

Effect of heavy metals on soil and crop pollution in Ukraine – a review

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ABSTRACT

The presented review discusses current situation with heavy metal pollution in the various regions of Ukraine and possible pollution of important crop. It is suggested that violent conflict of 2022 in Ukraine may cause development of polluted areas with Pb, Ni, Cr, Cu. Especially such tendency is dangerous for Ukrainian regions with high level of heavy metals level where is military conflict was in an active phase: Donetsk, Zaporizhia, Kyiv, Lugansk, Sumy, Kharkiv, Kherson, Chernihiv, Mykolaiv, Zhytomyr, Dnipropetrovsk, and Odessa regions. The analysis of monitoring data related heavy metals pollution has been described in regions of Ukraine. Current characteristics of major crop production areas in Ukraine regarding their possible yield production and presence of heavy metals in the soil are presented. Near 70% of planted areas for major exported plants in the areas of conflict may be under additional increased effects of heavy metals. The wheat, corn, barley, rapeseed, sunflower have been presented and discussed their cultivation potential as major crops in Ukraine. It is recommended to use modern technologies of phytoremediation with use crop rotation of plants hyperaccumulators of heavy metals at these areas afterword's.

Keywords: heavy metal pollution, phytoremediation, major crops, Ukraine

INTRODUCTION

Nowadays many scientists try to explore impacts of heavy metal contamination on agriculture range from the agricultural soil to the crop production. The presented review explores the current situation with heavy metal pollution in the various regions of Ukraine and complex linkages between heavy metals effects, agricultural production, and possible conflict onset, by focusing on the current conflict situation in Ukraine. Vasco et al. (2021) have been hypothesized that spatial differences in crop production within countries are a relevant factor in shaping the impact of climate variability on conflict in agriculturally - dependent countries. It was shown that the negative impacts of climate variability lead to an increase in the spatial concentration of agricultural production within countries. In turn, the combined effect

of climate extremes and crop production concentration increases the predicted probability of conflict onset by up to 14% in agriculturally dependent countries (Vasco et al., 2021).

Ukraine has six primary products with over a billion dollars in export sales: corn, sunflower seed, wheat, rapeseed, barley and sunflower meal. Ukraine and Russia account for more than 30% of world trade in wheat (Nykolyuk et al., 2021, FAO, 2022). EU countries will not only be affected by the halt in wheat imports from Ukraine, the meat and dairy industries are also poised to take a hit, as Ukrainian maize is essential for livestock feed, on top of the hike in prices caused by the reliance on Russian gas and fertilizers. Some of the main wheat importers from Ukraine are Egypt, Ethiopia, Yemen, Lebanon, Palestine, Israel etc. Vulnerable countries such as war-torn Yemen

look set to suffer the most from Ukrainian food exports halting in the aftermath of the Russian invasion (Leiva, 2022).

It is known strong effect of Chernobyl accident in 1986 on the heavy metal and radioactivity pollution in the different parts of Ukraine (Beresford et al., 2016). Nowadays scientists are still searching for the ways to eliminate it (Sytar and Prasad, 2016). Since 1998, European countries have aimed at supporting the policy of reducing heavy metals emissions and have already achieved significant results. Heavy metals are dangerous through possible involvement in carcinogenic, immunological, and reproductive effects, and due to long-range trans-boundary air pollution, this problem cannot be regarded as local. Accumulation of heavy metals in the reproductive organs of plants worsens their fertility, which is fraught with economic and environmental decline in a particular region. Furthermore, it can subsequently occur in the food chain because of specific effect on the plant quality and productivity (Taran et al., 2020).

It is a constant increase in heavy metal contamination around regions with aggressive and violent behaviors (Anyanwu et al., 2018). Warfare is associated with significant heavy metal contamination of the environment, due to destruction of built infrastructure and consequent release of heavy metals and direct contamination from exploded ordnance and leakage from unexploded ordnance (Bazzi et al., 2020). Therefore, the aim of current review was to highlight situation with heavy metals contamination and how violent conflict may affect cultivation of important crop plants in Ukraine which are directly connected with accessibility and quality of food resources in the world.

NATURAL AND ANTROPOGENIC SOURCES OF HEAVY METALS (HM) IN SOIL

In the natural ecosystems water, soil, and rocks are main sources of heavy metals. Heavy metals are existing in the Earth's crust (Fru et al., 2016). Due to volcanic eruptions, soil and rock erosion, industrial human activities such as petroleum combustion and coal burning the heavy metals content in the ecosystem is continuously

increased (Tchounwou et al., 2012; Pal et al., 2017). So destroyed ecosystem is unbalanced and may have different functions with increased level of heavy metals.

