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Invited Review

Research on Heavy Metals in Poland

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Abstract

The analysis of 238 papers published in the *Polish Journal of Environmental Studies* concerning investigations on heavy metals conducted in the years 1998-2008 suggests a steadily growing interest in the issue. Investigations on the environmental problems in question are carried out by means of more modern research methods and using the most recent analytical equipment. Research on the role of heavy metals and metalloids in the environment concerned analytical and legal problems. Research on the speciation of metals, their toxicity, accumulation, biomagnification, bioindication, migration, removal, phytoremediation and biomonitoring was conducted. The papers published in the *Polish Journal of Environmental Studies* were divided according to the range of topics mentioned above. At present, the paper is a review compendium and therefore current and important for every reader.

Keywords: heavy metals, problems, review, *Polish Journal of Environmental Studies*

Introduction

Heavy metals are a group of elements with a mass density greater than 4.5 g/cm^3, which tend to release electrons in chemical reactions and form simple cations. In the solid and liquid states they are characterized by good heat and electrical conductivity, and are glossy and opaque. They have high melting and boiling points. They are malleable with usually monoatomic pairs. The metals classified as heavy metals include: Cu, Co, Cr, Cd, Fe, Zn, Pb, Sn, Hg, Mn, Ni, Mo, V, W. Within the group of heavy metals one can distinguish both the elements essential for living organisms (microelements) and the elements whose physiological role is unknown, and thus they are "inactive" towards plants, animals and people. The metals serving as microelements in living organisms usually occur in trace amounts that are precisely defined for each species. Both their deficiency and excess badly affect living organisms. The strongest toxic properties are characteristic for inorganic metals compounds, which dissociate well and are easily soluble because they can easily penetrate through cell membranes and get into internal organs. These metals accumulate mainly in kidneys, the adrenal gland, liver, lungs, hair and skin, and they may cause high blood pressure, cancerous changes, damage to kidneys, liver and brain. In some cases they may also lead to mental disorders and loss of brain function.

The circulation and migration of metals in the natural environment are mainly related to such processes as rock decay, volcano eruptions, evaporation of oceans, forest fires and soil formation processes. The sources of anthropogenic contamination or pollution of the environment by heavy metals include different branches of industry, the power industry, transport, municipal waste management, waste dumping sites, fertilizers and waste used to fertilize soil. The heavy metals from these sources are dispersed in the environment and they contaminate soil, water and air. They also (directly or indirectly through plants) get into human and animal bodies.

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On the other hand, semimetals (metalloids) are the elements that have properties intermediate between those of metals and nonmetals. The known metalloids are: antimony, arsenic, astatine, boron, germanium, silicon, tellurium, selenium. The metalloids have a number of properties characteristic for metals, such as a glossy surface in the solid state and high melting points. Although their electric and heat conductivity is much lower than that of typical metals, it is still higher than the conductivity of typical nonmetals, hence their use in semiconductor materials. Their chemical properties are also intermediate, with the sources of origin similar to heavy metals. Metalloids may cause enzymatic disorders, skin and cancerous changes and gastrointestinal irritations.

The *Polish Journal of Environmental Studies* raises widely understood environmental issues such as analysis and controlling pollutants in all parts of the environment (air, water, soil), management of substances hazardous to people and the environment, circulation of pollutants in the environment, waste utilization and management, land reclamation, development of new methods and instruments for controlling pollutants, environmental engineering issues, etc.

Altogether, between 1998 and 2008 238 papers that concerned the problem of heavy metals and metalloids appeared in the journal.

