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LITHIUM AS A RISK FACTOR FOR HUMAN HEALTH AND MODERN ENVIRONMENTAL POLLUTION SOURCES (LITERATURE REVIEW)

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Introduction. There are no official documents in Ukraine that would regulate handling of lithium power sources. Two known ones, namely the Summary and the Act No. 1287 are merely declaratory and do not influence the processes of lithium power sources import and further recycling. In other words, exhausted lithium cells are thrown away along with waste that has no appropriate assigned regulations.

The aim of the study – the creation of an analytical review of the current state of environmental lithium pollution and to describe hazards for human health in the context of industrial and environmental exposure to the metal.

Materials and methods of the study. The study is based upon the analysis of domestic and foreign publications concerning the current state of environmental lithium pollution, the analysis of lithium content in environmental objects, the toxicity of the metal, the impact of industrial exposure, the regulatory and legal acts, guiding documents of international organizations and those that are established in Ukraine.

Results. There are a variety of main industrial uses for lithium ores. Currently, one of the main factors for lithium pollution of the environment is the waste from electronic products and devices. Lithium compounds do not have the ability to biologically concentrate in food chains due to their ionic nature. Lithium can be found in different objects of the environment and the general population can be exposed to lithium via atmospheric air, ingestion of food and drinking water. Industrial exposure to the element is possible via skin contact or breathing at the workplace during disposal, manufacturing or recycling of lithium products. Although there is few data on industrial exposure, there are known effects of skin hyperemia and tearing following of the skin due to breathing air polluted with lithium. Lithium exposure is known to heighten the risk of lowering the functionality activity of kidneys, hypothyroidism, hyperparathyroidism and body weight increase. European Union has guidelines of 22nd December, 1998 and of 24th November, 2003 which restricts the use and disposal of lithium products. There are no relevant regulatory documents in Ukraine, according to which the spent electronic waste would be subject to appropriate control.

Conclusions. The conducted analytical studies give way for evaluation of modern ways to utilize lithium compounds. In particular, they show that there are no regulations governing the use and disposal of lithium products in Ukraine. Manufacturers of lithium energy sources, taking care of their employees, must agree with the requirements of public and government organizations, must develop and comply with safety standards for toxic components of lithium energy sources. At the same time, the growth in the use of electronic technology in Ukraine has such a pace that the population should be informed about the potential danger of active environmental pollution, a threat to human health.

Key words: lithium, toxicity, permissible amounts in environmental objects and biological media, sources of pollution, regulation

Introduction

Lithium is the 3rd element of the periodic table and is the 27th most common element in nature. It is an alkali metal that does not occur in nature as a free element. It is found in trace amounts in many minerals, in most rocks and soils, and in many natural waters. The average value of lithium concentration in soils is estimated to be from 10 to 40 mg/kg, in

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the earth's crust – [20...70] · 10^{-4}% [1–4]. Lithium is found in small amounts in almost all igneous rocks and in the water of many mineral springs. The leading suppliers of lithium extracted from brines are Argentina, Chile, Peru (constituting the so-called «lithium triangle» of South America), as well as China and the United States; and for the supply extracted from pegmatites – Australia, Brazil, Canada, Portugal, China and Zimbabwe. Below is a Table 1 [20] outlining current mine production and mine reserves.

The production and use of lithium compounds has a wide industrial application: for the production of ceramics, glass and primary aluminum metal, lubricants, primary and secondary battery cells, production of synthetic rubber, polyester fiber, catalysts, electronic and electrical equipment. In medicine, lithium drugs have been used for a long time, mainly as antioxidants and antihistamines, as well as in the treatment of nervous disorders. In particular, lithium salts, especially carbonate (Li_2CO_3) and acetate (CH_3COOLi) are widely used in the treatment of manic-depressive disorders [6–10].

