

ARTICLES

ANTHROPOGENIC SOIL POLLUTION WITH LEAD¹Zenkina V.G., ¹Solodkova O.A., ¹Agibalova A.A., ²Zenkin I.S.¹*Pacific State Medical University, Vladivostok, e-mail: zena-74@mail.ru;*²*Far Eastern Federal University, Vladivostok*

The intensity and scale of anthropogenic and geochemical pollution of nature is constantly growing. Heavy metals occupy a special place among pollutants, as they actively participate in biological processes, being part of many enzymes and proteins. Soils are not the final stage of the influx of heavy metals, but the link in the chain of their migration, where they can stay for a long time, interacting with its components and leaving the consequences of this interaction, which often lead to a decrease in the productivity of terrestrial ecosystems and pose a real danger to humans. Determined the content of lead cations in soil samples on the territory of the Medical University of Vladivostok and the possibility of recovery. To determine the content of lead ions in the samples, the method of thin layer chromatography and flame atomic absorption analysis was used. The analysis of the quantitative determination of lead showed a significant excess of the norms by 6-60 times in soil samples taken at different parts of the university buildings, near and far from transport routes. The optimal and affordable method of soil recovery from lead contamination is the phytoremediation method, planting a dense "green curtain" near the roadway. Due to the discovery of plants that hyperaccumulate heavy metals, phytoremediation is an effective and cost-effective method of cleaning the environment.

Keywords: soil pollution, heavy metals, lead dust, environmental monitoring, phytoremediation

The intensity and scale of anthropogenic and geochemical pollution of nature is constantly growing. Heavy metals (HM) occupy a special place among pollutants, as they actively participate in biological processes, being a part of many enzymes and proteins. Most of them are necessary for living organisms, however, as a result of intense atmospheric dispersion in the biosphere and significant concentration in the soil, many of the metals become toxic to biological objects [1, 2].

Soil is a non-renewable resource, i.e. in case of loss or degradation, it cannot be restored in a period comparable to the duration of a human life. Soil conditions affect the food we eat, the water we drink, the air we breathe, our health and the health of all life on Earth. Without healthy soils, we cannot grow food. Indeed, it is estimated that 95% of what we eat is directly or indirectly produced on the soil. Healthy soils are key to food security and our sustainable future. They help sustain food production, contribute to climate change mitigation and adaptation, they help filter water, increase resilience to floods and droughts, and much, much more. But there is an invisible threat that jeopardizes the soil and everything that they can give [2].

The use of hydrocarbon products as fuel for power plants, transport, heating enterprises and residential buildings has led to chemical contamination of the biosphere, such substances as: carbon monoxide, hydrocarbon products, lead compounds, asbestos dust, mercury, cobalt, cadmium and other metals [3, 4]. Soils are, if not the final stage in the influx of HM, then, in any case, the link in the chain of their migration, where they can be for a long time. So, the half-time from the initial concentration is: for zinc –

70-510 years, for cadmium – 13-110 years, for copper – 310-1500 years and for lead – 740-5900 years! In the soil, HM interact with its components and leave the consequences of this interaction, which often lead to a decrease in the productivity of terrestrial ecosystems and pose a real danger to humans [2, 5, 6].

Heavy metals are highly capable of various chemical, physicochemical and biological reactions, are able to accumulate in plants, and enter the body of animals and humans with food [7, 8]. At present, HM pollution is becoming a serious problem all over the world, toxic metals enter the environment both as a result of natural phenomena and as a result of large-scale industrialization. Discharged wastewater containing toxic HM mixes with soil or water and changes its natural composition. These HM have an adverse effect on living things and cause damage to the vital organs of animals and humans, leading to serious diseases: asthenic syndrome, encephalopathy, movement disorders, polyneuritis, damage to analyzers, changes in the blood system, metabolic and endocrine disorders, damage to the gastrointestinal tract, of cardio-vascular system. Moreover, HM pollution prevents the biodegradation of chlorine-organic compounds (another type of environmental pollution), interacting with metabolizing enzymes and suppressing their action. Some studies have shown that HM cannot be completely removed from the environment, but they can be effectively reduced or converted to a less toxic form to reduce their harmful effects on the environment. In recent years, more and more works have been devoted to the transformation of heavy metals through the use of the bioremediation potential of genetically modified microorganisms. In addition, the use

of plants for bioremediation of HM from the environment is also discussed along with their detailed mechanism [9].

