Science, Engineering & Education, 10, (1), 2025, 75-82

Ecological Monitoring of Soil and Groundwater Areas Around the "Stomana Industry" Plant

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Received 27 March 2025, Accepted 27 April 2025
DOI: 10.59957/see.v10.i1.2025.10

ABSTRACT

Most heavy metals are characterized by a certain accumulation in soil and plants. Recent studies have shown that heavy metals are already dangerous pollutants of the urban environment. Along with the main pollutants (dust, SO_X, NO_X, CO_X, halogens, etc. [6]), such metals are also continuously discharged into the environment. Heavy metals also tend to accumulate in the hydrosphere, especially in bottom sediments and in the biomass of existing inhabitants. The uncontrolled discharge of sludge from metallurgical and chemical industries also leads to dangerous pollution of the natural environment with heavy metals. In the ferrous metallurgical industry, in addition to the main products (cast iron, steel, ferroalloys), numerous waste products are also produced. They contain to a certain extent all the elements used in this industrial sector.

The purpose of the study is to present the state of the area, in terms of polluting elements, around the largest ferrous metallurgical enterprise in Bulgaria.

Keywords: heavy metals, soil and groundwater pollution, metallurgy.

INTRODUCTION

Effect of elements-pollutants from ferrous metallurgy on the human body

Increasing mortality from lung cancer has been periodically reported from hematite mines and iron foundries. When ingested, iron is potentially toxic in all forms. Free ferroions are toxic to capillary walls and the liver, causing shock and toxic hepatitis [1, 2].

Workers with manganese by dermal and inhalation routes take manganese compounds into their bodies. They cause stress on the immune system and compensatory processes [3]. Manganese and its salts are highly toxic substances with selective damage to the central nervous system. Damage can also occur in the parenchymal organs - kidneys, peripheral blood vessels, lungs, blood. It has an irritating effect on the respiratory tract [2, 4].

Chromium dust, mainly containing Cr, that has entered the atmosphere through inhalation has a negative effect on the lymphoid organs. This effect is most pronounced in the spleen. All chromium compounds are toxic. They are

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in the bones, bone marrow, nails, teeth, etc. In chromium poisoning, local damage to the upper and deeper respiratory tract predominates. Skin damage is manifested by the development of ulcers, dermatitis, and eczema. Frequent kidney damage is characteristic of chromium poisoning [3, 5].

Lead is a toxic element that accumulates in the body [2]. Water-soluble lead compounds can enter animals and humans through drinking water and cause several dangerous damages to bone marrow cells and even chromosomes [3]. Lead can accumulate in the aorta, liver, and kidneys. Lead crosses the blood-brain barrier and accumulates in the central nervous system. It accumulates in bones and teeth [7].

Once in the bloodstream, nickel is deposited in the liver, spleen, and kidneys [4]. Nickel dermatitis is common among workers. It can cause asthma. It has an extremely bad effect on the lungs and nasal sinuses. A high risk of laryngeal cancer has also been reported [1, 2].

Zinc is an important mineral and plays a vital role in protein synthesis and in the regulation of the production of cells of the human body's immune system. The recommended daily intake of zinc for men is 9 -15 mg, and for women - 7-13 mg. Acute toxicity is observed when more than 200 mg day^{-1} of zinc is ingested. This can lead to abdominal pain, vomiting, stomach irritation, headaches, irritability, dizziness. Chronic toxicity - prolonged intake of zinc from 50 to 150 mg day^{-1} can lead to Cu deficiency with accompanying symptoms of anemia, etc. [8, 9].

It is assumed that zinc and copper compete for absorption from the digestive tract, so a diet that excludes one of these minerals may lead to a deficiency of the other. There is no evidence of toxicity of pure copper. All copper compounds are poisonous. Once in the body, they cause vomiting. The normal amount of copper for an adult per day is about 0.9 mg [5, 10].

Daily ingestion of more than the required dose of arsenic leads to chronic arsenic intoxication, which leads to Alzheimer's, diabetes, or death. It can enter the liver, lungs, kidneys, spleen, and walls of the digestive tract. Some of the As, although more slowly, reaches the bones, hair, nails, and skin, where it remains permanently. The fatal lowest dose of As is estimated to be 70–180 mg. Chronic As poisoning manifests itself in skin diseases, gastrointestinal disorders, anemia, and various carcinomas [5, 10].

