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HEAVY METALS CONCENTRATION IN THE WATER OF HUMAN-MADE OBJECTS

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Abstract. The study concerns with the changes of heavy metals concentration in the water of human-made objects (ponds and canals of drainage system). It has been revealed the exceeding of maximum permissible norm of Cu, Zn, Pb and Cd in the ponds, and the exceeding of maximum permissible norm of Pb and Cd in the canals of drainage system during the continuous time that certifies their permanent getting in the soils and waters from point and diffuse sources. The paper analyzes basic sources of heavy metals getting in the waters and their positive and negative impact on the biota. In order to increase ecological value of water objects and resources of agricultural lands it has been offered to use fertilizers and pesticides in a rational way, move to electric car use gradually, arrange landfills in a proper way, standardize algicidal fertilization, use fish fauna representatives to regulate number and algae biomass, equip the bioplateau and implement phytoremediation technologies with the aim to remove heavy metals from the soils and waters.

Keywords: ponds, canals of drainage systems, pollutants, permissible concentrations

1. Introduction

Heavy metals are constant components of water ecosystems. In optimal concentrations biogenic heavy metals have become necessary to provide the livelihood of all living organisms. Non-biogenic metals are highly toxic and cause irreversible changes even under the condition of very low concentrations (Malikula et al., 2022). A significant increase in toxic effects and breaking biochemical and physiological processes of biota occur as a result of exceeding maximum permissible concentrations of heavy metals in water objects and other environments of their depositing. Specific conditions for their emigration in water ecosystems (water, mud, soil), bioaccumulation (accumulation in tissues and organs of living organisms) and biomagnification (accumulation with trophic chains) are defined with physical and chemical characteristics of heavy metals, pH level, oxidation-reduction potential and the presence of ligands (Zotov et al., 2010; Dudnik et al., 2013; Paulet al., 2021). Sources of heavy metals in water objects significantly impact the mentioned processes. The most common sources are wastewater from lead-zinc factories, ore-concentrating plants, galvanic coating shops, chemical and metallurgical industries, production of parchment paper, mineral paints, artificial fibre and leather, metal-ceramics, polymers, glass pigments, porcelain and galvanic coatings (Kondratyuket al., 2009). The constant flow of heavy metals into the water objects provides the drains of agricultural land. Soils contain a Soil and water objects pollution takes place as a result of heavy metals flow from waste incineration plants, natural dumps, and solid waste landfills. The authors point out significant exceeding of geochemical background of Zn, Cd, Fe, Cu, Ni, Pb and Cr. The level

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of soil pollution near the solid significant amount of heavy metals that are intensively accumulated during continuous time intervals. Fertilization with phosphate, potash, nitrogen fertilizers and pesticides significantly increases their concentration. Only using superphosphate 7.3–170 mg/kg of cadmium, 50–1430 mg/kg of lead, 4–100 mg/kg of cuprum, 7–32 mg/kg of nickel and other heavy metals get into the soil (Floria, 2012). Besides, heavy metals are included in the composition of organic fertilizers. Slow removal of heavy metals from the soil causes their accumulation in high concentrations. 30–40 % of heavy metals and their derivatives get into groundwater from the soil and these derivatives are carried long distances (Puzik et al., 2012). Soil and water objects pollution takes place as a result of heavy metals flow from waste incineration plants, natural dumps, and solid waste landfills. The authors point out significant exceeding of geochemical background of Zn, Cd, Fe, Cu, Ni, Pb and Cr. The level of soil pollution near the solid waste landfills differ from mild to high ones, and concentrations of Cd and Pb often exceed maximum permissible levels (El Fadili et al., 2022). Without any doubt, water objects pollution by heavy metals depends on the physical and geographical characteristics of the territory, and, first of all, from the character of soil cover, the intensity of erosion processes, level of forest cover, water logging, and also the level of anthropogenic impact. The research of heavy metals concentration is of particular interest dealing with essential components of agricultural landscapes that are presented with the ponds and canals of drainage systems as there is not almost appropriate protection from heavy metals' getting and accumulation in the water and sediments for such human-made objects. Thus, the ecological value of these water objects and sources of agricultural land is decreasing (Savic et al., 2015). Considering mentioned items the aim of the research is to define heavy metals concentration in the water of human-made objects (ponds and canals of drainage systems) and to analyze their impact on the biota.

2. Materials and methods

While researching Rivne branch office of the State Institution "Soils Protection Institute of Ukraine" has selected water samples in 25 control section lines in the Hoshcha region. 200 water samples have been analyzed selected from the main canals of the drainage system of "HUK and Korchunok" that pass through the village of Tuchyn on the pasture and among the fields of heavy use, and also the ponds of "Staryi" (50°42'24.2"N, 26°34'54.1"E), "Novyi" (50°42'28.5"N, 26°35'30.0"E), and "Malyi" (50°41'31.6"N, 26°32'45.3"E) in the villages of Tuchyn and Zhalianka (50°44'37.2"N, 26°38'51.4"E) (Fig. 1).

