ABSTRACT: The article focuses on the research conducted on sewage sludge in Ternopil City, Ukraine, with a specific emphasis on its microelement composition and implications for disposal and utilisation. Bacterial contamination in both old and new sludge storage facilities is revealed by the study. It is found that the sludge holds potential as a fertiliser due to its nutrient content and organic matter, although adjustments may be necessary for specific soil conditions. However, it is determined that the permissible limits for agricultural use are exceeded by heavy metal concentrations, indicating pollution resulting from landfills, old pipes, and intensive agriculture. According to existing regulations, the sludge is considered suitable only for composting. The importance of sludge monitoring, treatment, and management is underscored by the findings, as they are crucial for ensuring safe disposal, mitigating environmental risks, and addressing potential health hazards.

KEYWORDS: sewage sludge, sewage treatment, heavy metals, sludge’s physical and chemical composition
Introduction

Sewage sludge poses a significant challenge resulting from population growth and industrial development. Large volumes of sediment are generated during wastewater treatment, posing environmental and human health risks. These sediments, accumulating on sludge sites, can result in soil, groundwater, and air contamination, as well as contribute to greenhouse gas emissions. Research reveals extensive sewage sludge production in different countries, with the United States producing 6.5 million tons annually, of which only 29% is properly treated (EPA, 2009).

Sludge undergoes stabilisation and, in most cases, dewatering processes to facilitate efficient handling and transportation. Stabilisation procedures usually decrease putrescibility, minimise potential odours, and reduce pathogens and vectors attractants. Dewatering methods transform solids containing at least 95% water into semi-solid material with a water content ranging from 50% to 85%.

China is currently facing challenges in the land application of sewage sludge due to inadequate treatment and disposal practices. This has resulted in environmental pollution and potential risks to human health. As China’s municipal wastewater treatment ratio increases, the production of sewage sludge is expected to rise rapidly, making the issue of disposal even more serious and unavoidable. However, if properly managed, stabilised sewage sludge can positively impact agriculture, forestry, horticulture, and urban development. The main obstacles to land application are the high concentrations of heavy metals, organic pollutants, and pathogens in sewage sludge resulting from wastewater treatment (Wang, 1997).

In Japan, approximately 2 million tons of sludge are produced yearly as a byproduct of wastewater treatment. However, despite this substantial volume, only a small fraction of the sludge is utilised as fertiliser. Efforts to maximise the utilisation of sludge as fertiliser can contribute to resource conservation, reduce environmental impact, and support the development of a circular economy in Japan’s agricultural sector (Nakamaru et al., 2023). Within the European Union, the quantity of sediment amounts to approximately 10 million tons annually, highlighting the magnitude of this resource. However, despite its vast volume, only around 36% of this sediment is currently being utilised in agricultural practices (Eurostat, 2023).

Ukraine, as a prosperous country with a well-established industry and a substantial population, is also confronted with the challenge of sewage sludge disposal. According to the data, 3 million tons of sediment are generated annually within the country, of which only 3 to 5% are used as secondary raw materials, mainly for the production of organic-mineral fertilisers.
This indicates an untapped potential that has yet to be fully utilised in Ukraine. It is crucial to explore and implement innovative strategies to optimise the utilisation of sewage sludge, thereby fostering sustainable practices and minimising waste in the country (Tymchuk et al., 2020).

In the processes of mechanical, biological, and physico-chemical purification of domestic, industrial, and agricultural wastewater at treatment plants, various types of sediments are formed, which differ in composition, properties, and impact on the environment. Mostly sediments from primary settling tanks, excessive activated sludge, and their mixtures, sediments from sludge maps are applied to the soil as fertiliser (Shevchenko et al., 2012).

Sewage sludge contains a wide range of bacterial species, surpassing the quantity found in sewage. Sediments contain many microorganisms and microscopic fungi, including pathogenic species. These sediments can contain up to 10 different types of parasitic pathogens, posing a potential threat to human health. Proper disposal or burial of sediments requires compliance with sanitary and hygienic standards to prevent direct or indirect risks. Storage of sediments on sludge cards for less than one year is not enough for their complete disinfection. Some pathogens can remain active for a long time, but after long-term storage (more than 3 years), the risk of infection with helminths is practically absent.

Sewage sludge from urban wastewater treatment plants contains many organic matter, macro- and microelements, and biologically active substances. Certain types of sewage sludge exhibit comparable effectiveness to conventional organic fertilisers. The availability of phosphorus in sewage sludge varies depending on its type, with fresh sludge displaying similar availability to monocalcium phosphate, while dried sediments provide less accessible phosphorus for plants (Kelley et al., 1984). Phosphorus content increases the most during the 2-3 year period of organic matter mineralisation in sewage sludge. Nitrogen within sewage sludge is predominantly found in organic compounds, with mineral nitrogen primarily as ammonium. This enhances nitrogen assimilation by plants from the soil, stimulates root system development, and boosts soil microorganism activity. These factors contribute to an additional 15-20% nitrogen uptake from fertilisers.