Brief description of the Stomana Industry plant

Since the beginning of the 1990s, the production of Stomana Industry has been completely reoriented to steelmaking using the electric arc method from metal scrap. Today, the plant operates an electric steelmaking workshop in continuous production mode. Next to it is a fully covered scrap workshop with a shredder installation unique for the region. The facility is a scrap separation and sorting installation with a capacity of 200 t h^{-1}. The main production facilities of Stomana Industry also include a workshop for sheet products and a long-rolling workshop. The workshop to produce steel spheres is also periodically included in the production. The plant also includes a workshop for cold-rolled steel, drawing and pressing lines, and a forming line. The largest project implemented in the recent history of Stomana Industry is the new rolling workshop for long products such as reinforcing bars, long-rolled products, circles and wire rod.

EXPERIMENTAL

Location of monitoring points around the Stomana Industry plant for soil condition

The large capacity of the company also requires mandatory monitoring of the state of the environment in and around the production areas. Below is presented and analysed the state of the soil and groundwater in several points around the plant, and their chemical composition is tracked, according to the main polluting elements most often generated by ferrous metallurgy.

For effective study of the state of the soil, a total of four monitoring points has been created, the coordinates of which are presented in Table 1.

The presented points are in accordance with the requirements of Regulation No. 6 / 27.08.2013 [12]. Soil samples were taken from them, on which a chemical analysis was performed, and the results are presented schematically in Fig. 1 - 7, where the maximum permissible concentrations (MPC) are also indicated, according to Regulation No. 3/01.08.2008, Art. 3, on norms for permissible content of harmful substances in soil [13]. The samples are from soil located at 0.00 to 0.10 m and from 0.10 to 0.40 m below the ground surface [11]. The studies were carried out in November 2017 (for the elements Cr, Ni, Cu, Zn, Pb, As, Fe) and December 2020 (for the elements Zn, Pb, As), respectively by the accredited Laboratory for Ecology and Technical Testing "Aquaterratest" and an accredited laboratory at the General Directorate for Environment in the Republic of Bulgaria [11]. The studies were carried out using the aqua regia method, in accordance with the BSS EN 13346:2003 standard, as well as subsequent spectrometric analysis [13].

Location of monitoring points around the Stomana Industry plant for the state of groundwater

Regarding the study of the state of groundwater, four monitoring points have also been established, the coordinates of which are presented in Table 2.

The presented points are in accordance with the requirements of Regulation No. 6 / 27.08.2013. Water samples were taken from them, which were subjected to chemical analysis, and the results are schematically presented in Fig. 8 - 15, where the maximum permissible concentrations (MPC) according to Regulation No. 1/10.10.2007 (amended and supplemented on 23.12.2016) for the study, use and protection of groundwater, Appendix 1 [14] are also indicated. The samples are from groundwater located at 0.00 to 9.90 m below the ground surface. They were taken and examined by an accredited Laboratory for Ecology and Technical Testing "Aquaterratest", Sofia in January 2017, as well

Table 1. Location of control points when monitoring soil condition.

Monitoring point	Geographic coordinates
TP 100	N 42°35'19.68274" E 23°05'23.19239"
TP 200	N 42°35'37.52511" E 23°05'31.66856"
TP 300	N 42°35'29.72144" E 23°05'20.02886"
TP 400	N 42°35'30.07954" E 23°05'31.70503"

Table 2. Location of control points when monitoring the state of groundwater.

