groups of amino acids. Biological degradation is not possible for heavy metals. In the process of body detoxification, the active metal ion “hides” within the protein or deposits in intercellular granules in an insoluble form or is excreted with faeces. The chemical form often decides which organ will be attacked. Mercury in a free form as well as in the form of an organic compound is fat-soluble and has a destructive effect on the brain and nervous system, and the Hg\(^{2+}\) ion can attack the kidneys. The form of free cadmium ions mainly determines their toxic effects. Metal ions are bound in tissues in a selective manner. Mercury and cadmium accumulate mainly in the liver and kidneys, while radioactive
radon and toxic lead primarily in bone tissue [Ociepa-Kubicka and Ociepa 2012, Arantes et al. 2016].

Heavy metals with the most severe toxic effects are most often lead, mercury, cadmium and arsenic. The liver and kidneys are organs responsible for detoxification of the body. Accumulation of these elements in the brain, muscles or bones is also often observed, and the nature of poisoning can be chronic or acute [Draghici et al. 2010, Vieira et al. 2011].

CHARACTERISTICS OF THE MOST DANGEROUS POTENTIALLY TOXIC TRACE ELEMENTS

Cadmium

Cadmium is not widely used in industry, but it is used indirectly in numerous manufacturing processes, so it can end up in sewage, ground and surface waters together with waste. It appears in phosphorus fertilizers. It is released during the combustion of crude oil and solid fuels, as well as in the process of obtaining metallic zinc (in the form of vapours). No method has been found to prevent this emission yet. The recognized effects of chronic cadmium poisoning include kidney, intestine and liver damage, hypertension, anaemia, bone decalcification, pregnancy complications, and changes in the circulatory system. Acute poisoning, caused by taking a single high dose of cadmium, is rare. Long-term exposure may lead to itai-itai disease. This disease occurs as a result of long-term effects of cadmium on the body and manifests itself in damage to the spine, femur and muscle atrophy. Poisoning most often concerns workers employed in metallurgy and electroplating plants (steel products are covered with cadmium) [Czeczot and Majewska 2010, Romanowska-Duda 2015, Rafati Rahimzadeh et al. 2017].

Cadmium is undoubtedly carcinogenic. The lethal dose depends on the form of the compound in which it appears, sensitivity of the body, and it ranges from 350 to 3,500 mg. This metal is absorbed in the form of vapours, dust or directly through the digestive system and easily bioaccumulates in the body. The presence of this element in the environment results in the contamination of many raw materials and food products. Due to the high degree of cadmium toxicity, constant control of food products is necessary [Czeczot and Majewska 2010, Apostoli and Catalani 2011].

Daily intake of cadmium with food by adults in different countries is at the level of 25–200 μg. In Poland values between 11 and 30 μg have been recorded [Wojciechowska-Mazurek et al. 2003]. The PTWI index (FAO/WHO) means the allowable weekly intake set for adults and children, for cadmium it is 7 μg·kg⁻¹ of body weight [Siebielec and Siebielec 2016].

The natural content of cadmium in drinking water is low, however, as literature indicates, this element is often found in surface waters. Usually, the cadmium form in solution is not stable, which causes rapid precipitation of this element or its sorption by clay minerals, metal oxides and hydroxides. Bacteria is mainly responsible for binding cadmium in sediments, usually precipitating it in the form of sulphides. In the case of severe river pollution, approx. 70% of cadmium is cationic. The ease of its maintenance in the form
Drinking water quality in the aspect of complex compounds formed with polyphosphates results from their introduction into waters together with wastewater, which increases the risk of water contamination with cadmium [Górski and Siepak 2014, Romanowska-Duda 2015, Michalski et al. 2018].

Lead

Lead is an element commonly used in industry. Its presence is observed in air, soil and water. Industrial emissions from cement plants, steel mills, smelters have caused it to be present in the atmosphere. However, increased communication and exhaust emissions contribute most to the increase in lead concentration in the atmosphere (tetraethyl lead is added to the fuels as an antiknock agent). Precipitation from the atmosphere is very easy, further entering the soil, from where it easily migrates to water. However, the threat exists in metallurgy, in the production of batteries, in the rubber, plastic and petroleum masses industries, in crystal glassworks and in the production of explosives and plant protection products. Acute poisoning is not common due to improved safety of technological processes. Lead is well absorbed through the skin and respiratory tract, has a lipophilic character, accumulates in the liver, bone and nerve tissue and the brain. Tetraethyl lead (Pb(C₂H₅)₄) may cause enzyme deactivation [Wani et al. 2015].