Pacific State Medical University (TSMU) in Vladivostok is located near the carriage-way, above and below the road level. Thus, the exhaust gases with HM are deposited in the lower relief part of the soil. There are no industrial enterprises or agricultural land near the educational institution. Consequently, the main source of HM and, in particular, lead, entering the soil is motor vehicles. Some gasoline companies add tetraethyl lead, an antiknock agent, to it, which increases its antiknock properties. When such fuels are burned, lead added to gasoline is released into the atmosphere along with carbon dioxide. Gases formed on the territory of the city spread from it in all directions. Vladivostok is located on the shores of Japan Sea with its numerous picturesque bays and bays, unique flora and fauna. Consequently, such an arrangement leads to direct pollution not only of the soil, but also of the water, since gases full of various metals settle on the ground and on the water surface of the sea [9, 10]. People, realizing the seriousness of the problem, are already beginning to think about replacing fossil fuels with natural ones.

Purpose of the study

Determine the content of lead cations Pb^{2+} in soil samples on the territory of TSMU and the possibility of phytoremediation.

Materials and research methods

Sampling was carried out using an aluminum cylinder, which was immersed in the soil of this image by 10 cm. The study of land samples was carried out from different parts of the territory of TSMU in order to identify lead cations in soil samples: № 1 – near the main building, № 2 – near buildings 3, № 3 – between buildings 5 and 6, № 4 – near building 2.

The soil, which was in the cylinder, was carefully removed and examined without disturbing the location of the soil layers. Then each sample was treated with hot water ($t = 90-100^{\circ}C$) and infused for 10 minutes. The resulting solutions were filtered first from mechanical impurities using calico, and then from the smallest particles using filter paper (blue ribbon) until the complete disappearance of turbidity in the solution. After filtration, the solutions were evaporated in a porcelain dish to a volume of 1 ml. The one stripped off solutions were poured into test tubes and marked with numbers.

To determine the content of lead ions in the samples, we used the method of thin layer chromatography. In this method, the chromatography of substances occurs in a thin layer of sorbent deposited on a solid flat substrate. The separation mainly takes place on the basis of sorption-desorption. In this case, the plate had an aluminum substrate. First, a “start line” is marked on the plate, which is 7 mm from the edge of the plate. Then points are marked on the line where the obtained one stripped off solutions are applied. We got 5 points: at points № 1-4 we applied solutions obtained from samples 1-4, respectively, at point № 5 we applied the “witness” $Pb(NO_3)_2$. Then a system of solvents was prepared: n-butanol, distilled water with the addition of CH_3COOH until $pH = 3$ (C-1). After applying the sample solutions, the plate was placed in a beaker with a system (C-1) for 30 minutes. Then the plate was removed and dried for 10 minutes. Then the plate was treated with a K_2CrO_4 solution.

For the quantitative determination of lead in the samples, flame atomic absorption analysis was used. Soil samples dried in a drying oven ($t = 105^{\circ}C$ for 1.5 hours) were placed in a glass and decomposed in aqua regia [(3V HCl: 1V HNO_3), 40 ml per sample], until the formation of wet salts. Then the contents of the beakers were transferred quantitatively into volumetric flasks with a capacity of 50 ml and made up to the mark with distilled water. The prepared samples were installed in a Shimadzu AA 6601F atomic absorption flame emission spectrophotometer.

Research results and discussion

As a result of the study, it was found that the content of lead in sample № 1 and № 4 is higher than in samples № 2 and № 3, as evidenced by the size of the spot on the plate, with the largest spot in the sample № 4. Therefore, it can be assumed that exhaust gases (one of the main sources of lead), after being thrown by machines into the soil, are not immediately absorbed, but gradually descend (there is a small slope near the university) and then settle to the ground. Since the “sample point” is located at the bottom, there is no “washout” of the contamination. And we are seeing the accumulation of lead cations. This is also evidenced by signs of plant poisoning, such as yellowing of leaves, their rapid death, various mutations. Probably, such an ecological picture unfavorably develops not only on the territory of the university, but also for the city, taking into account its landscape. It is necessary to take measures to eliminate or

reduce the penetration of gases into the territory of the TSMU. The most widely used soil clean-up and remediation method is the excavation and removal of the contaminated layer, which is then processed or removed for storage elsewhere. As a rule, these are expensive methods, accompanied by strong pressure on the environment. Moreover, in many cases, extraction is difficult for financial or technical reasons. Therefore, the priority task is to develop new technologies for removing pollutants from soils.

