Introduction

Metals are significant environmental pollutants, and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons Nagajyoti [1]; Bieby Voijant Tangahu [2]; Mamatha [3]; Metals, such as cadmium, copper, lead, nickel, cobalt and mercury are major environmental pollutants, particularly in areas with high anthropogenic pressure. Metal accumulation in soils and plants is of concern in agricultural production due to the adverse effects on food safety and marketability, crop growth due to phytotoxicity, and environmental health of soil organisms. The influence of plants and their metabolic activities affects the geological and biological redistribution of heavy metals through pollution of the air, water and soil Nagajyoti [1]; Gyuricza [4] Anthropogenic metals contamination of ecosystems as a result of the application of industrial, transport, agrarian and other technologies causes a damage of the functioning of plants as an important component in ecosystem Bradl[5]; Alloway [6]; Kabata-Pendias [7] Often plants are the main accumulator of metals in polluted ecosystem. In the same time, plants play an important role in ecosystem as biomass producers and as biodiversity creators Rombke [8]; Kabata-Pendias [7]; Sardar [9]. Usually phytotoxicity is considered as a harmful influence of metal on plant growth and development Kabata Pendias [7]; Nagajyoti [1]; Satpathy[10]; Gill [11]. However, the setting of a safe level of toxicant for the plant is also very important, because it can help to prevent and to control then negative effects of metals in the ecosystem. Today a methodology that would determine the safe concentration of metals directly for plants in the soil is absent. After all, the existing standards for the content of metals in environmental objects are sanitary-hygienic and focused just on human health Lewis [12]; Smirnov [13]; Warne [14]. Determination of the metals safe level in the soil for plants can help to objectively assess state of the ecosystem and prevent the metals dangerous influence on plant Ryzhenko [15]. The Phyto Maximum Allowable Concentration (PMAC) was suggested as safe level of metal in the soil for plants.
and calcareous deep chernozem on loamy loess (chernozem). Sod podzolic soil has the following physicochemical characteristics: pHsalt 5.5; organic matter by Turin 0.87%; CEC 6.3 mg eqv/100 g. Chernozem soil has the following: pH 6.2, organic matter by Turin 2.89%; CEC 27.1 mg eqv/100 g. Background concentration of metals in soil (1 M HCl, mg kg⁻¹) was: Cd - 0.1; Pb - 0.3; Cu - 0.92; Zn - 2.4; Ni - 1.1; Co - 1.5 (sod podzolic); Cd - 0.11; Pb - 0.32; Cu - 2.6; Zn - 5.3; Ni - 2.3; Co - 2.5 (chernozem). Studied trace elements: Cd, Pb, Zn, Cu, Co, Ni were applied separately in amount equal to the following concentration in the soils (Table 1).

### Table 1: Scheme of Experiment.

<table>
<thead>
<tr>
<th>Control (no HM application)</th>
<th>Cu²⁺</th>
<th>Zn²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 mg kg⁻¹ of the soils</td>
<td>600 mg kg⁻¹ of the soils</td>
<td></td>
</tr>
<tr>
<td>150 mg kg⁻¹ of the soils</td>
<td>900 mg kg⁻¹ of the soils</td>
<td></td>
</tr>
<tr>
<td>200 mg kg⁻¹ of the soils</td>
<td>1200 mg kg⁻¹ of the soils</td>
<td></td>
</tr>
<tr>
<td>300 mg kg⁻¹ of the soils</td>
<td>1500 mg kg⁻¹ of the soils</td>
<td></td>
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</tbody>
</table>

That amount corresponds with adopted in Ukraine Maximum Allowed Concentration (MAC) in soil [Medvedev [16]]. The following metals salts: Pb(NO₃)₂, ZnSO₄, H₂O, CuSO₄·7H₂O, CdSO₄·H₂O, NiSO₄·6H₂O, CoSO₄·7H₂O were used for the trace elements application. The investigation was conducted in green house conditions. Plants grew in plastic Mitcherlik’s pots. Soil preparation, pots filling, and trials were carried out in accordance with standard methodic Dospokhov [17]; Medvedev [16]. The metals were added to soil during soil preparation before filling the pots. Then, spring barley germinated seeds were planted into the pots and, in the stage of 3 leaves, the recommended population was established. The studied elements were extracted by 1 M HCl from the soils. The method of HM determination was thin layer chromatography (TLC). Method widely was used in our previous investigation and officially recognized in Ukraine Kavetsky [18].