The utilisation of fermented sludge as a substitute for or in conjunction with organic fertilisers proves to be highly beneficial. Sediments exhibit higher levels of phosphorus and calcium compared to manure. Moreover, nitrogen and phosphorus within sediments are readily absorbable by plants. Multiple researchers testify the feasibility of such an application. However, it is imperative to subject sewage sludge to specialised treatment to prevent the introduction of substantial quantities of pathogenic microorganisms and heavy metal salts. Additionally, strict control over their content is necessary.
when using sludge as fertiliser on land plots (Milieu Ltd et al., 2010; Ali et al., 2017; Chen et al., 2018).

In addition, there are different approaches to wastewater treatment methods used in different regions, which also affect sewage sludge composition and properties. For example, sewage sludge usually contains chemicals harmful to plants and soil in regions where chemical methods of wastewater treatment are used. At the same time, sewage sludge contains biologically active substances beneficial for plant growth if biological wastewater treatment methods are used in the region. Therefore, research on the suitability of sewage sludge as a fertiliser must take into account regional characteristics in order to determine their usage efficiency and safety. This research aims to assess the possibility of sludge use as fertilisers in agriculture, taking into consideration various factors such as quality, heavy metal content, etc. The study focuses on investigating the characteristics of sewage sludge in Ternopil City as a region in Ukraine and its suitability as a fertiliser in agriculture because research results on sludge suitability vary depending on regional and geographical characteristics.

Research methods

A technique of sewage sludge sampling. At the time of sampling (March 2021, May 2021), the sediments of the sewage sludge field were finely dispersed and loosely compacted, and, in some places, it was noticed as water-saturated sludge. A sampling of accumulated sediments was conducted using a cylindrical metal pipe with a lower valve. The sampler had a diameter of 128 mm and a length of 1 m. A pipe was attached to the upper part of the sampler, allowing for increased length through coupling connections. The sediment deposits had a thickness of 3 m or more. Sampling was performed at specific depth intervals: 0-0.2 m, 1.4-1.6 m, and 2.8-3 m. These intervals were selected to investigate the ecological, biogeochemical, and parasitological characteristics of the sediments in near-surface, mid-depth, and bottom conditions. Each sample had a volume of 2.5 dm$^3$ and was carefully packed in double polyethylene bags. A unique serial number was assigned to each sample, which was recorded in the sampling log. The selection points were geodetically measured and marked in the area (International Organization for Standarization, 2002). Fresh sediment samples were collected immediately after being unloaded from the centrifuge and placed into polyethylene bags for further analysis.
The techniques of analytical determination of sewage sludge composition

As a standard on the technique of sludge composition’s indices from the treatment plants determination hasn’t yet been developed, the study was carried out according to the current regulatory documents on soil analysis (Clesceri et al., 1998; Van Reeuwijk, 2002).

The organic substance content was determined gravimetrically after dry burning of the sample. The moisture content was determined gravimetrically after being dried to the constant mass at 105°C. The sludge acidity was determined potentiometrically by measuring water extract pH (water: soil ratio 1:5). Total content of metals (Cu, Ni, Pb, Cd, Mn, Cr and Zn) was determined by the atomic absorption method after samples acid decomposition in the hydrogen peroxide presence.

Mercury (Hg) from the sludge samples was removed by acids and determined in the obtained solution by the spectrophotometric method. The extraction of exchangeable forms of metals (Cu, Ni, Pb, Cd, Mn, Cr, Zn, Co, Fe) was conducted by ammonium-acetate buffer solution with pH 4.8 at the solution: soil ratio 1:5, with the further analysis of the obtained extracts by the atomic absorption method. Total and ammonium Nitrogen were determined by the titrimetric method. Phosphorus moving compounds were extracted from the soil by the ammonium carbonate solution of 10 g/dm³ concentration at the soil: solution ratio 1:20, and further, the phosphorus was determined as a blue phosphorus-molybdenum complex on the spectrophotometer. A bacteriological and parasitological study of the sewage sludge was carried out by the titrimetric and microscope methods, respectively.

During the correlation analysis, various statistical characteristics were calculated, including the arithmetic mean values of system parameters, the standard root mean square deviation, and the coefficient of mutual correlation. The confidence interval limits were determined by multiplying the root mean square deviation by the dimensionless Student’s coefficient. The calculations were performed using the standard Excel package.