Lithium does not accumulate biologically, but its high concentrations are dangerous for humans and the environment. The amount of lithium intake with food and drinking water has not been clearly described. Although there are individual reports that lithium can be considered as an essential microelement, the required daily dosage for this metal has not been established and the molecular mechanisms of lithium action in manic-depressive syndrome, heart muscle pathology and during pregnancy also have not been studied. Further research is needed to determine lithium requirements for different animal species and lithium concentrations in biological substrates on which their behavioral effects are observed, testing of subchronic sublethal toxicity during modeling process of toxicological studies aimed at studying the toxicokinetics of the biotic lithium ligand. The production of lithium-containing products and the disposal of lithium products, including electronic and

Table 1

Description current mine production and mine reserves

Tons	Mine Production			Mine Reserves	
	2018	2019	2020	2019	2020
Chile	17,000	19,300	18,000	8,600,000	9,200,000
Australia	58,800	45,000	40,000	2,800,000	4,700,000
Argentina	6,400	6,300	6,200	1,700,000	1,900,000
China	7,100	10,800	14,000	1,000,000	1,500,000
United States	W	W	W	630,000	750,000
Canada	2,400	200		370,000	530,000
Zimbabe	1,600	1,200	1,200	230,000	220,000
Brazil	300	300	1,900	95,000	95,000
Portugal	800	900	900	60,000	60,000
Other				1,100,000	2,100,000
World Total (rounded)	95,000	86,000	82,000	17,000,000	21,000,000

Source: United States Geological Survey

W – withheld by government not to disclose proprietary. The only lithium production in the United States was from a brine operation in Nevada.

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modern lithium-ion batteries (LIB) and waste, pose a toxicological hazard to workers. In addition, in the available scientific literature, information on this issue is sparse.

The aim of the study – the creation of an analytical review of the current state of environmental lithium pollution and to describe hazards for human health in the context of industrial and environmental exposure to the metal.

Materials and methods of the study

The study is based upon the analysis of domestic and foreign publications concerning the current state of environmental lithium pollution, the analysis of lithium content in environmental objects, the toxicity of the metal to humans and other animals, the impact of industrial exposure, the regulatory and legal acts, guiding documents of international organizations and those that are established in Ukraine.

Results of the study and their discussion

Content of lithium in the environment and bioaccumulation

Although lithium is found in minerals and various types of rocks, various clays are capable of accumulating small amounts of Li^+ cation, especially in conditions of increasing pH values. Other alkali metals quite easily replace adsorbed lithium, leaching it into the aqueous layer. In general, the degree of sorption by clays and humus increases for the cations in the series: Li < Na < K < H < Ca. There is also an observed reduction of the proportion of lithium with increasing levels of water mineralization. It is known that the composition of trace elements in natural waters correlates with their content in the rocks from which they are eventually washed away. In surface waters, the concentration of lithium may be increased as a result of, for example, locally available minerals or brines saturated by it.

Surface waters of technologically polluted areas can also be characterized by a high lithium content. In particular, due to the release of large volumes of mine wastewater into the ecosystem of the Donbas river basin, lithium levels of 11.8 to 13.7 mg/l were registered as of 2014.

The impact of the lithium extraction process on the environment can be the result of both the extraction process and the raw material processing [9]. The subject of concern is air and soil pollution, as well as the depletion of water reserves, which often depend on the viability of the population near the mining facilities. Lithium compounds do not have the ability to bioconcentrate in food chains due to the nature of their ions. Impact from industrial exposure to lithium compounds can occur by inhalation and skin contact in the workplace. Because lithium is found in a variety of environments, the general population will be exposed to lithium through inhalation of air, food and drinking water [11, 12].

It was found that inner tissue of a mature human body contains around 69–71 mg of lithium. With water a possible recommended daily intake amount of lithium would be of 65–105 μg. Main portion of the metal comes with food. High concentrations of the metal are found in tomatoes, potatoes, dairy products, meat, liver, fish and eggs. Because these foodstuffs form the dietary basis for people intake of lithium from water should, preferably, be limited.

The maximum threshold limit value for lithium in drinking water is no more than 0,03 mg/l, but this value does not always meet the standard, especially in tap water in large cities. According to experts, **bottled drinking water** (treated or natural spring water) **often has much bigger lithium content** than tap water [5, 7]. The physiological limit of

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lithium in water is defined as 90–200 μg, and the content of 600 μg/day and above is a direct danger to health. Ingestion of 200 mg of lithium leads to toxic damage to the body. Such a wide range is established due to the fact that the effect of the metal on the body depends on the age of the person, his weight, state of health and diet. Lithium belongs to the second level of hazardous substances in terms of danger to humans [15, 16].