Fig. 1. Schematic map of water objects placement

Water samples have been selected according to conventional methods once a year in the spring period during 2011–2018. The water has been filtered through a membrane filter with a pore diameter of 0.45 µm, concentrated by 10 times and it has been defined heavy metals concentration using the method of atomic and absorption spectrophotometry with the help of spectrophotometer C-115 M1 according to the wavelength that was appropriate to the maximum of absorption of each researched metal according to the standard methodic (Novikov et al., 1990). Metal concentration (C) was presented in mg/dm^3 of the studied samples.

3. Results and Discussion

Figs. 2–9 show the comparison of the average concentration of biogenic (Cu, Zn) and non-biogenic (Pb, Cd) heavy metals in the water of ponds and canals of drainage systems during 2011–2018.

The ponds. 80 % of Cu in the Earth's crust is presented with its compounds with sulfur, and 15 % are revealed as oxides, carbonates, and silicates that are the products of primary sulphide copper ores weathering (Dudnik et al., 2013; Perepelytsia, 2004). Unreasonable use of pesticides and fungicides causes Cu pollution of agricultural lands (Adrees et al., 2015) with the following leaching to the water objects.

Cu concentration in the water of the pond of "Staryi" of the village of Tuchyn varies from 0.0044 mg/dm3 (2016) to 0.0160 mg/dm^3 (2015). The highest Cu concentration in the water of the pond of "Malyi" of the village of Tuchyn is 0.0260 mg/dm^3 (2014), and the lowest one is 0.0059 mg/dm^3 (2012). Cu concentration in the water of the pond in the village of Zhalianka changes from 0.0031 mg/dm^3 (2013) to 0.0150 mg/dm^3 (2011, 2014) (Fig. 2). In general, the highest Cu concentrations in the water of the studied ponds have been observed in 2013 and 2014, however, the excess of standard indicators has not been revealed (MPC(Cu) household purposes=1,0 mg/dm^3). The excess of Cu MPC has been singled out for the fishery waters and is 3.1–26 times (MPC(Cu) fishery purposes=0.001 mg/dm^3).

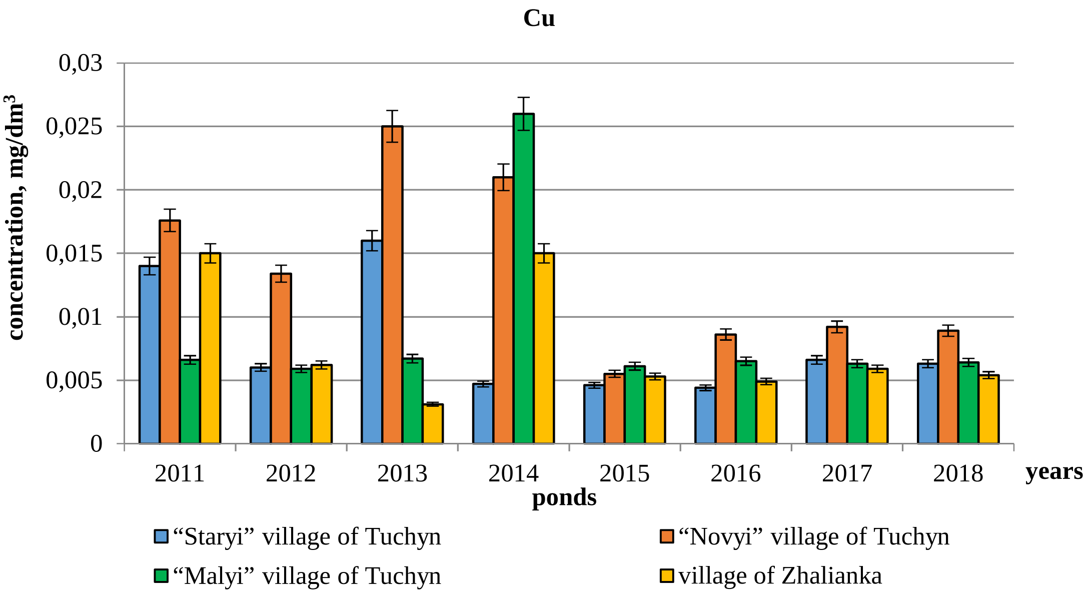

Fig. 2. Cu concentration in the water of the ponds of "Staryi", "Novyi", "Malyi" in the villages of Tuchyn and Zhalianka (2011–2018)

Cu is a component of a lot of enzymes. It catalyzes oxidation-reduction reactions and impacts the intensity of photosynthesis, growth and ageing processes, nitrogen metabolism of algae, higher aquatic vegetation and fish (Linnik, 2014; Waggoner et al., 1999; Maksymiec, 1998; Dudnik et al., 2013). In metabolic reactions, Cu is an electrolytes carrier and component of enzyme-substrate complexes. Cytochrome oxidase is of high importance among copper-containing enzymes as it catalyzes the final stage of tissue respiration. At the same time, increased Cu concentrations harmfully impact the biota. Blue-green algae, diatoms, invertebrates and fish demonstrate high sensitivity. Green algae are presented as more resilient to high Cu concentrations. However, the process of algae photosynthesis is suppressed, and the algae composition and their amount change when Cu concentration is 0.05 mg/dm^3 and more (Kondzior et al., 2018; Romanenko, 2001). The use of algicides to regulate biomass and algae population causes the excess in Cu concentration in the water of the studied ponds (Dudnik et al., 2013). Besides, Cu concentration in the ponds changes as a result of accumulation in sediments as a component of complexes with organic substances and deposition of suspended solids with adsorbed copper forms (Linnik et al., 2012; Paul et al., 2021). Due to chelates, suspended solids and humic acids, Cu concentration may decrease 1.0–1.5 times (Dragun et al., 2009).