The analysis of the quantitative determination of lead was carried out in the mode of flame atomic absorption analysis, which resulted in the following data: all soil samples exceed the maximum permissible concentration for lead concentration; in sample № 4 – 60 times, in sample № 3 – 20 times, in sample № 2 – 6 times, in sample № 1 – 25 times. The results of the content of lead in the soil are not very encouraging, therefore, the priority task is to develop new technologies for removing pollutants from soils. Various microorganisms have been used quite successfully for a long time to neutralize toxic organic substances that enter the environment with wastes from chemical enterprises. However, they are not able to remove heavy metals harmful to health from soil and water – for example, cadmium, copper, mercury, selenium, lead, as well as radioactive isotopes of strontium, cesium, uranium and other radionuclides. Another thing is green plants, which extract from the environment and concentrate various elements in their tissues [3, 8, 11]. The plant mass is not difficult to collect and burn, and the resulting ash is either buried or used as a secondary raw material. This method of cleaning the environment was called phytoremediation – from the Greek “fiton” (plant) and the Latin “remedium” (to restore). Phytoremediation became an effective and cost-effective method of cleaning up the environment only after the discovery of heavy metal hyperaccumulator plants capable of accumulating in their leaves up to 5% nickel, zinc or copper in terms of dry weight – that is, dozens of times more than ordinary ones [10, 11, 12]. The biological significance of this phenomenon has not yet been fully disclosed: it can, for example, be assumed that a high content of toxic elements protects plants from pests and makes them more resistant to diseases. Based on this property, you can clean the soil from HM. Birch, manchurian ash, western thuja, juniper, Sakhalin buckwheat, corn, Indian mustard will help cleanse the soil from lead.

With the development of science, people have learned to influence the germination of the crop, its growth, composition; learned to isolate new species of plants and animals with even higher productivity. But behind these advantages are huge disadvantages, indicating the price of all these innovations. The biological relationship between soil and man is carried out by metabolism, since with the harvest, man removes mineral and organic substances from the soil. Thus, the soil provides food for many representatives of flora and fauna. Consequently, the deterioration of soil quality, its contamination with HM, pesticides and other harmful substances can lead to adverse consequences in the biological system: new diseases can arise, existing ones become complicated, various mutations are possible. This is due to the fact that some of the substances introduced into the soil are washed out and enter underground waters, lakes and rivers, from where they directly affect animals, including humans, which negatively affects his health.

To determine the nature of the effect of Pb^{2+} on plants, we studied the growth and development of cress seeds (*Lepidium sativum* L.) sown in soil samples taken on the territory of the educational institution [12, 13]. For the purity of the experiment, a purchase of “clean” soil was made, the content of HM in which corresponds to GOST, in which the seeds were sown. All soil samples were placed in plastic containers labeled with the corresponding sample numbers. For sowing the soil, 125 large watercress seeds were selected and sown, 25 seeds in each container. After planting all 125 seeds, the soil was watered with purified warm water.

The duration of the experiment was 10 days with regular watering (after 2 days), measuring the height of each stem and daily records of plant development (Fig. 1).

In the course of the experiment, the following results were obtained: the plants of samples № 2 and № 3 turned out to be the closest to the norm of their development. The highest germination rate № 3, and the lowest – № 4. At the initial stage of their development, some № 4 and № 1 died or stopped in development (Fig. 2). Based on the results obtained, it can be assumed that Pb^{2+} has a negative effect on plants, reducing germination, slowing down growth and inhibiting development. Therefore, the optimal and affordable method of soil recovery from lead contamination is the phytoremediation method, planting a dense “green curtain” near the roadway.