The methodology of publications review was systematized according to the following classification:

1. Methods for heavy metals and metalloid determination.
2. Research problems.
3. Analytical problems.

Methods for Heavy Metals Determination

The methods that dominate the papers presented in the *Polish Journal of Environmental Studies* used in quantitative determination of heavy metals and metalloids includes methods based on spectrophotometric techniques. They are based on the interaction of electromagnetic radiation with matter in all its macro- and microscopic forms. The most common technique in this group is atomic absorption spectrometry (AAS) [1, 3, 7, 8, 9, 11, 13, 17, 18, 21, 23, 25, 29, 39, 46, 48, 51, 60, 61, 63, 67, 71, 72, 76, 84, 88, 103, 104, 114, 117, 124, 125, 130, 131, 137, 140, 141, 153, 159, 162, 169, 170, 175, 195, 199, 207, 208, 211, 224, 230]. It is an analytical technique based on the absorption of radiation by free atoms in the thermal plasma created in an atomizer, characteristic for a given element of spectral lines emitted by the source of radiation such as a hollow cathode lamp (HCD) or electrodeless discharge lamp (EDL).

The popularity of AAS in quantitative analysis of elements is not surprising due to the high sensitivity and selectivity of the technique. Moreover, the technique is characterized by low detectability limit and high precision. The basis for more detailed classification of atomic absorption spectrometry is the type of atomizer used. The most common atomization technique was definitely flame atomization (F-AAS), where air or N_2O was used as the oxidizing gas and acetylene was usually flammable gas [15, 20, 22, 35, 36, 44, 47, 54, 57, 62, 64, 68, 69, 75, 97-99, 101, 107, 109, 111, 118, 121, 128, 135, 139, 145, 146, 151, 152, 154, 155, 161, 164, 165, 168, 172, 180, 191, 192, 193, 197, 200, 215, 217-220, 222, 227, 232, 235, 236, 238]. Another type of atomizer is electrothermal (ET-AAS), also readily used in determinations of metals [97, 101, 144, 150, 154, 161, 173, 180, 205, 223]. Electrothermal atomization most often occurs in so-called graphite furnaces (GF-AAS) [34, 44, 55, 64, 74, 81, 96, 109, 116, 146, 204, 215, 218, 220]. The furnaces are shaped like small tubes 4-6 cm in diameter with a hole placed in the upper part used for sample introduction. Hydride generation atomic absorption spectrometry in the papers published in the *Journal* was only used in quantitative determination of metalloids (selenium, arsenic, antimonium in the aquatic samples collected from surface and ground waters [12, 50, 56, 66, 78, 89, 90, 119], or from ash landfill leachate [133]. Cold vapour AAS technique (CV-AAS) was used in mercury determinations [16, 31, 40, 94, 128, 161, 171, 198, 225]. Special flow cells (quarz or glass with quarz windows) are used in the technique, and Hg must occur in ion form or in gases. Atomic Fluorescence Spectrometry is also worth mentioning here as it enables mercury determination when combined with the above atomization technique [210]. The papers raising the problem of heavy metals determinations also mention the use of spectrophotometric techniques that involve quantitative measurement of light absorption or emission by a sample. However, spectrophotometric techniques [39, 73, 185, 206], including ultraviolet and visible light spectrophotometry [5, 19, 24, 42, 122, 140, 142, 164], are rarely used in the analyses of environmental samples presented in the *Journal*. The cause of such tendencies are the requirements concerning constant lowering of sample determination limits, as well as the large time expenditure necessary for the analysis [105]. That is the reason why spectrophotometric techniques are becoming less and less competitive in comparison to other methods. Classic atomic emission spectrometry (AES), which was presented only once [137], does not seem very popular. However, combining it with a plasma spectrochemical source in the form of inductively coupled plasma (ICP-AES) was a breakthrough in the development of this method. As a result, a very sensitive and selective technique was created and used for the quantitative determination of metals in a variety of environmental samples [6, 77, 143, 148, 167, 176, 184, 187, 188, 201, 203, 204, 209, 212, 214, 216, 221, 228, 229, 231].

Another group is electroanalytical techniques. They usually enable the determination of metals concentration at the level of their natural occurrence in the environment and they make it more difficult to determine the particular elements in the matrix, which quite seriously limits their use in the research problem in question [105]. The most common example in this group is DPASV (differential pulse anodic stripping voltammetry) [30, 41, 49, 75], while other techniques such as voltammetry [59], stripping voltammetry (SV) [108], potentiometry [110], and polarography [122] are used sporadically. On the other hand, the flow-through coulometry may be useful in the determinations of trace elements, and especially in aquatic environment samples where low concentrations may be expected [129].