Zinc gets into water objects as a result of damage and dissolution of rocks and minerals. Wastewater from concentration enterprises, metallurgical plants, production of mineral paints and artificial fibre production contain high concentrations. As a result of coal combustion, zinc gets into the atmosphere. It is carried over long distances, deposited and washed away from the catchment area with surface runoff to the water object. Every year, 72 kg of Zn per 1 km^2 of the territory get with atmospheric precipitation, which exceeds Cu flow 12 times and for lead it is 3 times (Dudnik et al., 2013). In water objects, the increase in Zn concentration is caused by its additional getting with melted snow waters and rainwater (Hüffmeyer et al., 2009; Aryalet al., 2010; Codling et al., 2020). Finally, Zn concentration in atmospheric precipitation can be 0.008–0.330 mg/dm^3 (Chen et al., 2007).

The highest Zn concentration is 0.1070 mg/dm^3 (2014) in the water of the pond of "Staryi" in the village of Tuchyn, and the lowest concentration is 0.0034 mg/dm^3 (2016). Zn concentration in the water of the pond of "Novyi" in the village of Tuchyn varies from 0.0079 mg/dm^3 (2012) to 0.1150 mg/dm^3 (2014). The lowest Zn concentration in the water of the pond of "Malyi" in the village of Tuchyn is 0.0042 mg/dm^3 (2013), and the highest one is 0.0760 mg/dm^3 (2012). In the water of the village of Zhalianka, Zn concentration changes from 0,0135 mg/dm^3 (2013) to 0.0370 mg/dm^3 (2014) (Fig. 3). The highest Zn concentration have been observed in the water of the pond of "Staryi" in the village of Tuchyn which does not exceed maximum permissible concentrations (MPC(Zn)household purposes=1.0 mg/dm^3). The exceeding of MPCfishery purposes Zn is 1.7–11.5 times (MPC(Zn)fishery purposes =0.01 mg/dm^3).

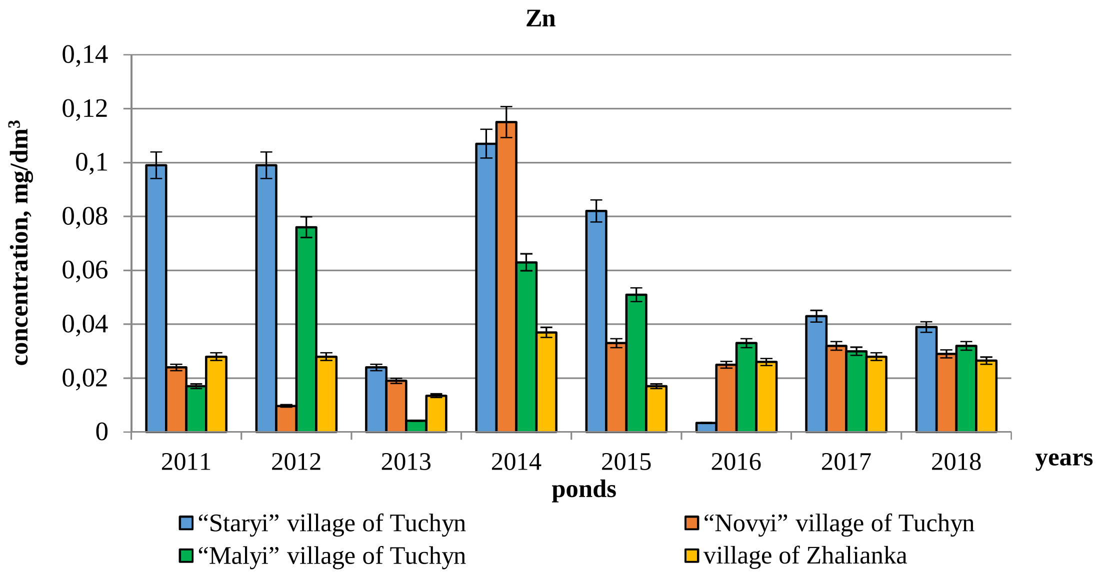

Fig. 3. Zn concentration in the water of the ponds of "Staryi", "Novyi", "Malyi" in the villages of Tuchyn and Zhalianka (2011–2018)

It is known that zinc belongs to essential metals and is actively assimilated by the biota, which causes the change of its concentration in the water. Zinc impacts the processes of photosynthesis, the synthesis of nucleic acids and proteins provides the regulation of starch synthesis and other reactions that are related to carbohydrate and phosphoric metabolism in plants (López-Millán et al., 2005; Romanenko, 2001). Zn is a vital co-factor for a lot of ferments, so it takes part in plant metabolism processes (Natasha et al., 2022). In particular, zinc is a component of carbonic anhydrase that catalyzes the reaction of dehydration of carbonic acid. High Zn concentrations inhibit the synthesis of nucleic acids (López-Millán et al., 2005; Romanenko, 2001), decrease the concentration of Chl a and b, and also the relation of a/b (Khudsar et al., 2004; Vaillant et al., 2005). Toxic impact on the growth, photosynthetic activity and biota oxidative stress increase with high Zn concentrations and increased concentrations of other metals (Tsonev et al., 2012).