It is known about high contents of Pb and Hg [Mercury(II) fulminate] in the explosives harbour (Navy U. S., 2008; Gebka et al., 2016). In the production of missiles, gun barrels, coat bullets and military vehicles are used such heavy metals as Zn, Cu, Ni, Pb, and Cr (Audino, 2006; Casey, 2009, Barker et al., 2021). Ba, Sb, and B are weapon main compounds (Fitchett, 2019). Due to the high density (19.3 g/cm³) of W is used for kinetic bombardment (Rowlatt, 2014). In general, the use of heavy metals in weapons has raised since the end of World War II (Gebka et al., 2016).

Metal emissions may differ depending on the type of ammunition. For example, significant emission of Cu and Zn may occur from firing with NM229 containing a steel core results. At the same time, high quantity of Pb particles is produced by SS109 with soft lead core (Mariussen et al., 2021). In a significant emission of particulate matter consisting predominantly of Cu, Zn, and Fe take part firing lead-free small-calibre ammunition (Wingfors et al., 2014).

Regarding all these previous data analyses it was concluded that military activity results in soil contamination with Pb, Cu, Cd, Sb, Cr, Ni, Zn. Bio-monitoring studies have demonstrated increased metals accumulation in biological organisms. Metals mediate adverse effects in military personnel and exposed civilian population (Skalny et al., 2021).

ENVIRONMENTAL POLLUTION WITH HM

The impacts of high concentrations of heavy metals on agricultural production are well established in the scientific literature (Sytar et al., 2013, 2019, 2021). The monitoring of heavy metal pollution in soil in Ukraine based on the available literature of national and international scientific reports was presented (Sytar and Prasad, 2016).

ICP-OES was used for the analysis of metal concentration in the soils. For example, elemental and

thermo-gravimetric measurements of heavy metals in soils and leaves were used as bio-indicators of pollution in Kyiv City (Tarik et al., 2021). It was observed that some leaf and soil samples shown similar level of essential mineral elements and metals. In other samples the concentrations of metals were different. The concentration of metals was found to be higher in soil samples than in leaves. Thermo-gravimetric analysis (TGA) data helped to further characterize both types of samples. The metal removal during the incineration of the leaves was studied by coupling a thermo-gravimetric analyzer to an inductively coupled plasma optical emission spectrometer (TGA-ICP-OES). The dispensation of Cd, K, Na, Pb, and Zn during incineration at temperatures up to 960 °C was online monitored, and some insights were discovered about the behavior of such metals and the chemistry implicated in the volatilization process (Tarik et al., 2021). At the same time, in the other monitoring studies the mobile forms of Cd, Cu, Pb and Zn were determined in ammonium acetate buffer extract by atomic absorption spectrometry (Maksimtsev et al., 2021).

The monitoring analysis shows Pb, Cr, and Cu are dominant contaminants/pollutants in soil. In Ukraine the regions of Kharkiv, Zaporizhia, Donetsk, and Chernivtsi show a high level of Cr due to their high concentration of industries. In many areas of Ukrainian territory, the content of Ni, Zn, and Co in the soil is at less than maximal permissible level (Syta and Prasad, 2016). Research in 2020 by Czech and Ukrainian ecologists found increased levels of heavy metals in the rivers and soils of Pavlograd city, Dnipropetrovsk region (Kharytonov et al., 2020). The Ukrainian Carpathians are also have a significant air pollution caused by emissions from numerous industries. In the Ivano-Frankivsk region, Cd and Mo accumulate in forest soils; Cr, Mo and Zn soil concentrations are higher than their limit levels; and Pb concentrations exceed toxic levels close to industrial areas (10% of the region territory) (Shparyk and Parpan, 2004).

Recently, crop rotation in the right-bank Forest-Steppe of Ukraine also includes milk thistle, the vegetative mass, and seeds used mainly as medicinal raw materials (Devi, 2019; Bhattacharya, 2020). It is known that milk thistle

actively accumulates heavy metals, which helps to reduce their concentration in soils. It was found that the content of Pb, Cd, Zn, and Cu in the vegetative mass of milk thistle when grown on gray forest soils in the right-bank forest-steppe of Ukraine (Vinnitsya region) was 6.2 mg/kg, 1.25 mg/kg, 32.5 mg/kg, and 12.0 mg/kg, respectively. The high accumulation of heavy metals by milk thistle had a positive effect on the removal of Pb, Cd, Zn, and Cu due to phytoremediation (Razanov et al., 2021).