High-performance ion chromatography (HPIC) with a UV-VIS spectrophotometer as a detector and 2,6-pyrido dicarboxylic acid as an eluent was used to determine the speciation form of chromium Cr (VI) [112] and ion forms of different heavy metals [202]. The system of inductively coupled plasma mass spectrometry [ICP-MS] is a perfect tool for the analysis of trace quantities of metallic elements. It is characterized by a low detectability limit and good selectivity. For that reason it is a common technique used for the determination of metal contents in different environmental samples (water, soil, tissues and ashes) [83, 84, 85, 106, 136, 158, 173, 176, 182, 183, 186, 196].

X-ray spectrometry (XRF) is characterized by good selectivity and low detectability limit of ppm-ppb [10, 26, 27, 132, 213]. Additionally, it belongs to the non-destructive analytical techniques, i.e. techniques that do not damage the sample under study. This last feature is also characteristic for neutron activation analysis (NAA). It enables the simultaneous determination of up to 40 elements, which makes it one of the most universal analytical techniques [168]. Another technique, energy-dispersive XRF (EDXRF), is very useful in the in-situ analysis of trace elements at the measurement site, which enables shortening of the analytical process [113].

Flow injection analysis (MHS-FIAS) coupled with a spectrophotometric detector enables limiting the use of reagents and automatization of the analytical process [220].

Iron and nickel were also determined by means of complexing titration with EDTA as titrant [206]. Analytical techniques used in determinations of metalloids [74, 105] and other metallic elements [2, 14] were also discussed in articles published in the *Journal*.

Research Problems

The scope of issues and problems concerning heavy metals and metalloids raised in the *Polish Journal of Environmental Studies* is very wide and it comprises all parts of the natural environment. The environment should be defined as the totality of animate and inanimate elements, both natural ones and ones that have been created as a result of anthropogenic activities that occur in a given area. The elements interact and are interdependent. The environment is thus everything that surrounds people, including people themselves. The environment comprises waters, soils, animals and plants, atmospheric air, pollutants, etc. Each of the above-mentioned parts includes heavy metals and metalloids, which not only affect each of the parts, but can also change interactions between them. It is therefore clear that the considerations concerning metals in the environment have a very wide spectrum that requires a certain classification of the publications. The classification presented in this paper is an attempt to address the problem of heavy metals and metalloids raised in the *Journal*.

Speciation Analysis

The term 'speciation' refers to the occurrence of various physical and chemical forms of an element in the material under study [239]. Speciation analyses in publications concern the elements that form toxic compounds or whose compounds are necessary for the normal functioning of living organisms. Speciation analysis (the identification and determination of these forms of elements) most often deals with the compounds which occur in the studied material in trace quantities. That is why this analysis becomes a research problem, as these forms are only a part of the trace content of the element. Hence the errors made in the analytical procedure may change the relative content of these forms in a sample.

The research on speciation forms of heavy metals and metalloids presented in the *Journal* mainly focuses on surface waters and bottom sediments. However, the speciation of metals in sewage or industrial leachates [46, 122] and in soil [155] was also the subject of investigations. A wide review of analytical methods, techniques and procedures in speciation analysis was also presented [2, 66], as well as the environmental problems related to speciation forms of mercury in different environmental samples [70, 86]. However, the main problem was the determination of speciation forms of heavy metals in bottom sediments, which may be an indicator of the condition of surface waters from which the bottom sediment samples were collected [36, 54, 146, 209, 233]. The research on speciation forms also concerns metalloids. Surface water samples were collected from both non-urban [90] and urban areas, to a great extent changed by people [12]. Also the differentiation of relative content of metalloids speciation forms in surface waters (lake) in terms of seasons of the year and lake zones [119] seems interesting.