Symptoms of poisoning can be both physiological and mental. A metallic taste in the mouth, nausea, vomiting, abdominal and headache as well as attention deficit disorder, memory impairment and anxiety are observed. Lead can cause kidney damage and disrupt haemoglobin synthesis. A daily dose of up to 1 mg absorbed through inhalation is relatively safe, while a higher one can cause chronic poisoning. Symptoms of acute poisoning include drooling, burning in the mouth, metallic taste, intestinal colic (lead poisoning – strong and very painful intestinal spasm), vomiting, diarrhea. Other symptoms that may occur include a drop in blood pressure and body temperature, haematuria, proteinuria, brain problems with poor vision, as well as seizures and coma, which can be fatal. The most characteristic external manifestations of chronic poisoning are the lead line on the gums (blue-black sulphide lead rim) and pale grey skin [Romanowska-Duda 2015, Knollmann-Ritschel and Markowitz 2017].

Lead may appear in soft and hard waters. Soft waters with strong buffering capacity and low alkalinity may contain lead in the form of soluble salts. In hard waters (with high alkalinity) there may be insoluble lead salts – sulphate, phosphorus, carbonate [Górski and Siepak 2014, Wani et al. 2015].

Mercury

Mercury, one of the most toxic trace elements, has no physiological function in the human body. It is difficult to determine the safe concentration of this element because it occurs in many forms with different toxicity. Characteristics, such as chemical form, amount of the element, exposure time, route of entry and individual susceptibility, determine the toxicity of this element. Mercury enters the human body along with consumed seafood and fish. The main sources through which mercury enters the environment are coal-fired power plants, the paper, chemical and pharmaceutical industries as well as gold mining and waste incineration (all are anthropogenic sources). Studies have shown
that between 4,400 and 7,500 t of Hg can be released into the environment annually. Sources of this element in the environment are also natural processes. These include rock weathering, volcanic emissions, evaporation from land and oceans, underwater fumes and biomass combustion and geothermal processes [Bonsignore et al. 2016, Kim et al. 2016, Ha et al. 2017].

Methylmercury is the most toxic form of this element. Its main characteristics include the ability for bioaccumulation and biomagnification in the trophic chain and the ability to penetrate biological barriers, including the placental barrier, which affects the proper development of the foetus. Mercury has a negative effect on the nervous system, reproductive system, liver and kidneys. The aquatic environment is not free from mercury. Mercury in water is transformed by microorganisms into an organic form. It is collected by fish and marine invertebrates in which mercury is collected (biomagnification process) [Mania et al. 2012, Bonsignore et al. 2016, Ha et al. 2017].

Mercury enters the human body by ingestion, inhalation and through the skin. The chemical form and the quantity taken determine its toxicity. Organic compounds are more easily absorbed than inorganic ones. Inhalation of vapours with high concentration of mercury can lead to acute poisoning. The main symptom is respiratory failure. Chronic poisoning (with chronic exposure) leads to depressive states, excessive arousal, whole body tremor, memory impairment and anxiety. Other symptoms include gastrointestinal disorders, the possibility of a blue-violet mercuric sulphide deposit on the gums. Poisoning with an inorganic form usually leads to acute poisoning. In this group, it is usually mercury chloride poisoning, the lethal dose when administered orally is 0.2–1 g. The main symptoms of mercury chloride poisoning are acute gastroenteritis and renal failure. Methylmercury is the main form of the organic form of mercury, causing poisoning. When mercury reaches $0.2 \mu \text{g} \cdot \text{cm}^{-3}$ in the blood, the first signs of poisoning are observed. These include tingling in the extremities, numbness of the lips and tongue. The highest permissible mercury content in the human body in the urine is: not higher than $100 \mu \text{g} \cdot \text{dm}^{-3}$ and not higher than $0.04 \text{mg} \cdot \text{kg}^{-1}$ of body weight. The lethal dose for humans is 0.2–0.4 g of total mercury [Sapota and Skrzypińska-Gawrysiak 2010, Cyran 2013, Kot et al. 2016].

Arsenic

Arsenic is one of the elements from the group of nitrites. Its basic features are lack of taste and smell. It has been used for thousands of years. It is used for the preservation of wood and leather, as well as for the production of glass and paints. Thanks to its antiseptic, antipyretic, as well as antispasmodic and tonic properties, it is used in medicine [Litwin et al. 2009, Hoffman and Mielicki 2013]. It has a strong toxic effect, is absorbed into the body through the respiratory and digestive systems. This element, found in soil or minerals, can be released into the water. Human anthropogenic activities (mining, metallurgy, use of pesticides) mainly contribute to the presence of arsenic in nature [Bizoń et al. 2013].