Lithium compounds have a pronounced irritating effect. First of all, they affect the gastrointestinal tract, kidneys and central nervous system; exhibit a cholinomimetic effect, increase the serotonin content in the brain, affect carbohydrate metabolism and tissue respiration. Lithium is a biological antagonist of sodium, and it is especially toxic when there is a lack of the latter in the diet. Lithium chloride irritates human skin, lithium hydroxide can cause ulcers on the skin and nasal mucosa, similar to exposure to sodium hydroxide. The toxicity of lithium increases in the following sequence: $Li < LiCI < Li_2CO_3 < LiOH$. Lithium hydride in a concentration of 5–55 mg/m^3 has a pronounced irritating effect on laboratory animals, in a number of cases damage to the nasal septum was observed. Lithium hydride solution at a concentration of 0.01 mg/l causes skin burns [12–16].

Inhalation of air contaminated with smoke from the burning of lithium batteries can lead to poisoning similar to lithium hydride poisoning at a concentration of 0.2–0.5 mg/m^3, which leads to hyperemia of the skin, lacrimation followed by persistent conjunctivitis and even rupture of the nasal membrane.

The safe level of lithium in the blood is from 4.1 to 8.3 mg/l. Lithium toxicity occurs when this level reaches 10.4 mg/L or higher. Severe lithium toxicity occurs at the level of 13.9 mg/L and above, which in rare cases can be life-threatening. Levels of 20 mg/L and above are considered to require immediate medical attention. The safe dose of lithium varies from person to person, but most people are prescribed between 900 milligrams (mg) and 1,200 mg per day in divided doses for therapeutic purposes. Some take more than 1,200 mg per day when treating acute mental disorders. Others may be more sensitive to lower doses. These adverse effects of lithium are associated with serum concentrations ranging from 0.5 mM lithium/L (3.5 mg lithium/L) to more than 2.5 mM lithium/L (17.4 mg lithium/L) (see Table 2).

People taking lithium drugs need to carefully monitor how much they take and when. It's easy to accidentally overdose on lithium by taking an extra pill, mixing it with other medications, or not drinking enough water. For example, in 2014, 6,850 cases of lithium toxicity were reported in the United States.

When the doses of lithium drugs used to treat mental disorders were exceeded, weakness, drowsiness, loss of appetite, thirst and dry mouth, and in some cases even nausea, vomiting, and diarrhea were observed. This was accompanied by tremors of the lips and lower jaw, hyperflexia, dizziness, dysarthria, and impaired vision. In critical cases, this resulted in epileptic seizures, convulsions, coma and even death. But in conditions of manufacturing or living in areas where the air is polluted by waste incineration products containing lithium products, cases of chronic poisoning are possible.

The industrial application of lithium is quite diverse, from the manufacture of lithium drugs to the production of light alloys in the aeronautics industry. During a long historical period, the main application of lithium ores was the production of glass, glass ceramics, porcelain enamels, fritted glazes and refractories, batteries, lubricants, etc. The glass-ceramic industry remains the main con-

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Table 2

Derivation of biomonitoring equivalents for lithium in plasma and whole blood [19]

BE Derivation Step	U.S. EPA (2008) – PPRTV[2]	ICH (2014) (adopted by Health Canada, 2016a) – PDE[3]
Species, endpoint	**Humans, Kidney toxicity**	**Humans, Kidney toxicity**
Fraction absorbed	100 %	100 %
POD (LOAEL), external dose (mg Li/kg-bw/d)	2.1	0.8
Clearance - Adults (L/kg-bw/day)	0.5	0.5
BE-POD (LOAEL), plasma concentration (mg Li/L plasma)[a]	4.2	1.6
UF (intraspecies, LOAEL)	100	100
UF (database deficiency)	10	-
BE, plasma concentration (mg Li/L plasma)	0.0042	0.016
Partition coefficient (blood to plasma) (Pbp)	0.65	0.65
BE-POD (LOAEL), blood concentration (mg Li/L blood)	2.73	1.04
BE, blood concentration (mg Li/L blood)	0.0027	0.0104

Note. [a]Computed using the equation: plasma concentration (mg Li/L plasma) = [POD (mg Li/kg-bw/day)] • [fraction absorbed]/ Clearance (L/kg-bw/day); [2]PPRTV = provisional peer reviewed toxicity value; [3]PDE = Permitted Daily Exposure.

sumer of lithium even today. The addition of flux from spodumene ore or from pure lithium salts to the smelting mixture makes it less elastic, reduces the coefficient of thermal expansion and the minimum processing temperature, and also increases the transparency, rigidity and durability of the finished product. In addition, lithium plays an important role for specialized optics, where it is used in insulating metal films for glass, directly added to the composition of future glass lenses, or used for lenses material when in the form of monocrystalline lithium fluoride, which, compared to other materials, is the most transparent to UV radiation [7, 10].