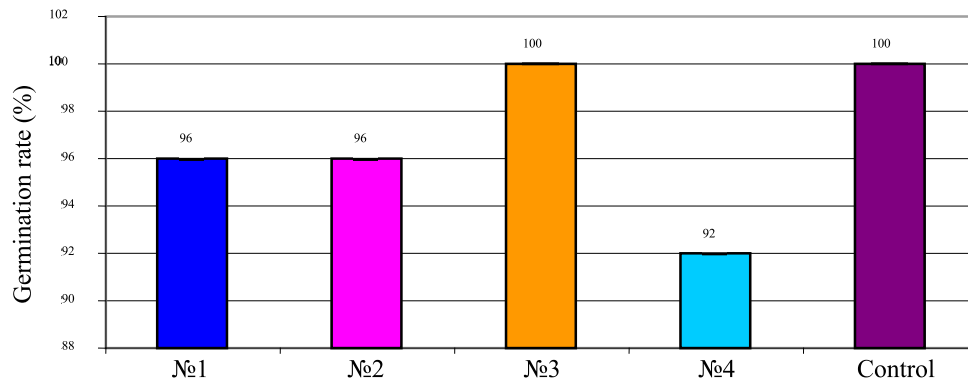
Germination of seed of *Lepidium sativum* L.

Fig. 1. Germination of watercress seeds in different soil samples

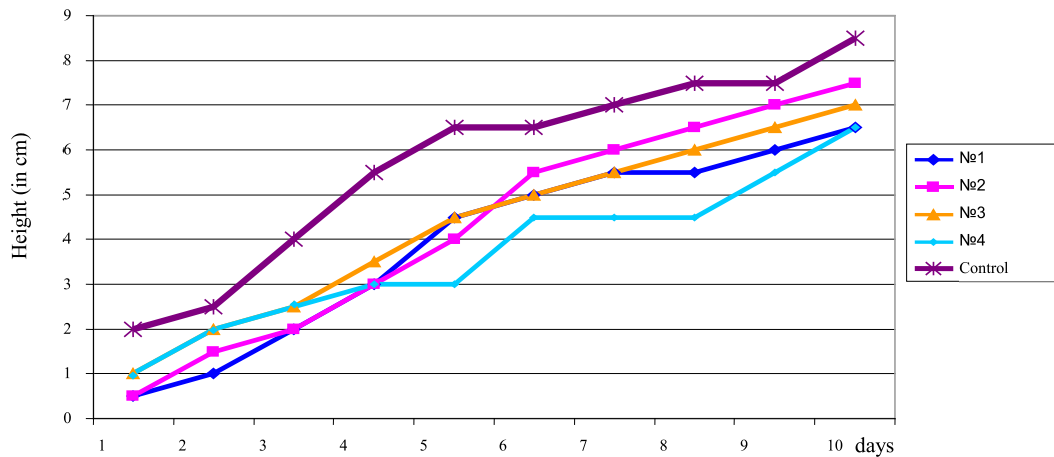
Growth of *Lepidium sativum* L.

Fig. 2. Growth dynamics of watercress in different soil samples

Conclusion

In the 21st century, world civilization has entered a stage in its development when the problems of survival and preservation of the natural environment, rational use of natural resources have come to the fore. The modern stage of human development has exposed the problems caused by the growth of the Earth's population, the contradictions between the traditional economy and the growing rate of use of natural resources, pollution of the biosphere with industrial waste and the limited capacity of the biosphere to neutralize them. These contradictions hinder the further scientific and technological progress of mankind, become a threat to its existence.

The main problem of a modern city is transport. During the operation of internal

combustion engines, nitrogen oxides, lead, hydrocarbons and other substances are intensively released, which settle on the soil surface or are absorbed by plants. Lead is deposited on plants, penetrates into the soil, where it remains for a long time, since it dissolves slightly. People living in cities near highways with heavy traffic run the risk of accumulating toxic substances in their bodies, which leads to a deterioration in their health.

Self-cleaning of soils is usually a slow process. Toxic substances accumulate, which contributes to a gradual change in the chemical composition of soils, disruption of the unity of the geochemical environment and living organisms. Toxic substances from the soil can get into the organisms of animals and people and cause serious illnesses and deaths.

In our studies, it was possible to identify foci of lead dust pollution and it turned out that the exhaust gases settle at the lowest point near the surface of the earth and “spread” over it. Based on the results of quantitative analysis, we can talk about total soil contamination with lead and other metals. In this regard, it is necessary to reduce as much as possible the level of input of heavy metals into the soil ecosystem and the human body, since this causes not only external changes, but also internal ones. To achieve this goal, we believe that the simplest and most inexpensive method of cleaning soil from HM is the phytoremediation method, which will allow cleaning not only the soil, but also the air, thereby contributing to the improvement of the ecological situation. The implementation of constant monitoring of the territory, the use of modern cleaning technologies, landscaping along transport routes, of course, will help mitigate the negative impact of harmful factors, including heavy metals, on the human body.

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