Toxicity

Heavy metals are commonly considered the simulators or inhibiting factors of life processes, due to which they may appear toxic for living organisms. This depends on their concentration, ability to form complexes and degree of oxidation. The excessive content of heavy metals in the human body may in many ways affect the body and psychophysical development. For instance, Norska-Borowka and Behrendt in their paper state that a large amount of lead in the blood of children living in heavily polluted areas affects their performance at school [11]. The excessive content of heavy metals in a mother's body increases the risk of locomotor system defects in children [97]. Moreover, lead may also disturb metabolism of purines [127] and increase oxidative stress in patients with pollenosis [173].

When analyzing toxic properties of heavy metals, it is often impossible to perform experiments on people due to certain threats to their health and life, as well as the consent of the Bioethical Commission. Experimenting on animals is a solution to the problem. The most commonly used animals are rats, then hamsters, birds and in the investigations involving aquatic pollution – fish.

The experiments conducted on animals confirm that heavy metals cause oxidative stress [211]. The tests conducted on trout also confirm that heavy metals have a toxic influence on the ontogenesis of the specimens under study [226]. The research on reproduction of rats conducted by Slovakian scientists [237] partly confirmed this thesis: the specimens given small doses of Pb and Hg had a lot of offspring (more than the specimens from the control group), although their survival rate was low. On the contrary, the specimens taking small doses of Cd had a much lower reproduction rate and a higher survival rate. The explanation of the above may be the use of an adaptation mechanism. The properties of cadmium were most often investigated, due to its high toxicity and ability to accumulate in particular organs [102]. A too high content of cadmium has an inhibiting effect on the biochemical parameters of an organism [80]. Cadmium also has a hepatotoxic effect [189]. Due to its high accumulation abilities, a small dose of cadmium causes a strong toxic effect on thyroid and parathyroid glands [223]. The compounds that may function as biomarkers of a chronic exposure to cadmium may be the isoenzyme B N-acetyl-β-D-glucosaminidase [116] or a kynurenine-tryptophan metabolite [144, 150]. Such a bioindicator for copper may be the body circumference of a carp. But as it was shown, Cu has more toxic properties than Cd or the combination of Cu and Cd, which may indicate antagonistic properties of both metals [234]. The copper itself has neurotoxic properties [28].

Lead decreases enzymatic activity in the body. At the same time, zinc does not have such properties, and additionally its presence reduces the negative influence of Pb [44]. Lead, the same as cadmium, accumulates not only in the body's kidneys and liver, but also in bones and hair [62]. This disturbs the micro- and macroelement balance in the body and the effect is intensified by the presence of ethanol [95]. The striking fact is that supplementation of melatonin (an effective antioxidant) in young rats did not significantly lower the content of lead in their blood and bones [224].

The experiments on young rats showed that the excessive absorption of zinc by young rats causes disorders and badly affects brain development and the dopaminergic system [175, 181]. Also nickel taken orally in excessive doses causes intensified excretion of microelements from the body [101].

The toxic properties of heavy metals in a biological system such as soil determine its enzymatic activity in the first place [58, 100, 157, 194]. This is also true in the case of other systems [163]. Lowered enzymatic activity slows down the growth of plants, seeds germination and decreases the abundance of crops [38, 115, 126, 174]. The excessive contamination of soil with heavy metals results in changes to the parameters of agrarian soils [172], changes in denitrification processes [120, 138] and may also influence microelement metabolism in plants [123, 221]. However, the disorders may be minimized by the addition of different biocomponents such as compost [147]. Heavy metals such as lead may change the carbohydrate metabolism in plants [197]. Fungi seem not to be sensitive to soil contamination with heavy metals as regards the concentrations occurring in Poland; higher concentrations have a toxic effect [91, 166].

According to observations, the body fights the stress caused by excessive Cd content by increasing the production of antioxidants such as glutathione, metallothioneine, flavonoids and other chemical compounds [149, 179, 190]. Vitamins C and E also have antioxidant properties [156]. Another method alleviating the effects of the stress caused by large contents of cadmium is selenium supplementation [29], while quercetin stops the destructive influence of this metal on lymphocyte DNA [53]. The strong toxicity of cadmium may be inhibited by a single, previusly approved, dose of zinc [153]. Plants defend themselves against the excessive Cd doses through mycorrhizas, using fungi, which accumulate metal [108].