Pb gets into water objects as a result of the dissolution of galenas, anglesites, cerussites and other metals with wastewater of ore-concentrating plants, chemical enterprises, metallurgical plants, and also with coal combustion (Linnik et al., 2012; Perepelytsia, 2004). Pb concentration in the water of the pond of "Staryi" in the village of Tuchyn varies from 0.0160 mg/dm^3 (2015) to 0.0306 mg/dm^3 (2018). The highest Pb concentration in the water of the pond of "Novyi" in the village of Tuchyn is 0.030 mg/dm^3 (2014), and the lowest one is 0.010 mg/dm^3 (2015). In the water of the pond of "Malyi" in the village of Tuchyn, the highest Pb concentration is 0.047 mg/dm^3 (2011), and the lowest one is 0.027 mg/dm^3 (2018). The maximum Pb concentration in the water of the pond in the village of Zhalianka is 0.041 mg/dm^3 (2011), and the minimum one is 0.017 mg/dm^3 (2015). The excess in MPC for Pb concentration 1.2–1.6 times is revealed in the water of the pond of "Malyi" in the village of Tuchyn and the water of the pond in the village of Zhalianka 1.3–1.4 times ($MPC(Pb)_{household\ purposes}$=0.03 mg/dm^3) (Fig. 4). Pb concentration exceeds $MPC_{fishery\ purposes}$ ($MPC(Pb)_{fishery\ purposes}$=0.01 mg/dm^3) for the ponds 1.7–3.9 times. Pb concentration excess in the water of the ponds may be related to their close placement to the highways. It is known that to increase petrol anti-detonation characteristics, lead combinations that get to soils and reservoirs with exhaust engine fumes are used (Puziket al., 2012). In the water of the ponds, the excess in regular Pb concentrations is caused by exhaust engine fumes (Puziket al., 2012) and natural dumps (El Fadili et al., 2022). High Pb concentrations disrupt mineral nutrition, water balance and the growth of plants, impact membrane structure and permeability and the photosynthesis process (Nas et al., 2018).

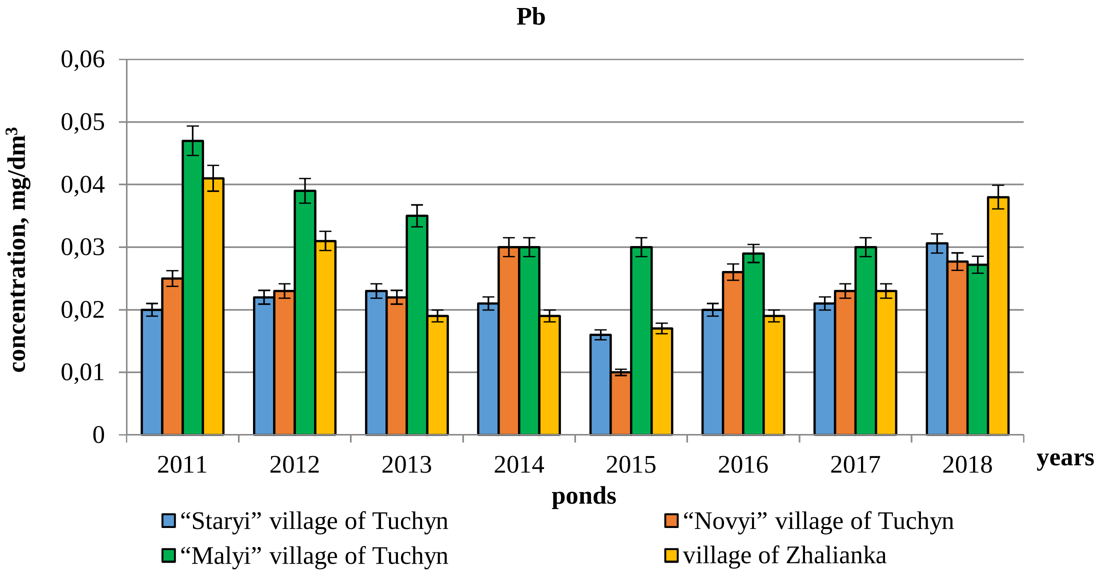

Fig. 4. Pb concentration in the water of the ponds of "Staryi", "Novyi", "Malyi" in the villages of Tuchyn and Zhalianka (2011–2018)

Cadmium may accumulate in soils over the centuries (Dudnik et al., 2013). That is why its concentration in water objects depends on the content of rocks and soils. Cadmium compounds pollution increases as a result of the unreasonable use of mineral fertilizers, pesticides, and wastewater for irrigation works (Klimas, 1995). Besides, Cd may get with wastewater from the mining industry, concentration and electrolysis industry, atmospheric precipitation (Perepelytsia, 2004), and products of combustion of diesel fuel and lubricants (Puzik et al., 2012).