Monitoring point	Geographic coordinates
MP 1	N 42°35'37.90" E 23°05'31.67"
MP 2	N 42°35'29.95" E 23°05'31.65"
MP 3	N 42°35'19.69" E 23°05'23.38"
MP 4	N 42°35'29.59" E 23°05'20.07"

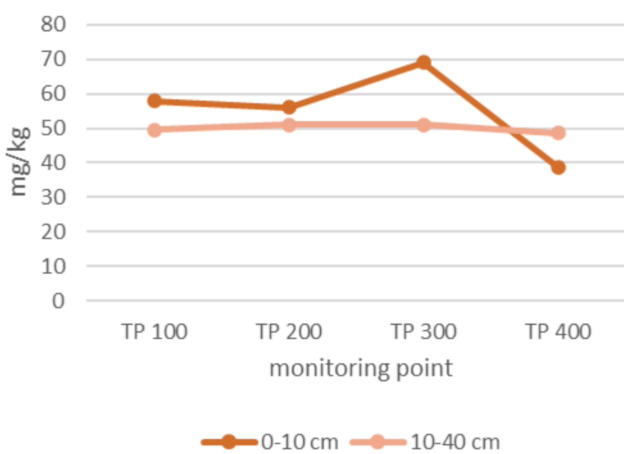

Fig. 1. Chromium content, 2017 year, MPC - 300 mg kg^{-1} soil.

as by an accredited laboratory at the General Directorate for Environment in the Republic of Bulgaria in November 2017 [11].

The locations of the monitoring points, both for soil and groundwater, are linked to the national grid in the WGS 84-BL system.

RESULTS AND DISCUSSION

Results of the analysis of soil samples from the monitoring points

All soil samples taken were analysed by a specialized laboratory [11] in compliance with the requirements of Regulation No. 3/01.08.2008.

The diagrams (Fig. 1 - 7) show that chromium, nickel, copper and iron retain a constant and relatively unchanging nature of presence in the soil around Stomana Industry. They are within the permissible limits for both studied layers. In the upper soil layer (from 0.00 m to 0.10 m) zinc and lead are in the permissible concentrations according to the regulation. At point TP 400, their values in 2020 are about, respectively, 202 % and 183 % higher than their concentration at the same monitoring point in 2017, while at the other points they are without sharp fluctuations. At the same point and the same soil layer, arsenic has a similar behaviour, with its content increased by about 259 % compared to 2017. But at point TP 200 in 2017 and 2020 it is, respectively, 42.7 mg kg^{-1} and 44.1 mg kg^{-1} soil for the layer from 0.00 to 0.10 m and 46.2 mg kg^{-1} and 46.3 mg kg^{-1} soil for the layer from 0.10 to 0.40 m.

Results of the analysis of water samples from the monitoring points

All water samples taken were analysed by a specialized laboratory in compliance with the requirements of Regulation No. 1/10.10.2007 [11].

In the groundwater around Stomana Industry (Fig. 8 - 15), the elements copper, zinc and arsenic are within the norm. In the studies at the beginning of 2017, zinc in two of the four monitoring points -MP 2 and MP 4 was more than twice as high as in the other two points. The

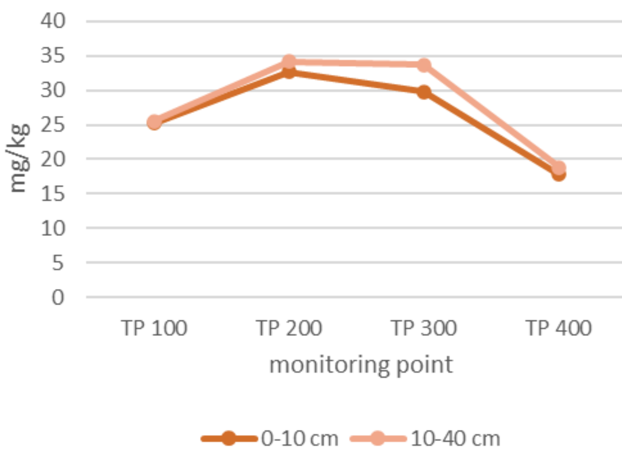

Fig. 2. Nickel content, 2017 year, MPC - 250 mg kg^{-1} soil.