Although direct data on the role of metal overexposure in military-related plant and human hazards are still limited, the existing evidence of metal overexposure upon military activities along with demonstrated metal toxicity are indicative of significant contribution of metals to adverse decrease in crop production associated with military activity. The geochemical properties of heavy metal-contaminated soils from a Korean military shooting range were analyzed. All soils were strongly contaminated with Pb with minor concentrations of Cu, Ni, Cd, and Zn. Arsenic was rarely detected. The obtained results are indicated that the soils from the shooting range are contaminated with heavy metals and have evidence of different degree of anthropogenic sources of Pb (Moon et al., 2021).

Syta and Prasad (2016) presented situation of Pb pollution in Ukraine where Kyiv, Chernihiv, Sumy and Zhytomyr were regions in Ukraine with level of Pb in the soil more than 20kg per hectare. Kherson, Kharkiv, Lugansk, Mykolaiv, Zaporizhia regions were characterized by average level of Pb (more than 10 kg per hectare) (Syta and Prasad, 2016). It is known that after Chernobyl accident such areas are still sensitive and recovering of ecosystems take time. After such military conflict in these regions of Ukraine 2022 we supposed significant increase of Pb level in the soils of these regions. The period of heavy metal removal from soil is near 740 to 5900 years (for example, cadmium and lead) (Dobrovolsky, 1997).

The greatest Ni content found in soils of the regions of Zhytomyr, Kyiv, Zaporizhia Donetsk, and Lugansk (in the soil 25-50 mg/kg when maximal permissible level 50 mg/kg). At these regions it was possible to get relatively safe crops with tolerance to Ni but in limited quantities.

HEAVY METAL POLLUTION IN CROP PRODUCTION

High level of copper found in Kyiv, Chernihiv, Zhytomyr, Volyn, Zakarpatiya regions. Chernivtsi, Kharkiv, Donetsk and Zaporizhya regions has been characterized high level of Cr (Sytar and Prasad, 2016). In the situation during and after military conflict in these Ukrainian regions special crop rotation agricultural treatment during two years with plant hyperaccumulators of heavy metals may be needed (Sytar et al., 2016).

Crop-level adaptation and technological innovation can moderate losses to some extent (Rosenzweig and Parry, 1994) but adaptive capacity is projected to be exceeded in regions under military conflicts because of higher temperature and higher heavy metal concentrations. Current characteristics of major crop production areas in Ukraine regarding their possible yield production and presence of heavy metals in the soil are presented in Table 1.

Table 1. Characteristics of main crop production areas under military conflict in Ukraine (2022) regarding their possible yield production and possible heavy metals contamination (State Statistics Service of Ukraine (2021), Sytar and Prasad (2016), Kharytonov et al. (2020))

Crop type	Planted area under the harvest in 2021 under military conflict in 2022	Possible areas under conflict influence (thsd.ha)	Harvesting of wheat as of 01 December 2021 (yield, quintal per ha of the harvested area)	High level of heavy metals	Average level of heavy metals
Wheat	Donetsk region	381.1	40.6	Pb, Ni, Cr	
	Zaporizhia region	709.3	38.8	Cr	Pb, Ni
	Kyiv region	207.5	52.6	Pb, Ni, Cu	
	Lugansk region	279.5	39.2	Ni	Pb
	Sumy region	195.5	48.2	Pb	Ni
	Kharkiv region	587.5	48.6	Cr, Ni	Pb
	Kherson region	502.6	42.5	-	Pb
	Chernihiv region	187.7	51.6	Cu, Pb	Ni
	Mykolaiv region	479.0	42.3	-	Pb
	Zhytomyr region	169.5	49.6	Ni, Pb, Cu	
	Dnipropetrovsk region	559.8	44.1	-	Cd, Ni, Pb, Cu
	Odessa region	675.4	40.5	-	-
Corn	Donetsk region	55.8	44.3	Pb, Ni, Cr	
	Zaporizhia region	36.2	75.1	Cr	Pb, Ni
	Kyiv region	345.9	95.2	Pb, Ni, Cu	
	Lugansk region	55.8	29.1	Ni	Pb
	Sumy region	461.4	72.8	Pb	Ni
	Kharkiv region	286.5	52.8	Cr, Ni	Pb
	Kherson region	58.8	90.7	-	Pb
	Chernihiv region	568.9	95.2	Cu, Pb	Ni
	Mykolaiv region	121.9	50.7	-	Pb
	Zhytomyr region	279.4	92.0	Ni, Pb, Cu	
	Dnipropetrovsk region	303.5	51.7	-	Cd, Ni, Pb, Cu
	Odessa region	137.6	62.7	-	-