Over the past 15 years, global lithium consumption for the production of lithium chemical power sources has grown from approximately a quarter to half of all mined reserves. The demand for lithium power sources in recent years has been driven by the needs in the production of consumer electronics and electric vehicles. Cathodes of lithium power sources can be made from oxides, sulfides, even chlorides and fluorides of such elements as Manganese, Copper, Vanadium, Titanium, Bismuth, Nickel, Lead, etc. The forms of cathodes are extremely diverse.

Electrolytes of chemical power sources can be solid, liquid, gel-like, and melted. However, the most common type is liquid electrolytes. The basis of liquid electrolytes for lithium current sources is most often aprotic dipolar solvents. In most cases, they have a dual function: they dissolve lithium and simultaneously restore it at the cathode. $SOC1_2$, $POFC1_2$, $POC1_3$, SO_2C1_2, as well as SO_2 or $C1_2$ dissolved in electrolytes are most often used [4, 10, 18]. Among the organic solvents used are propylene carbonate, dimethoxyethane, gamma-butyrolactone, dimethylformamide, etc. The electrolyte is formed as a result of dissolving $LiClO_4$ or $LiA1C1_4$,

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less often – $LiBF_4$, LiPF6, $LiAsF_6$. For pacemakers, the Li/I_2 system-based cells are used, where the cathode consists of a mixture of iodine and polyvinylpyridine, and the LiI layer plays the role of a solid electrolyte and separator.

Gel electrolytes have a higher conductivity than solid electrolytes; Chemical power sources employing them have a high current density. Thermal reserve batteries have electrolytes formed by melting at a temperature of up to 650 °C mixtures of lithium compounds in the presence of thickeners (substances that do not melt at these temperatures).

Recently, lithium-ion batteries have been widely used as current sources for industrial and household appliances [3, 6, 7, 18]. The credit for the development of modern lithium-ion batteries (LIAs) belongs to Prof. John B. Goodenough. His design, using ions instead of metallic lithium, solved the problem of dendrite formation. Today, LIAs are used in most everyday portable electronic devices. The current design uses a lithium metal oxide cathode, a graphite anode, and an electrolyte in a mixture of solvents (usually $LiPF_6$ in a mixture of organic carbonates).

In 2002, 5 billion dollars' worth of such batteries were sold globally (60 % of all batteries) for the needs of household appliances. This type of power source is rapidly spreading and Li-ion batteries for cars, for military and space equipment are already in operation and are being developed further.

The unique lightness of the lithium ion, due to its small size and ability to intercalate – that is, to migrate from one crystalline body to another, made it possible to develop and then implement a new type of battery. In the process of charging, the lithium cation leaves the anode and migrates to the cathode, when using the battery to obtain electricity, the reverse process is carried out. Lithium-ion batteries were mass-produced for the first time in the early 90s of the 20th century by the «Sony» company. Carbon was the key element for this type of batteries. First, coke, then graphite and other carbon materials became the basis for creating lithium-ion batteries. Theoretically, the mass and volume specific charge density of lithium-graphite is 372 A • h/kg and 819 A h/dm^3, respectively. The first stage of charging, which is carried out at the enterprise, is accompanied by the transfer of up to 50 % of lithium to the surface layer consisting of lithium carbonate. The oxidation treatment of the surface of carbon materials makes reduction of the amount of lithium and simultanious increase of the discharge capacity by 25 % possible. In modern batteries, the material for the anode is $LiCoO_2$. In the process of charging the battery, the potential of the electrode may drop to zero, which leads to the restoration of lithium to the metallic state, the interaction of metallic lithium with the components of the environment, heating of the system, depressurization and release of battery components.

In order to prevent such processes, special electronic potential control systems are installed in modern models of lithium-ion batteries, which increase the cost of the end products. If we compare lithium-ion batteries with nickel-hydride batteries, then the voltage in the former is 2.9 times higher, the energy density relative to the mass is 1.3 times higher, the self-discharge is 30 times higher, which makes their cost still three times higher than metal hydride batteries, as a consequence. Nickel-cadmium cells are even cheaper, but due to the danger of cadmium contamination, interest in them is gradually decreasing. Lithium-ion batteries are used, first of all, as power sources for portable computers, mobile means of communication, photo and video equipment, etc. Despite the high cost, their use in automotive industry, medical

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equipment, vehicles, etc. is growing rapidly. It is clear that the demand for these batteries in military and scientific equipment is increasing rapidly.