In 1988, Joint FAO/WHO Expert Committee on Food Additives (JECFA) determined the value of provisional tolerable weekly intake (PTWI) of arsenic from all sources at $15 \mu \text{g} \cdot \text{kg}^{-1}$ of body weight. However, in recent years it has been shown that even lower...
doses of inorganic arsenic can cause skin and lung cancer. Therefore, based on epidemiological studies, the lowest doses were determined by determining BMDL (benchmark dose lower confidence limit, i.e. the lowest doses associated with inducing a specific effect on the human body) at 0.3–8 μg·kg\(^{-1}\) of body weight daily, and JECFA decided to withdraw PTWI values [Wojciechowska-Mazurek et al. 2012]. Arsenic mainly occurs in the third or fifth degree of oxidation. Pentavalent arsenic compounds are less toxic than trivalent, and methylated trivalent arsenic compounds are more harmful than inorganic compounds. Poisoning can lead to death by inhibiting the proper functioning of the enzymes (pyruvate and α-ketoglutarate dehydrogenase) responsible for metabolism. Arsenic can penetrate the placental barrier and has the ability to accumulate in foetal epithelial tissue at the beginning of pregnancy [Bizoń et al. 2013, Jang et al. 2016].

Occurring in high doses in the air (several hundred μg·m\(^{-3}\)), arsenic leads to disorders in the nervous system, peripheral vascular disease, pharyngitis, laryngitis and bronchitis, as well as perforation of the nasal septum. Long-time exposure can damage peripheral nerves, leads to changes in the heart muscle, damages the liver and contributes to damage to mucous membranes and skin. The International Agency for Research on Cancer (IARC) has recognized arsenic and its compounds as carcinogenic substances with epidemiologically proven carcinogenic effects. The form in which arsenic appears, as well as the degree of tolerance of individual organisms, determines its toxicity. The safe daily dose is 10–15 μg and the toxic daily dose is 5–50 mg. A single lethal dose of arsenic trioxide is between 100 and 200 mg [Hoffman and Mielicki 2013, Kulik-Kupka et al. 2016].

WATER QUALITY IN POLAND

In the EU Member States, the primary and binding directive regulating the quality parameters of water intended for human consumption is Council Directive 98/83/EC. According to its provisions, drinking water should be free of microorganisms, parasites and harmful substances that could be dangerous to human health. Every three years, member states are obliged to report to the EU Commission on the quality of local drinking water. On this basis, once every five years, microbiological, chemical and indicator parameters as well as methods of their monitoring are verified. The directive does not apply to natural mineral waters and waters considered curative (Council Directive 98/83/EC). On the basis of the Directive, Polish legal regulation was created. The quality requirements for drinking water are directly derived from the Regulation of the Minister of Health of 2017. In contrast, Directive 2000/60/EC sets out rules that are intended to stop the deteriorating condition of waters in the European Union. It covers the protection of all waters: surface, underground, inland and transitional. It aims to restore ecosystems in these water bodies. It also indicates ways to reduce the level of water pollution and ensures sustainable water use by individuals and enterprises. The Polish regulation based on Directive 2000/60/EC is the Act of 20 July 2017 Water Law which. The Act regulates water management in accordance with the principle of sustainable development, in particular the shaping and protection of water resources, water use and management of water resources [Kłos 2015].

In 2016, the Supreme Chamber of Control (Najwyższa Izba Kontroli – NIK) presented a report on the protection of the quality of water taken to supply the population
with drinking water. The report has been prepared on the basis of research carried out between 2013 and 2016 by the laboratories of the Sanitary Inspection and the Water Supply and Sewerage Enterprise. Control studies covered 30 units, including 12 water supply companies, 12 municipal offices and six poviat sanitary and epidemiological stations. As a result, it was found that the activities carried out by water supply companies and municipalities do not guarantee proper protection of the quality of water taken and fed into the water supply network intended for human consumption. It is related to, among others, the lack of protection zones around water intakes and poor supervision of municipalities over sewage management in their area. In the controlled period, in five enterprises the permissible water quality parameters were exceeded in locations where water was introduced into the water supply system. Tests of the quality of water covered by the supervision of sanitary inspectors, conducted between 2013 and 2015, showed from 113 to 175 cases exceeding the permissible water quality parameters. The number of places where these parameters were exceeded ranged from 38 to 56, which constituted from over 17% to nearly 26% of the number of such points covered by supervision. In the first quarter of 2016, 32 such cases were found in 20 locations where water is introduced into the water supply network. The concentration of iron and manganese was most often exceeded [NIK 2016].