Cd concentration in the water of the pond of "Staryi" changes from 0.0010 mg/dm^3 (2012, 2013) to 0.0020 mg/dm^3 (2014). The minimum Cd concentration in the water of the pond of "Novyi" in the village of Tuchyn is 0.0009 mg/dm^3 (2012), and the maximum one is 0.0028 mg/dm^3 (2014). Cd concentration in the water of the pond of "Malyi" in the village of Tuchyn varies from 0.0009 mg/dm^3 (2013) to 0.0038 mg/dm^3 (2014). The lowest indicators of Cd concentration in the water of the pond in the village of Zhalianka are 0.0008 mg/dm^3 (2011), and the highest ones are 0.0024 mg/dm^3 (2014). The author points out that the highest Cd concentrations were observed in 2014 in all researched ponds (Fig. 5). During 2011–2018 one could observe the excess of MPC for Cd concentration in the water of the pond of "Staryi" in the village of Tuchyn 1.2–2.0 times, of the pond of "Novyi" in the village of Tuchyn 1.5–2.8 times, of the pond of "Malyi" in the village of Tuchyn 1.3–3.8 times, of the pond in the village of Zhalianka 1.1–2.4 times ($MPC(Cd)_{household\ purposes}$= =0.001 mg/dm^3). Cd concentration did not exceed MPC for the waters of fishery purposes ($MPC(Cd)_{fishery\ purposes}$=0.005 mg/dm^3).

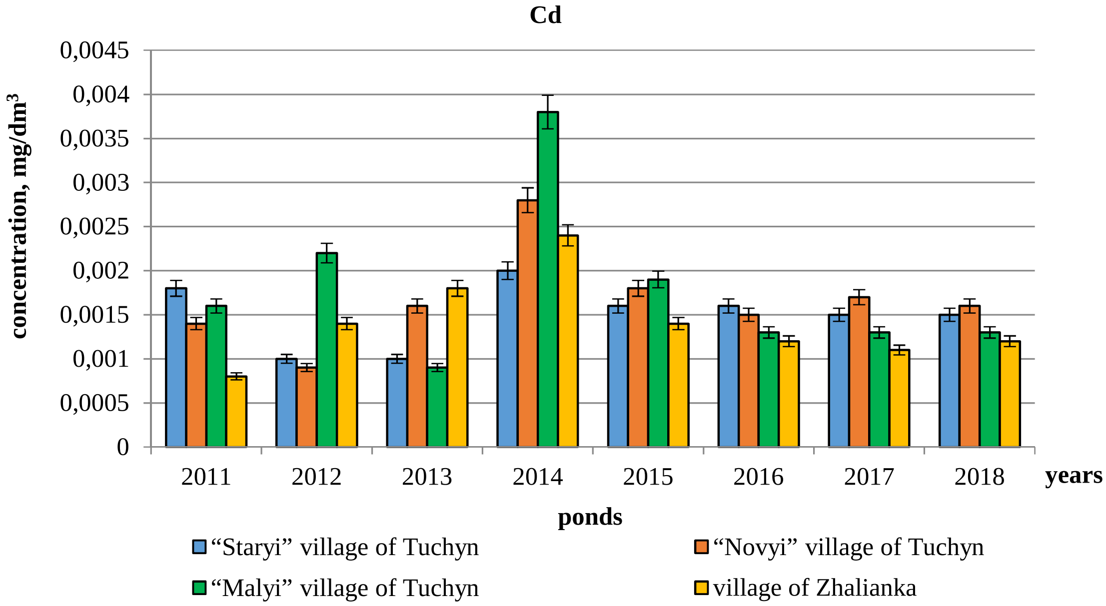

Fig. 5. Cd concentration in the water of the ponds of "Staryi", "Novyi", "Malyi" in the villages of Tuchyn and Zhalianka (2011–2018)

Cadmium belongs to the most toxic metals, so even in small concentrations, it inhibits the physiological and biochemical processes of the biota. Harmful Cd impact deals with its fast absorption by the organism and slow filter out that causes a significant accumulation of metals in tissues. The liver and kidneys accumulate Cd most, and the period of its half-filter out may continue for about 30 years (Barbier et al., 2005; Komarnicki, 2005; Paranyaket et al., 2007). Cd concentration in water that is 0.003–0.5 mg/dm^3 causes the death of 50 % of freshwater invertebrates during 72 hours. Cd toxicity sharply decreases only due to complex formation with organic substances, in particular with humic and fulvic acids (Romanenko, 2001).

Canals of the drainage system of "HUK and Korchunok". In the water of the canals of the drainage system on the pasture during 2011–2018, Cu concentration changed from 0.0024 mg/dm^3 (2015) to 0.0150 mg/dm3 (2014). Cu concentration in the water of the canals of drainage systems among the fields of heavy use varied from 0.0031 mg/dm^3 (2015) to 0.0150 mg/dm^3 (2014). In general, in the water of all canals of the drainage system, the highest Cu concentration was observed in 2014, and the lowest one was in 2015, although it does not exceed regular indicators (Fig. 6).