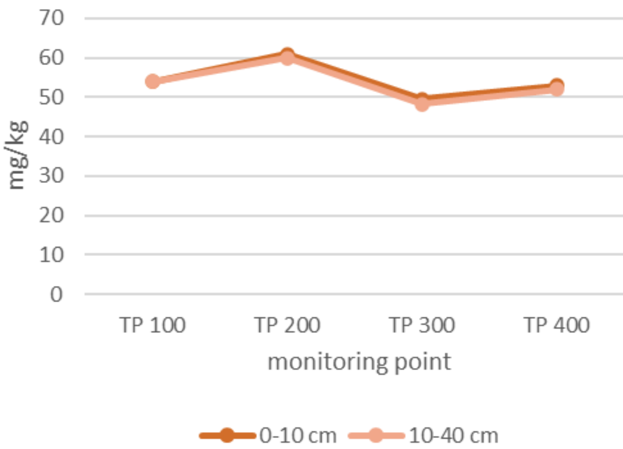

Fig. 3. Copper content, 2017 year, MPC - 500 mg kg^{-1} soil.

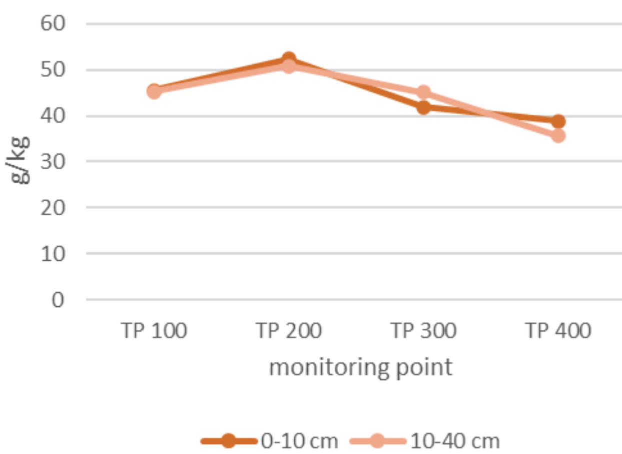

Fig. 4. Iron content, 2017 year, g kg^{-1} soil, MPC - not regulated.

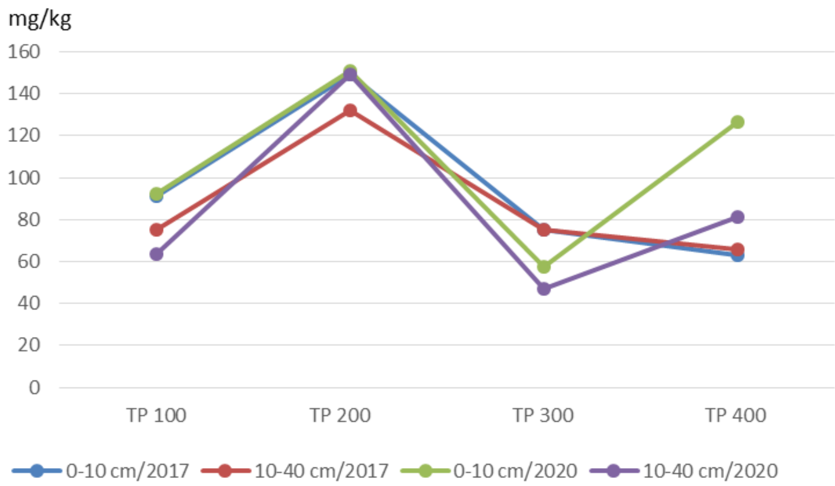

Fig. 5. Zinc content, 2017 and 2020 year, MPC - 600 mg kg^{-1} soil.