Nowadays, anodes made of lithium metal are used in lithium power sources based on irreversible electrochemical reactions. Another method of using metal lithium anodes is their application in all-solid-state lithium-ion batteries (ASS-LIBs), where the side processes of dendrite growth can be prevented by the structural rigidity of solid electrolytes. Due to the possibility of achieving energy capacities that are significantly higher than traditional batteries, this next-generation energy storage technology is considered one of the most promising. However, it is also possible to use other types of electrochemical energy storage systems that can reach the capacities of LIB and can be easier to manufacture – with sodium, aluminum, magnesium and other metals as anode materials. As an example, sulfur-sodium solid-state batteries that could not find proper use for electric cars in the 1990s due to the fragility of the materials and the subsequent interaction between the electrolyte and the anode with the occurrence of undesirable reactions, can be improved by including a stable interface between the solid electrolyte of the NASICON structure and sodium.

Hygroscopic lithium halides (chloride, bromide) can be used in air conditioning systems to release or absorb moisture into the environment, depending on the concentration and temperature of the solutions. LiBr solutions in a concentration of about 55 % (891 g/L) are used for air conditioning systems of large buildings, while LiCl is mainly used as an industrial desiccant. Lithium hydroxide or peroxide is used in the closed living space of submarines and space stations for the purpose of absorbing carbon dioxide and simultaneously releasing oxygen, respectively. Lithium-based lubricants are heat- and water-resistant and durable, have a low melting point. Saponification of triglycerides is used to produce lithium stearate and 12-hydroxystearate, which are often used in the automotive industry in mechanisms with direct metal contact [6].

Lithium, compared to cadmium, is a much less dangerous pollutant, and small batteries using lithium have not been considered toxic. Moreover, the tasks of disposal of lithium-ion batteries were started not due to danger they pose to the environment, but in order to return lithium to production and thereby make products cheaper. The fact is that the demand for lithium in the world is constantly growing, and this is confirmed by the volume of lithium consumption in Japan, which is now about 400 tons annually [3, 4]. At first glance, the technology of processing lithium cells is seemingly simple. It consists of the operations of opening the elements, draining and neutralizing the electrolyte, rectification of the electrolyte from the cathode mass, leaching of the residue, dissolving metallic lithium into a solution. Two methods are used to regenerate metallic lithium: electrolytic or aluminothermic. Opening the battery cells is dangerous due to fire and explosion hazard. Therefore, during this operation, it is necessary to completely exclude contact with air. Another danger is the possibility of the cathode materials, lithium metal, and electrolyte reacting with each other. This may cause an explosion. Practically, the technology of processing lithium cells is multi-stage and includes several operations of increased hazard [3, 4].

Sources for lithium pollution of the environment

Today, one of the main factors of environmental pollution with lithium is the waste of electronic products and electronic equipment.

In the review article from 2021 by W. Mrozik et al. [17] authors present the following figure that illustrates both direct and secondary possible

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pathways for pollution of the environment by Li-ion batteries (Figure).

It should be noted that back in 1994, the «Rechargeable Battery Recycling Corporation» was created in the states of Massachusetts and Maine to promote battery recycling in North America. This non-governmental organization collects batteries from consumers and companies and transfers them to the enterprises of «TOXCO» and «Battery Solutions Inc» for recycling. The basis of its activity is the directives of the Massachusetts Department of Environmental Protection. According to them, lithium is classified as hazardous waste, able to react with water. A similar document of the state of Maine prohibits the improper storage of these wastes. While in the United States, practical activities are carried out to process lithium energy sources in accordance with directive documents, in Europe they are still limited by regulations only.

Thus, in the European Union there is a directive from December 22, 1998 and November 24, 2003 on batteries and accumulators (primary and secondary cells) containing certain hazardous substances. The directive requires companies producing such batteries to include in their price the cost of further recycling and to carry out such recycling. The directive also requires the deployment in Europe of an extensive network of collection points for such energy sources. In Ukraine, there are no official documents that would regulate the handling of lithium chemical energy sources. It is only known that lithium chloride is included in the list of substances for the emission of which a fine is established.