Continued. Table 1

Crop type	Planted area under the harvest in 2021 under military conflict in 2022	Possible areas under conflict influence (thsd.ha)	Harvesting of wheat as of 01 December 2021 (yield, quintal per ha of the harvested area)	High level of heavy metals	Average level of heavy metals
Barley	Donetsk region	117.0	30.5	Pb, Ni, Cr	
	Zaporizhia region	195.0	34.8	Cr	Pb, Ni
	Kyiv region	70.6	42.4	Pb, Ni, Cu	
	Lugansk region	41.1	28.4	Ni	Pb
	Sumy region	33.9	39.8	Pb	Ni
	Kharkiv region	136.3	37.5	Cr, Ni	Pb
	Kherson region	209.7	40.2	-	Pb
	Chernihiv region	21.3	41.9	Cu, Pb	Ni
	Mykolaiv region	308.6	37.8	-	Pb
	Zhytomyr region	31.8	40.7	Ni, Pb, Cu	
	Dnipropetrovsk region	250.0	33.0	-	Cd, Ni, Pb, Cu
Odessa region	371.9	42.0	-	-	
Rapeseed	Donetsk region	5.3	16.9	Pb, Ni, Cr	
	Zaporizhia region	73.1	24.7	Cr	Pb, Ni
	Kyiv region	33.3	31.0	Pb, Ni, Cu	
	Lugansk region	-	-	Ni	Pb
	Sumy region	22.2	32.2	Pb	Ni
	Kharkiv region	3.7	23.3	Cr, Ni	Pb
	Kherson region	95.3	26.0	-	Pb
	Chernihiv region	34.5	33.8	Cu, Pb	Ni
	Mykolaiv region	62.2	26.1	-	Pb
	Zhytomyr region	41.0	28.0	Ni, Pb, Cu	
	Dnipropetrovsk region	84.0	23.6	-	Cd, Ni, Pb, Cu
Odessa region	118.7	25.3	-	-	
Sunflower seeds	Donetsk region	360.3	22.2	Pb, Ni, Cr	
	Zaporizhia region	532.5	19.9	Cr	Pb, Ni
	Kyiv region	200.9	31.2	Pb, Ni, Cu	
	Lugansk region	400.2	18.9	Ni	Pb
	Sumy region	265.6	30.9	Pb	Ni
	Kharkiv region	573.3	24.9	Cr, Ni	Pb
	Kherson region	345.0	19.5	-	Pb
	Chernihiv region	240.4	30.9	Cu, Pb	Ni
	Mykolaiv region	495.1	22.7	-	Pb
	Zhytomyr region	147.1	24.7	Ni, Pb, Cu	
	Dnipropetrovsk region	598.1	23.4	-	Cd, Ni, Pb, Cu
Odessa region	404.8	23.5	-	-	

* Data exclude the temporarily occupied territory of the Autonomous Republic of Crimea, the city of Sevastopol and a part of temporarily occupied territories in the Donetsk and Luhansk regions

For March 2022 near 70% of planted area under the wheat harvest, 50% of corn planted area, 70% of barley planted area, 43% of rapeseed planted area and near 70% of sunflower seeds planted area in Ukraine may be affected by military conflict (State Statistics Service of Ukraine, 2021).

The increased level of Pb, Ni, Cr may show detrimental effects towards plant growth and yield (Okereafor et al., 2020). For example, Pb, Cd, Cr and Co during a study were observed to be responsible for the poor growth of corn plants (*Zea mays* L.) (Ghani, 2010). At extreme levels, toxic metals could result in oxidative stress in plants, mutilation of cell structure through the substitution of deficient elements with toxic metals and slow down photosynthetic processes in plant cells (Sytar et al., 2016). Pb exerts detrimental effects on the morphology, growth and photosynthetic processes of corn and wheat plants through interference with vital enzymes, thus inhibiting seed germination (Hussain et al., 2013). Cd in the wheat decline seed germination and support reduction in nutrient content of plant (Yourtchi et al., 2013). Cr is stunted shoot and root growth of wheat (Panda and Patra, 2000). Ni support reduction in acquisition of wheat plant nutrient (Barsukova and Gamzikova, 1999).

Therefore, it is important to plan ways of mitigation of negative effects of possible increase heavy metals concentrations in the soils of described regions via use in the future crop rotation techniques with crop plants with remediation potential for selected heavy metals.

CONCLUSION

Due presented data and their analysis is clear that current military conflict may influence increase of heavy metals in the air, water, and soil. Especially such tendency is dangerous for Ukrainian regions with high level of heavy metals. Near 70% of planted areas for major exported plants under military invasion effects which may cause increase of heavy metals in the soil. As result can be significant decrease of yield in the major exported crops such as wheat, corn, barley, rapeseed, and sunflower seed. It should be developed and used modern technologies of phytoremediation with use crop rotation of plants hyperaccumulators of heavy metals at these areas.

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