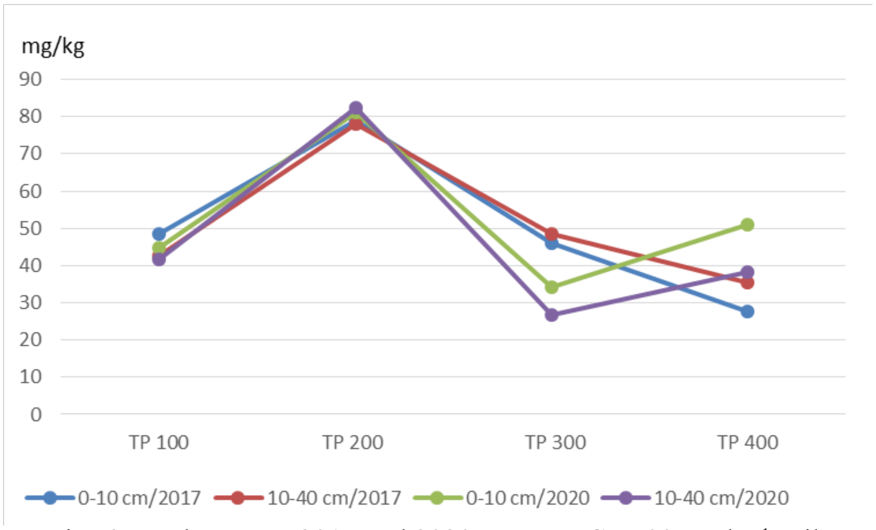

Fig. 6. Lead content, 2017 and 2020 year, MPC - 500 mg kg^{-1} soil.

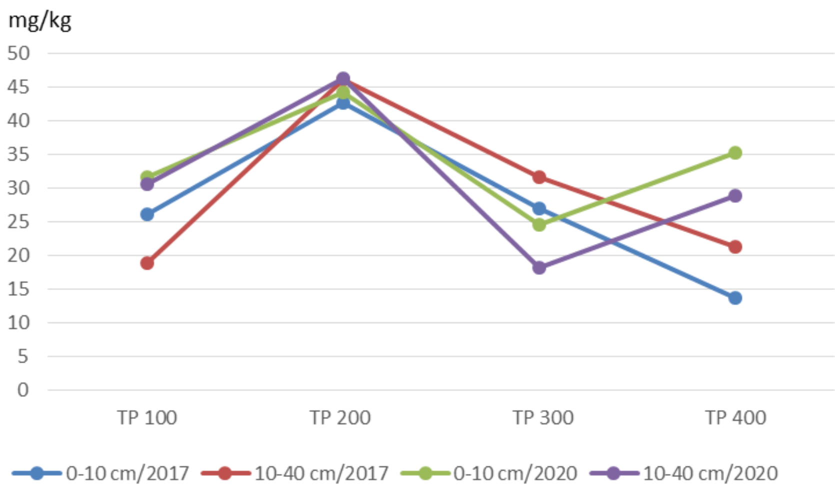

Fig. 7. Arsenic content, 2017 and 2020 year, MPC - 40 mg kg^{-1} soil.

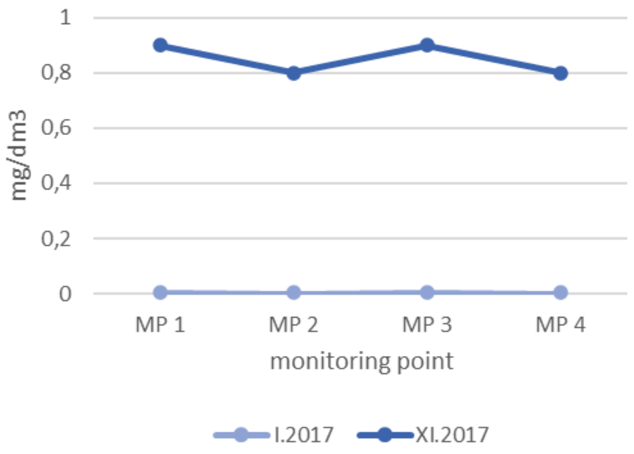

Fig. 8. Chromium content, MPC - 0.05 mg dm^{-3}.

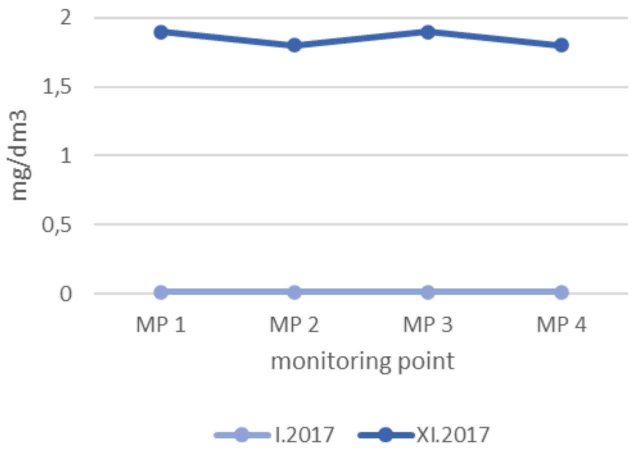

Fig. 9. Nickel content, MPC - 0.02 mg dm^{-3}.