The content of heavy metals in plants may also be reduced using herbicides, which form complexes with metals [236]. The inhibiting influence of cadmium on enzymatic activity in soil may also be delayed by increasing the content of magnesium in soil [100].

The resistance of different bacteria strains to tellurium was also investigated [178]. The compunds of tellurium in the environment are rare and of limited quantity. Due to this fact, the investigations were conducted using hospital waste because many medicines contain the compounds of this element. Most bacteria strains tolerated the concentration of tellurium compounds of 55 μg/ml. Other investigations of bacteria collected from water sediments and the sea showed the correlation between the concentration of mineral oils in water (their source was, for instance, spillage from leaky ship engines) and bacteria resistence to lead and cadmium [195]. Oil in higher concentrations inhibited the growth of bacterial colonies.

Determination of the Content of Heavy Metals and Metalloids

Analysis of environmental samples is continuously facing new challenges. Increasing knowledge in the field of environmental pollution compels scientists to improve analytical techniques, use combined techniques and introduce automatization and miniaturization in order to minimize the human error factor. Thanks to the above, the detectability and determitation limits of elements may be constantly lowered, which facilitates monitoring of the environment and helps prevent negative changes to the environment [43].

Monitoring the influence of contamination by heavy metals and metalloides on the human body involves the measurement of their content in tissues and organs. The obtained results show that diet, the quality of atmospheric air and smoking cigarettes increase the content of heavy metals in teeth, hair and skin [132, 136, 199].

The above-average content of some metals may also be revealed in urine [81, 96, 205]. However, the comparative analysis of the content of Cd, Pb, Cu, and Zn in the lungs of persons living in different regions of Poland shows that there is not always a direct ratio in which the inhabitants of more polluted regions have a higher content of these elements in their bodies [49].

The deficiency of selenium in blood and blood plasma was also observed [48, 185]. Selenium is an element necessary for body functioning, but its higher concentrations are harmful. The content of metals in blood is especially important in pregnant women; an increased content of lead in babies whose mothers smoke cigarettes and have inappropriate diets may be observed [18].

The state of aquatic environment may be perfectly evaluated by means of the analysis of metal contents in fish [63, 180, 218, 229] and other aquatic organisms such as crabs and mollusks [94]. Fish accumulate mercury in their bodies and the degree of accumutation depends on their size [31]. Heavy metals tend to accumulate in different organs and tissues, depending on the type of element [183, 220].

Land animals and birds also make good biomarkers [55]. The metal content in their bodies reflects the threat of pollution [114, 184], but it may also confirm the good condition of the environment in the region [23, 98].

Investigations of the content of heavy metals in soil are mainly focused on heavily urbanized areas such as industrial regions and city agglomerations, as well as on the areas of constant and linear emitters, which include industrial plants, waste landfills and roads. The investigations also concern the soils used for agricultural purposes [103, 145], and they take into consideration the genetic layers of soil [17, 124, 148, 159]. The results confirm degradation of urban and industrial areas where the concentrations of the studied elements are usually high [76, 89, 113, 155, 201], but sometimes they stay within the norms[1] [5, 129, 164]. The high variations in the content of elements in soil within one urbanized area were also observed [171]. Constant emitters may also heavily contaminate soil, although this is not a rule [219]. The pollution tracks run mainly through ash deposits and migrate in soil, caused by washing out waste from unsecured landfills or sewage tanks [7, 47, 191, 213, 230].

Interestingly, communication tracks do not pose such a serious threat. As the investigations show, the deposition of heavy metals occurs mainly directly at the roads and it does not do any particular harm while moving away from the road [152]. The investigations on the lead and cadmium content in urban family gardens confirm this viewpoint [24, 42]. It is also interesting that even in the relatively clean area of the Tatra Mountains, high concentrations of heavy metals whose content often exceeded the acceptable norms were observed [77].