### Results and Discussion

In this study, the algorithm of calculation of PMAC was proposed similar to the existing approach of calculation of Maximum Allowable Toxic Concentration (MATC) (equation 1) Rand [19]. In the toxicology practice, the scheme to substance toxicity assessment using the LOEC and NOEC is quite effective and widely used Smirnov [12]; Warne [13] Environment Canada. Guidance document on statistical methods for Environmental Toxicity Tests [20]; Globally Harmonized System of Classification and Labeling of Chemicals (GHS), fourth revised version [21]. These indicators are used also for calculate the Maximum Allowable Toxic Concentration (MATC) on behalf of assessing the toxicity of substances in the aquatic environment. MATC is calculated by the formula Rand [19]:

\[
\text{MATC} = \sqrt{\text{NOEC} \times \text{LOEC}}
\]

where NOEC is No Observed Effect Concentration;

LOEC is Lowest Observed Effect Concentration.

We propose to determine the Phyto Maximum Allowable Concentration by the formula:

\[
\text{PMAC} = \sqrt{C_{\text{contr}} \times (\text{PhLD}_5 \text{Contr} - \text{PhLD}_5 \text{Background})}
\]

where \(C_{\text{contr}}\) - background concentration (on the control variant of experiment–without additional metal input);

The PhLD₅ is phytotoxic dose 5% (PhLD₅) caused reduction of 5% of initial weight (height, length of root etc.).

In our opinion, 5% reduction of initial weight (height, length of root etc.) is the minimal effect, which is similar to the LOEC shows the preliminary changes in the productivity of the plant population. Moreover, the level of significance of deviations, which are considered sufficient for ecological and biological research at the level of 5% (p < 0.05) was chosen. The algorithm of obtaining the PhLD₅ was represented in previous papers Ryzhenko [22]. Table 2 shows the values of PhLD₅ and PMAC for all investigated metals, as well as the background concentration in soil (0-20 centimeters). PMAC was obtained with the help of equation 2. The PMAC for Cd in sod podzolic soil was calculated in this way:

### Table 2: PhLD₅, PMAC, and background concentration in soil (0-20 centimeters, 1N HCl, mg kg⁻¹).

<table>
<thead>
<tr>
<th>Metal</th>
<th>PhLD₅</th>
<th>Ccontr (Background concentration in soil, 0-20cm)</th>
<th>PMAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sod podzolic (1M HCl, mg kg⁻¹)</td>
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</tr>
<tr>
<td>Cd</td>
<td>14.72</td>
<td>0.10±0.02</td>
<td>1.21</td>
</tr>
<tr>
<td>Pb</td>
<td>186.64</td>
<td>0.30±0.05</td>
<td>7.48</td>
</tr>
<tr>
<td>Zn</td>
<td>394.46</td>
<td>2.40±0.30</td>
<td>30.77</td>
</tr>
<tr>
<td>Cu</td>
<td>62.91</td>
<td>0.92±0.10</td>
<td>7.60</td>
</tr>
<tr>
<td>Co</td>
<td>57.94</td>
<td>1.50±0.15</td>
<td>9.77</td>
</tr>
<tr>
<td>Ni</td>
<td>50.12</td>
<td>1.10±0.10</td>
<td>7.40</td>
</tr>
<tr>
<td>Chernozem (1 M HCl, mg kg⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>19.25</td>
<td>0.11±0.02</td>
<td>1.46</td>
</tr>
<tr>
<td>Pb</td>
<td>264.24</td>
<td>0.32±0.05</td>
<td>9.20</td>
</tr>
</tbody>
</table>
The PMAC for Ni, Pb, Cu, Co, Zn in two soils were calculated similarly.

The lowest value of the PMAC had Cd, the highest value of the PMAC had Zn in two studied soils. The chernozem soil ad higher values of the PMAC than Sod podzolic soil. It could be explained by higher content of organic matter, granulometric composition of soil and other properties of chernozem soil. According to the value of PMAC, the metals can be ranked in the following descending order: Zn>Co>Cd>Ni>Pb>Cd. The PMAC could be used as an environmental standard that regulate the safe level of pollutants in the soil for plant [23-25].

Conclusion

As a result of this investigation, it was proposed to use the Phyto Maximum Allowable Concentration as a permissible level for plants in soil in the polluted ecosystem. The algorithm of calculation of Phyto Maximum Allowable Concentration based on the approach of the existing calculation of Maximum Allowable Toxic Concentration (MATC). The Phyto Maximum Allowable Concentrations were obtained for Hordeum vulgare L for all researched metals in two soils (mg kg⁻¹; 1 N HCl): Cd–1.21; Cu – 7.60; Co–9.77; Zn – 44.90; Ni – 12.69; Pb –9,20 calcareous deep chernozem on loamy loess). The Phyto Maximum Allowable Concentrations give the possibility to estimate the danger of metal to soil and other properties of chernozem soil. According to the value of PMAC, the metals can be ranked in the following descending order: Zn>Co>Cd>Ni>Pb>Cd. The PMAC could be used as an environmental standard that regulate the safe level of pollutants in the soil for plant [23-25].

References