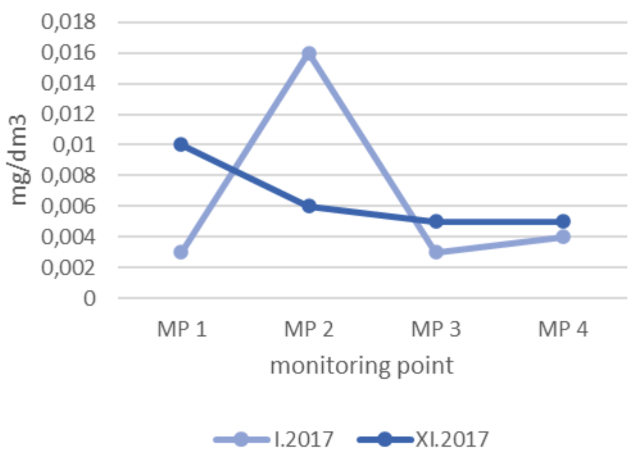

Fig. 10. Copper content, MPC - 0.2 mg dm^{-3}.

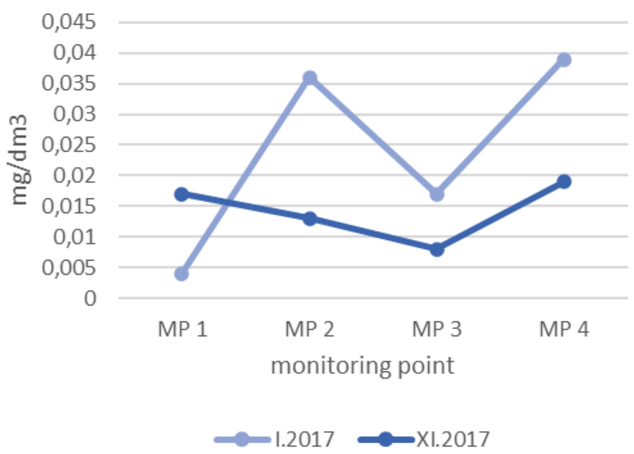

Fig. 11. Zinc content, MPC - 1.00 mg dm^{-3}.

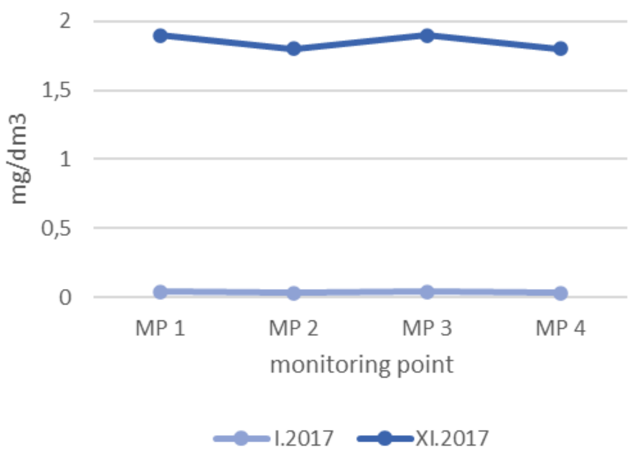

Fig. 12. Lead content, MPC - 0.01 mg dm^{-3}.

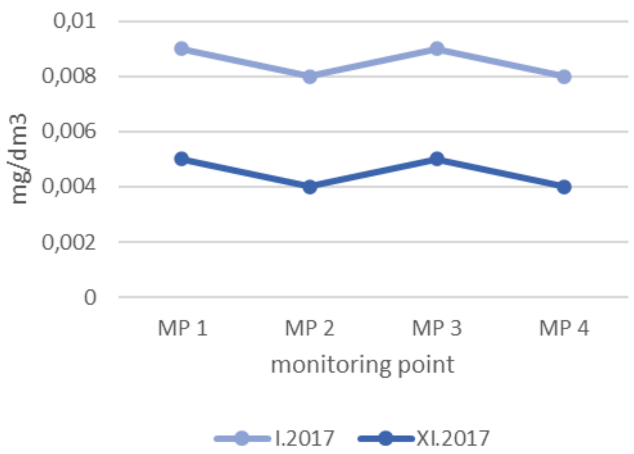

Fig. 13. Arsenic content, MPC - 0.01 mg dm^{-3}.