CONTAMINATION OF DRINKING WATER WITH METALS IN EUROPE

Drinking water tests carried out between 2005 and 2006 in Poland in the city of Szczecin for the content of metals (iron, manganese, copper, lead, cadmium, nickel, chromium, arsenic, aluminium) showed sporadic excess of iron content, and other elements were at the level of approx. 10% of the maximum allowable concentration [Herasimowicz-Bań and Brzeski 2009].

Kelepertsis et al. [2006] showed elevated levels of arsenic (125 μg·dm−3) and antimony (21 μg·dm−3) in drinking water in Eastern Thessaly, Greece, where more than 5,000 people consumed water containing arsenic and antimony above USEPA guidelines. Also, Jovanovic et al. [2011] found that 63% of all water samples exceeded Serbian and European standards regarding the presence of arsenic in drinking water. Cavar et al. [2005] reported that in three cities in eastern Croatia, the average concentrations of arsenic in drinking water samples were 38, 172 and 619 μg·dm−3, which is a serious threat to the health of approx. 3% of the Croatian population.

Tests conducted by Tamasi and Cini [2004] of drinking water in southern Tuscany in Italy showed that the concentration of arsenic at the final recipient is higher than in water samples at the treatment plant. These studies have shown that poor condition of the water supply can cause leaching of this metal from pipes. Similar results were obtained by Haider et al. [2002] in Austria and Etxabe et al. [2010] in Spain. The authors concluded that the concentration of lead in drinking water at the recipient is higher because it is leached from the pipelines.

Nielsen [2009] presented the results of research from Denmark in which he stated that nickel was detected in 3,362 wells. In addition, when testing European bottled water...
Drinking water quality in the aspect...

and tap water for heavy metal content, it was found that 4.63% of all water samples exceeded the limits for one or more of the following metals: arsenic (9 samples), manganese (8 samples), nickel (1 sample) and bar (1 sample) [Birke et al. 2010].

SUMMARY

As a result of civilization development, more and more toxic compounds, including trace elements, are accumulated in the aquatic environment. They are often difficult to remove during routine treatment methods. The literature analysis shows that the problem of the presence of these elements in surface waters as well as in drinking water is still valid and occurs in many regions of Europe. Water law is based on EU directives and national regulations limiting the maximum permissible content of these pollutants in drinking water. Water contamination with trace elements is one of the most important threats to human health. Trace elements can cause immediate acute poisoning or chronic conditions.

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JAKOŚĆ WODY PITNEJ W ASPEKCIE OBECNOŚCI POTENCJALNIE TOKSYCZNYCH PIERWIASTKÓW ŚLADOWYCH

Streszczenie. Źródłem wody pitnej mogą być wody powierzchniowe (jeziora, rzeki, zbiorniki retencyjne) oraz podziemne. Wymagania jakościowe w stosunku do wody pitnej wynikają bezpośrednio z rozporządzenia Ministra Zdrowia z 2017 roku, które określa maksymalne dopuszczalne stężenia wybranych pierwiastków zawartych w niej. Woda pitna znajduje zastosowanie w celach konsumpcyjnych, a także jest bazą przemysłu spożywczego. Jej jakość na potrzeby gospodarcze i higieniczne stanowi jeden z elementów zapewnienia bezpieczeństwa zdrowotnego żywności i żywienia. Spadek jakości wód powierzchniowych i podziemnych ujmowanych do spożycia związany jest głównie z działalnością gospodarczą człowieka. Wynika to z intensywnego rozwoju przemysłu, szczególnie metalurgicznego, elektrotechnicznego, chemicznego i wydobywczego, a efektem takiej działalności jest często zanieczyszczenie wód powierzchniowych, a w konsekwencji wody pitnej. Ze względu na stopień zagrożenia można wyróżnić pierwiastki o bardzo wysokim stopniu potencjalnego zagrożenia (kadm, rtęć, ołów, miedź, cynk, arsen), wysokim stopniu potencjalnego zagrożenia (mangan, żelazo, molibden) i średnim stopniu potencjalnego zagrożenia (nikiel, kobalt). Akumulacja tych pierwiastków w środowisku jest różnicą, a więc przede wszystkim od rodzaju pierwiastka, pobranej dawki oraz jego formy chemicznej. Stężenie pierwiastków śladowych w wodzie zależy w głównej mierze od ich właściwości fizykochemicznych, rozpuszczalności w wodzie, a także od pH i potencjału utleniająco-redukującego oraz zdolności do tworzenia rozpuszczalnych kompleksów. Przemieszczanie pierwiastków do organizmu człowieka poprzez kolejne ogniwa łańcucha pokarmowego...

Słowa kluczowe: woda pitna, bezpieczeństwo konsumentów, pierwiastki śladowe