The list approved by Order No. 104 of the Ministry of Environment and Natural Resources dated March 14, 2002. By Resolution No. 1287 of the Cabinet of Ministers of Ukraine dated August 17, 1998, is a list of particularly dangerous chemicals, the manufacture and sale of which is subject to licensing, including lithium and its inorganic salts. So far, both documents are only declarative and do not affect the processes of importing lithium

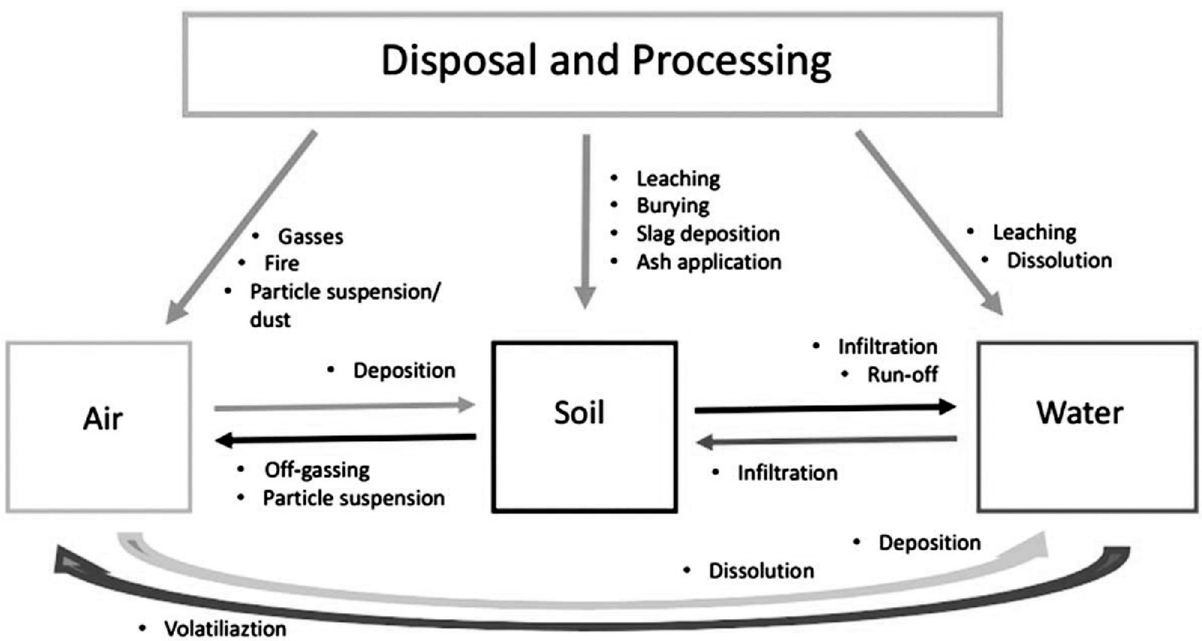

Figure. Possible emission routes of pollutants from LIBs into the environment [17]

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energy sources and their further fate. That is, spent elements are thrown into the waste for which there is no appropriate control. At the same time, the growth in the use of electronic technology in Ukraine has such a pace that if not informed about the potential dangers of active environmental pollution, and threats to human health, population can endanger itself or other populations of living organisms. It is a vivid example of how using foreign technical inventions, people do not want to assess the consequences of uncontrolled disposal of residues, which often contains dangerous substances.

On the other hand, manufacturers of lithium power sources, taking care of their employees, must agree with the requirements of public and state organizations, must develop and implement safety standards for toxic components of lithium energy sources. The population, as a typical user of foreign products, which includes the population of Ukraine, simply does not pay attention to the potential danger that pollutes the environment more and more every year. It should be informed about the ways of disposal, the health hazards due to inaction and ignorance concerning the problem.

Conclusions

The conducted analytical studies made it possible to evaluate the modern areas of application of lithium compounds. Particularly, they showed that in Ukraine there are no regulatory documents regulating the use and disposal of lithium products.

The safe daily requirement of lithium has not been established. Although lithium can be considered an essential trace element, the molecular mechanisms of action of lithium have not been studied. Therefore, further research is needed to determine the lithium requirements of different animal species and humans.

It is necessary to establish reference levels of lithium in biological substrates and markers of exposure under conditions of toxic action, testing of subchronic sublethal toxicity during modeling in experiments to study the toxicokinetics of lithium.

The growth of electronic equipment usage in Ukraine is at such a pace that the population must be informed about the potential dangers of the corresponding active pollution of the environment and threats to human health. Approaches to the disposal of products containing lithium must be safe for those working in these enterprises.

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