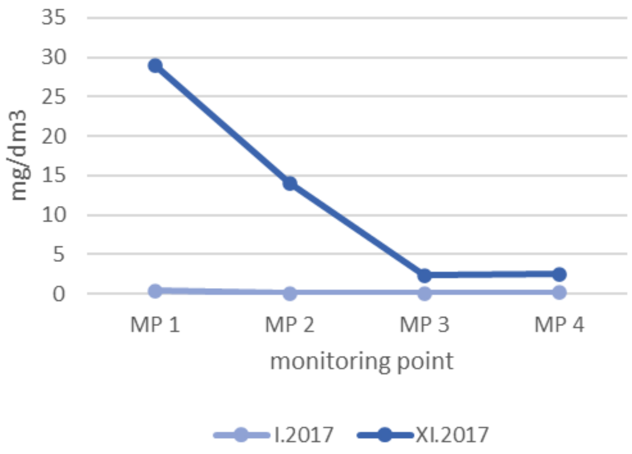

Fig. 14. Manganese content, MPC - 0.05 mg dm^{-3}.

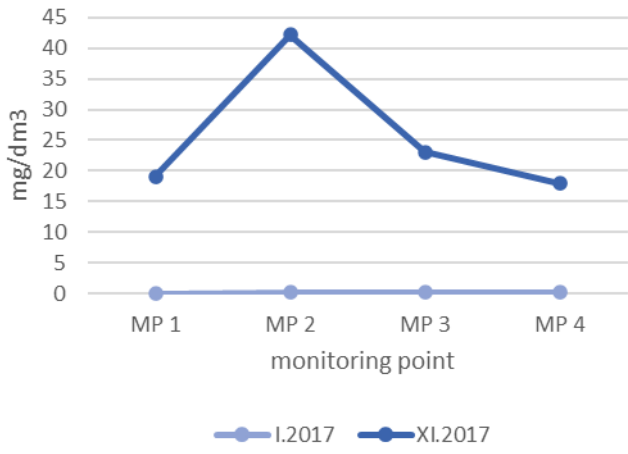

Fig. 15. The content of petroleum products, MPC - 0.05 mg dm^{-3}.

measured values at the four points towards the end of the year for nickel and lead were in the range of 1.5 to 2.0 mg dm^{-3}, which is significantly above the MPC. The data for chromium are in a similar range. At point MP 1, the manganese content was increased above the permissible concentration - nearly 600 times. Manganese is also outside the permissible values at point MP 2, where an increase of about 300 times compared to the limit quantity was observed. It is very worrying that at all four monitoring points, the content of petroleum products is above the maximum permissible concentration, especially at point MP 2. There the increase is over 800 times.

CONCLUSIONS

As a result of the study conducted regarding the soil around Stomana Industry, the following conclusions can be drawn:

- The zinc and lead content, although within acceptable limits, in one of the points have greatly increased concentrations compared to the study at the point three years earlier.
- At point TP 200, arsenic in both studied soil layers is above the maximum permissible concentration, respectively by an average of over 8% and over 15%, as this was observed in both years of study - 2017 and 2020.
- The remaining trace elements-pollutants are within normal limits.

There is also a certain excessive pollution in groundwater, expressed in the following conclusions:

- According to the presented chemical analysis, the concentrations of chromium, nickel and lead do not comply with the requirements of Regulation No. 1.
- Manganese levels are increased hundreds of times in half of the points for measuring the state of groundwater, but according to [15] this is likely due to the qualities of the natural background of groundwater.
- Very high pollution with petroleum products is found in all study sites.

In accordance with the above, it can be said that there are probably technological gaps, leading to undesirable levels of some of the studied elements in the soil and groundwater zones in the area of the Stomana Industry plant. For some of them, the natural background at the monitoring points also has an impact. Environmental studies should not be interrupted, and investments should be made in more effective purification facilities.

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