Important sources of Cu getting to water objects are wastewater from enterprises of the metallurgical and chemical industry, corrosion products of copper buildings and technical devices. A possible source of Cu getting to the canals of the drainage system may be soils that are cultivated with Cu-containing pesticides and agrochemicals (Dudnik et al., 2013).

In the water of canals of drainage system on the pasture Zn concentration varies from 0.013 mg/dm^3 (2015) to 0.076 mg/dm^3 (2014). In the water of canals of the drainage system that pass through the village of Tuchyn, Zn concentration varied from 0.011 mg/dm^3 (2011) to 0.025 mg/dm^3 (2018). In the water of canals of drainage systems among the fields of heavy use, it varied from 0.014 mg/dm^3 (2015) to 0.054 mg/dm^3 (2014). In the water of canals of the drainage system of "HUK and Korchunok", during the period of research (2011–2018), Zn concentration did not exceed MPC ($MPC(Zn)_{household\ purposes}$=1.0 mg/dm^3) (Fig. 7).

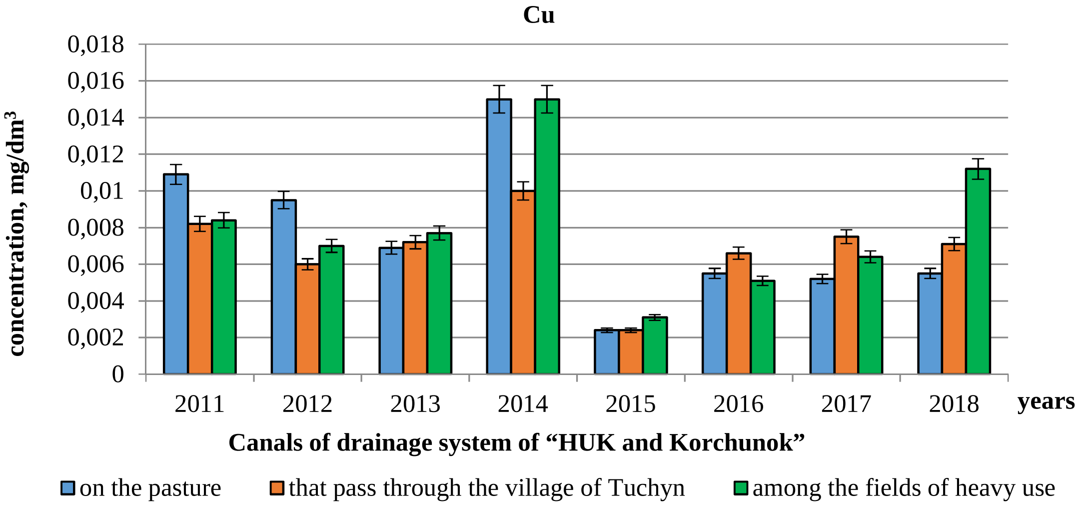

Fig. 6. Cu concentration in the water of canals of drainage system of "HUK and Korchunok" on the pasture that pass through the village of Tuchyn and among the fields of heavy use (2011–2018)

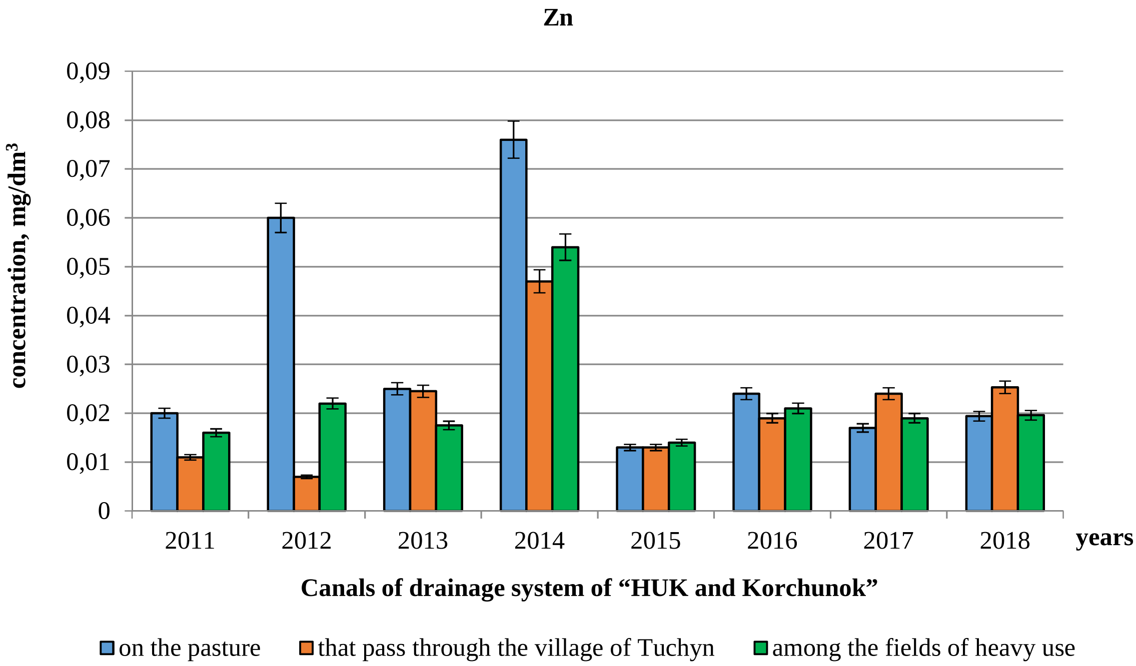

Fig. 7. Zn concentration in the water of canals of the drainage system of "HUK and Korchunok" on the pasture that pass through the village of Tuchyn and among the fields of heavy use (2011–2018)