The soil contaminated with heavy metals in the urbanized areas located on rivers poses a threat of these contaminants migrating to water and littoral vegetation [210, 225]. It is apparent that heavy metals often commonly occur in high contents in soil. However, their bioaccessibility for organisms depends on their form [170].

[1]Whenever the norms are mentioned, the authors refer to the norms given in the quoted publications.

The relatively clean Isle of Spitsbergen may serve as a reference for the contaminated areas. The isle's content of heavy metals is either at the level of natural occurrence in the original rock or exceeds it slightly [106].

The surface and ground waters are a significant area of investigation [66, 112, 198]. The contamination of surface and ground waters is particularly dangerous due to the use of these waters for consumption and municipal purposes. Therefore, their state may directly influence human health. Water, similar to soil, may be contaminated by the inflow of undesirable substances from industrial plants and leaky waste landfills and sewage tanks [7].

Water samples collected from the lakes in scarcely urbanized areas were used to determine metalloid forms. Their low content was determined in water [12, 56, 78, 90, 119]. The content of heavy metals in water reservoirs is usually lower than in the vegetation overgrowing the reservoirs and the animals living there. This is explained by their ability to accumulate metals [229].

The investigations conducted in rivers show their diverse state. The excessive content of heavy metals, deposited in bottom sediments, is mainly caused by the inflow of waste from nearby farms and industrial plants [6, 83, 137]. On the other hand, the state of ground waters in terms of heavy metals and metalloid concentration should be described as good [50, 193, 198]. However, there is always a risk of pollutants migrating to the water-bearing level [191].

Plants may be contaminated by metals through the absorbtion from soil or ash deposition [7, 25, 44, 125, 141, 201, 235]. It was observed that motor traffic does indeed contaminate roadside plants, but no corelation was stated between the traffic intensification and increased pollution [121, 125]. It is quite possible that this results from the plants' adaptation to stressful conditions, which was observed by Samecka-Cymerman and Kempers based on their research [204].

In the areas with little or no signs of antropogenic pressure, the content of heavy metals in plants stayed within the norm, sometimes slightly exceeding it in the vicinity of the communication routes [72, 75, 168] or in the case when genetic factors and not environmental conditions determined contamination by metals [217]. In aquatic vegetation, in the case of mercury, the excess of acceptable concentrations also was not observed [94]. The plants which have the ability to accumulate large quantities of metals may be used in the recultivation processes of degraded areas [176].

The study of fruit and vegetables shows that the norms of metal contents are not exceeded as a rule, and consequently they do not pose a threat to human health [27, 203, 212]. However, an increased content of mercury in wild mushrooms from non-urbanized areas was observed, which may put the health of people who eat them at risk [40].

The bottom sediments in aquatic reservoirs and rivers are where heavy metals accumulate, that is why metals content may be the pollution indicator for these elements in the whole ecosystem [86, 229]. The contents of heavy metals and metalloids in bottom sediments vary, which depends on where the reservoir or watercourse is located and on whether there are no potential pollution sources in the vicinity [26, 154, 180, 192, 215]. However, it should be undelined that the presence of pollution sources does not necessary have to increase the metals content in sediments, which was demonstrated by the example of mercury in the paper by Falandysz [16].

The research provides both the results which stay within the norm [10, 57, 171] and those which exceed it [84, 128, 161, 238]. A particular role in investigating bottom sediments is credited to granulometric fractionation [227] and speciation analysis of metals. It enables the determination of bioavailable forms that are at the same time potentially toxic for living organisms [20, 36, 54, 86, 146, 209, 233]. The considerable contamination of bottom sediments with heavy metals may result in changes to the morphology of a river bed [130, 131].

Due to their granulometric and mineral composition, dust and ashes pose a threat not only to the atmospheric air, but also to other elements of the environment, such as soil and water [196]. The sources of this pollution are mainly power stations, combined heat and power plants, old coal-fired furnaces and car combustion gases [35, 121, 186].