In the water of canals of the drainage system on the pasture, the minimum Pb concentration was 0.0160 mg/dm^3 (2015), and the maximum one was 0.0380 mg/dm^3 (2015), which exceeds MPC 1.8 times. The lowest Pb concentration was 0.0210 mg/dm^3 (2015). Pb may pass through the canals of the drainage system from the natural dumps and as a result of car fumes. The excess of Pb concentration MPC has been observed in the water of the canals of drainage systems among the fields of heavy use. The maximum Pb concentration was 0.0470 mg/dm^3 (2011) which exceeds MPC 1.6 times, and the minimum one was 0.0290 (2013). The authors highlight that in the water of all canals of drainage system of "HUK and Korchunok" maximum Pb concentration has been observed in 2011 and 2014 (Fig. 8). Pb belongs to extremely persistent polluters that stay in the soil for a long period of time and reveal high toxicity in low concentrations. That is why and first of all the exceeding of regular Pb concentrations is related to its getting to the soil.

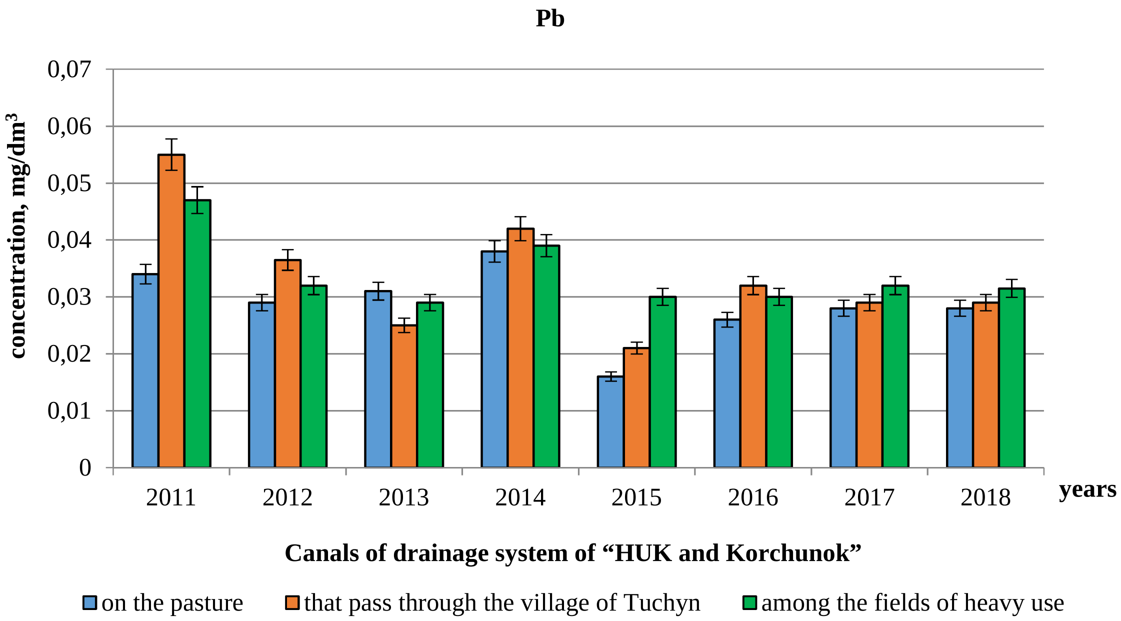

Fig. 8. Pb concentration in the water of canals of the drainage system of "HUK and Korchunok" on the pasture that pass through the village of Tuchyn and among the fields of heavy use (2011–2018)

In the water of the canals of the drainage system of "HUK and Korchunok" during the whole period of the research (2011–2018), Cd excess of MPC ($MPC(Cd)_{household\ purposes}$=0.001 mg/dm^3) was observed. In particular, in the water of the canals of the drainage system on the pasture, the minimum Cd concentration was 0.0014 mg/dm^3 (2017–2018), and the maximum one was 0.0037 mg/dm^3 (2014), which exceeds MPC 1.4–3.7 times. In the water of canals of the drainage system that passes through the village of Tuchyn, Cd concentration varied from 0.0011 mg/dm^3 (2017) to 0.0036 mg/dm^3 (2014), which exceeds MPC 1.1–3.6 times. In the water of the canals of the drainage system among the fields of heavy use, Cd concentration varied from 0.0012 mg/dm^3 (2012–2013) to 0.0034 mg/dm^3 (2014), which exceeds MPC 1.2–3.4 times (Fig. 9).

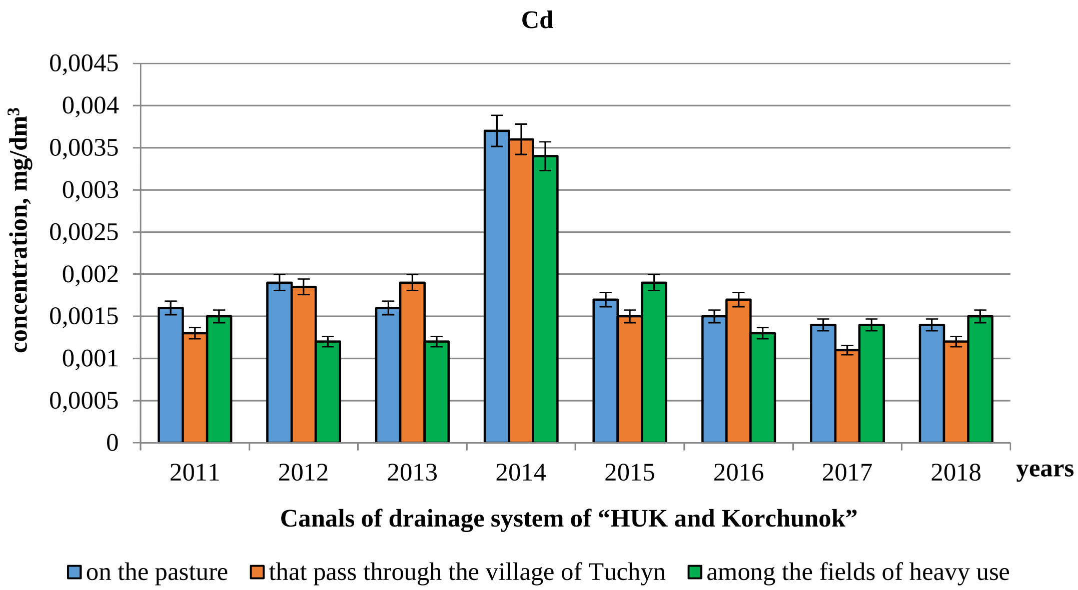

Fig. 9. Cd concentration in the water of the canals of the drainage system of "HUK and Korchunok" on the pasture that pass through the village of Tuchyn and among the fields of heavy use (2011–2018)

In the water of ponds and canals of the drainage system, Cd high concentrations are related to its getting from agricultural lands sewage. In particular, phosphate fertilizers that are applied to the soil contain high Cd concentrations. For example, 100g of superphosphate contains 720.2 µg of Cd (Floria, 2012). Uncontrolled fertilization causes the accumulation of Cd and other heavy metals in the soils and their following leaching to water objects. Also, Cadmium getting into water objects happens as a result of forest fires and straw burning in the fields. Wood ash contains from 2 to 30 mg/kg of Cd (Aronsson et al., 2004), and straw ash contains 10 mg/kg (Adrees et al., 2015; Hansen et al., 2001).

Wood ash is often added to the soil as a fertilizer and protection from diseases and pets. Ash alkaline reaction causes poor Cadmium absorption by the plants, and as a result, it accumulates in the soil and gets into the water objects (Adrees et al., 2015). Besides, the significant source of these territories' pollution with heavy metals is the active military training area. During the explosions of bombs (Cd, Cu, Pb), missiles (As, Ba, Cd, Cr, Cu, Fe, Ni, Pb, U, V, Zn), and training shootings (Cu), heavy metals get into the soils (Bordeleau et al., 2008) and reservoirs.

To reduce heavy metals concentration in ponds and canals of drainage systems, it is important to regulate fertilization and pesticides for all adjacent territories, arrange the landfills only at specially designated places, and also gradually move to electric cars. Besides, it is necessary to standardize algicidal fertilization regulating the number and algae biomass in ponds or rationally use fish fauna representatives with this aim. To increase the ecological value of water objects it is necessary to arrange a bioplateau using species that can accumulate and remove high concentrations of heavy metals. In general, it is possible to reduce the number of heavy metals in the soils and water objects using modern phytoremediation technologies.

4. Conclusions

In the ponds, the quality of water according to Pb and Cd concentration is not appropriate to permissible levels as it exceeds maximum permissible concentrations for the waters of agricultural and household purposes 1.2–1.6 and 1.1–3.8 times. In the ponds, the excess of the maximum permissible concentration of Cu, Zn and Pb 3.1–26 times, 1.7–11.5 times and 1.7–3.9 times was observed for fishery waters General concentration of heavy metals in the water of the ponds is as follows: "Staryi", "Novyi", and "Malyi" in the village of Tuchyn – Zn>Pb>Cu>Cd; in the village of Zhalianka – Pb>Zn >Cu>Cd.

In the water of the canals of the drainage system, the excess of Pb and Cd concentrations 1.3–1.8 and 1.1–3.7 times was revealed. The highest Pb concentrations are presented in the water of canals of the drainage system that pass through the village of Tuchyn, and Cd concentration is observed on the pasture. In the water of the canals of the drainage system, heavy metals concentration has changed in the following way: Zn>Pb>Cu>Cd (on the pasture); Pb>Zn>Cu>Cd (in the water of the canals of the drainage system that pass through the village of Tuchyn and among the fields of heavy use).

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