Groceries such as milk and dairy products, honey, juices, fruit, spices and herbs were also analyzed. These products meet the norms concerning the metals content and therefore do not pose a threat to human health, although the exceedance of norms was observed in several cases [158, 165, 200, 222, 228].

Accumulation

The problem of heavy metals accumulation is raised in many publications in the *Polish Journal of Environmental Studies*. Heavy metals can accumulate in animal bodies. Therefore, the consumption of meat which contains large concentrations of metals poses a threat to human health. For example, the excess of cadmium, which accumulates in the kidneys of cattle, may lead to heart disorders or osteroporosis [23]. Fish, on the other hand, are good organisms for the accumulation of heavy metals, and especially mercury [51]. The process of biomagnification, which involves the increase of metals concentration in organisms on the upper level of the trophic chain, is most visible in the aquatic environment [51].

Heavy metals tend to accumulate in different organs and tissues depending on the type of element [183]. This concerns plant tissues as well [45]. Moreover, plants also make good bioindicators [60, 121, 143, 151, 187, 221]. This property may be used in the phytoremediant processes, which shall be discussed further. Heavy metals also accumulate in soil, in the industrial areas or those situated along communication routes [107, 139].

Sorption

The contamination of soil with heavy metals results from the soil's ability to sorb their ions. This sorption depends on physicochemical parameters of soil as well as the properties and forms of metals [37]. The sorption of metals in soil may pose a risk of migration to ground waters, which is why this problem is the subject of numerous studies that aim at understanding the processes occurring in soil and at determining the sorptive properties of different types of soil and peat in relation to heavy metals ions [1, 21, 37, 64, 85, 99, 169]. It is also important to describe the conditions of ions desorption from one soil layer and migration to another, which gives a chance to implement the phytoremediation processes and inhibit the migration of bioavailable forms of metals to other parts of the environment [33, 118]. The *Journal* also has published papers concerning investigations of the sorptive properties and effectiveness of biosorbents [71, 117, 142, 188].

Bioindication

Bioindicators are a good tool for monitoring the state of the environment. Plants are commonly used as biomarkers [25, 30, 47, 141, 167]. Fish are good bioindicators of pollution in potable water reservoirs [180]. Bottom sediments are the place of the largest accumulation of mercury, and therefore they may be a valuable indicator of water pollution [86]. The content of metals in blood or urine, as well as enzymatic activity, may also reflect the state of the environment, which is the habitat of the organisms under study [3, 109, 205].

Metals Removal

The publications presented in the *Journal* raise the problem of the removal of heavy metals from selected parts of the environment. The methods of removing heavy metals ions from the matrix, such as the use of new ion-exchanger in an ion-exchange column, metallic iron, calcite or base-treated juniper fibre, membrane and biological methods, reversed osmosis process, extraction, leaching, immobilization and others were developed and improved [8, 9, 59, 61, 67, 88, 92, 104, 122, 140, 182, 206-208, 216]. These methods enable effective minimization of the content of heavy metals in municipal and industrial sewage, both in water and soil.

Migration in Soils

Heavy metals accumulated in the surface soil layer may migrate into the deeper layers, and consequently pose a threat of groundwater contamination [13, 37]. The highest risk is related to the soil located under the constant pollution emitters such as sewage tanks [191]. The speed and other parameters of pollutants transportation depend on the type of soil and its properties [64].

Phytoremediation

Phytoremediation is a technology of treating the environment in which some plant species use their large abilities to accumulate pollutants [22]. A relatively small number of papers concerning the problem of phytoremediation is observed. The investigations were mainly focused on a comparative analysis of species and on checking their effectiveness in the process of phytoremediation [22, 135, 151, 231]. As already mentioned in point 3.3, heavy metals tend to accumulate in different organs and tissues, depending on the type of element. This was the basis for research on the determination of the parts of plants where particular metals accumulated [111, 162].

Biomonitoring

Biomonitoring involves long-term observations of the selected parts of an ecosystem, which aims at evaluating its condition. One of the largest undertakings of this type was the "International Odra Project," which involved the monitoring of the Oder River [82, 83]. The monitoring of heavy metals usually concerns urbanized areas and it basically involves the analysis of their content in soils and plants [34, 167] as well as in food and agricultural products [93]. The biomonitoring of aquatic ecosystems is mainly restricted to the analyses of bottom sediments and vegetation [57, 225]. Valuable information is provided by the publications presenting new trends in monitoring and pollution analysis [43, 65] and providing complex information on the toxicity, biological role and influence of the selected heavy metals on the human body [4, 52, 134, 177].

Analytical Problems

The analytical problems raised in the Polish Journal of Environmental Studies concerns above all the implementation or improvement of analytical procedures, the comparison of the effectiveness of different methods, the review of new trends in environmental samples analysis and the optimization of statistical data processing.

In the publications of the *Journal*, different comparative analyses of various sequential extraction methods on the example of chromium and zinc were conducted. The following methods were compared: Tessier, Tessier modified by Kersten and Förster, Rudd, BCR, Gatehouse, Psenner, Sposito and McLaren and Crawford [87, 155]. The attempts to optimize the procedure conditions such as extraction time, eluent volume, eluation and drying temperature and the soil grain diameter are made [69]. The effectiveness of metal compounds extraction from soil by the chelating agents EDTA, HEDTA, EGTA and NTA was also evaluated [9].

In their publication Wódzki, Szczepański and Pawłowski developed a new system of liquid and polymeric membranes which, using Donan dialysis, can effectively treat some kinds of sewage with a simultaneous recovery of metals [8].

The comparison of four different mineralization methods of industrial sewage samples was also made. Among them there was a method included in the Polish norms (PN), appropriate for the determination of particular elements [39]. It was demonstrated that the mineralization methods included in the PN are not always the most appropriate and valid ones. The effectiveness of particular methods depends on the degree of metal content in a sample and on the matrix load with other metals.

The removal of metals from industrial sewage is a serious challenge for contemporary chemistry and environmental engineering. Alginate adsorbents are one of the alternatives. Klimiuk and Kuczajowska-Zadrożna conducted experiments on adsorption and desorption of cadmium in the aquatic environment and they stated a high effectiveness of alginate adsorbents with an admixture of polyvinyl alcohol [71].

In *Journal* publications a lot of emphasis is placed on the improvement of analytical techniques. A new type of arylenevinylene membrane used in ionoselective electrodes with liquid membranes was presented [110]. The membrane is used in the determination of lead ions. The innovation results in better selectivity and sensitivity of this technique. The energy dispersion X-ray fluorescence (EDXRF) was also discussed and compared in terms of effectiveness with other common techniques such as AAS and WDXRF [113].

Another research paper concerned the quality and validation of the whole analytical procedure according to the rules of Good Laboratory Practice [81]. The paper also dealt with the determination of arsenic in urine samples using GF-AAS.

As already mentioned, the *Polish Journal of Environmental Studies* also raises the problems concerning statistical data processing [68, 160, 202]. Furthermore, a lot of emphasis is placed on the review of analytical techniques used for the determination of heavy metals in different environmental samples, the harmfulness of these metals and legal regulations [14], their adsorption, accumulation and migration in soil [37], the new trends in monitoring and analysis of pollutants [43, 65] and their influence on the human body [52]. The separate research was devoted to metalloids, analytical techniques and procedures used in their determination [74, 105].

Conclusions Drawn from the Review of the Literature on the Study of Metals and Metalloids

- The *Polish Journal of Environmental Studies* includes an extensive collection of publications concerning the study of heavy metals and metalloids in the environmental context.
- A number of new trends in environmental analytics have been presented.
- At present, a tendency toward using combined techniques in environmental analytics is observed.
- New or improved methods enabling more effective removal of metals from the environment or restricting their transport (migration) have been presented.
- Greater importance of research on environmental monitoring has been observed due to a growing ecological awareness of the society and continuously tightening legal requirements.

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