Results of the research

The main sanitary and biological, physical and chemical and agrochemical indices of six obtained samples have been determined during the research of Ternopil city sewage sludge (Tables 1-3).
Table 1. Sanitary-biological indices of sewage sludge in Ternopil City

<table>
<thead>
<tr>
<th>№ of lot</th>
<th>Time of sample obtaining</th>
<th>№ of sample</th>
<th>Area of sample obtaining</th>
<th>Number of bacteria</th>
<th>Titre coliform bacteria</th>
<th>Helmints eggs</th>
<th>Titre Cl. perfringes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>March 2021</td>
<td>1</td>
<td>Storage platform (old)</td>
<td>94100</td>
<td>&lt;0.00001</td>
<td>none</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>Storage platform (new)</td>
<td>52000</td>
<td>0.001</td>
<td>none</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>Sludge lagoon №21 – 2 years</td>
<td>77200</td>
<td>&lt;0.00001</td>
<td>none</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>May 2021</td>
<td>4</td>
<td>Storage platform (new)</td>
<td>119200</td>
<td>0.0001</td>
<td>none</td>
<td>&gt;0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>Sludge lagoon №1 – V. Myshkovychi</td>
<td>6520</td>
<td>0.01</td>
<td>none</td>
<td>&gt;0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>Sludge lagoon № 25 – 4 years</td>
<td>79200</td>
<td>0.01</td>
<td>none</td>
<td>&gt;0.1</td>
</tr>
</tbody>
</table>

The common feature of all six sludge samples is their bacterial contamination (titer coliform bacteria less than 0.1), although its extent varies.

Table 2. Sludge agrochemical characteristics city

<table>
<thead>
<tr>
<th>№ of lot</th>
<th>Time of samples obtaining</th>
<th>№ of sample</th>
<th>Samples obtaining area</th>
<th>pH</th>
<th>Humidity %</th>
<th>% of dry substance N</th>
<th>P2O5</th>
<th>K2O</th>
<th>C</th>
<th>Ash content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>March 2021</td>
<td>1</td>
<td>Storage platform (old)</td>
<td>7.1</td>
<td>68.6</td>
<td>1.13</td>
<td>2.1</td>
<td>0.48</td>
<td>10.66</td>
<td>22.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>Storage platform (new)</td>
<td>7.6</td>
<td>84.8</td>
<td>1.41</td>
<td>2.11</td>
<td>0.49</td>
<td>15.96</td>
<td>31.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>Sludge lagoon №21</td>
<td>7.2</td>
<td>77.6</td>
<td>1.10</td>
<td>2.41</td>
<td>0.46</td>
<td>16.91</td>
<td>24.32</td>
</tr>
<tr>
<td>2</td>
<td>May 2021</td>
<td>4</td>
<td>Storage platform (new)</td>
<td>7.1</td>
<td>32.3</td>
<td>1.39</td>
<td>2.62</td>
<td>0.45</td>
<td>10.94</td>
<td>28.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>Sludge lagoon №1 – V. Myshkovychi</td>
<td>7.3</td>
<td>85.4</td>
<td>1.42</td>
<td>2.35</td>
<td>0.58</td>
<td>13.26</td>
<td>24.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>Sludge lagoon № 25</td>
<td>6.7</td>
<td>20.9</td>
<td>1.66</td>
<td>2.21</td>
<td>0.29</td>
<td>11.2</td>
<td>24.01</td>
</tr>
</tbody>
</table>

It is important to note that the possibility of sewage sludge being used as fertiliser also depends on the presence of any contaminants or heavy metals. Specific information about heavy metal concentrations is presented in Table 4.
Table 3. Heavy metals content in the Ternopil city sewage sludge, mg/kg of dry substance

<table>
<thead>
<tr>
<th>№ of lot</th>
<th>Samples obtaining time</th>
<th>№ of sample</th>
<th>Samples obtaining area</th>
<th>Sr</th>
<th>Cr(^{3+})</th>
<th>Ni</th>
<th>Co</th>
<th>Cd</th>
<th>Mn</th>
<th>Pb</th>
<th>Cu</th>
<th>Fe</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>March 2021</td>
<td>1</td>
<td>Storage platform (old)</td>
<td></td>
<td>214</td>
<td>196</td>
<td>25</td>
<td>26</td>
<td>47</td>
<td>47</td>
<td>476</td>
<td>248</td>
<td>249</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>2</td>
<td>Storage platform (new)</td>
<td>123</td>
<td>106</td>
<td>188</td>
<td>25</td>
<td>26</td>
<td>487</td>
<td>118</td>
<td>101</td>
<td>13220</td>
<td>888</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>3</td>
<td>Sludge lagoon №21</td>
<td>356</td>
<td>226</td>
<td>26</td>
<td>35</td>
<td>47</td>
<td>486</td>
<td>520</td>
<td>448</td>
<td>13430</td>
<td>1568</td>
</tr>
<tr>
<td>4</td>
<td>May 2021</td>
<td>4</td>
<td>Storage platform (old)</td>
<td>368</td>
<td>307</td>
<td>526</td>
<td>0</td>
<td>54</td>
<td>468</td>
<td>489</td>
<td>418</td>
<td>14540</td>
<td>1327</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>5</td>
<td>Sludge lagoon №1 – V. Myshkovychi</td>
<td>326</td>
<td>24</td>
<td>327</td>
<td>0</td>
<td>36</td>
<td>487</td>
<td>450</td>
<td>316</td>
<td>13800</td>
<td>1218</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>6</td>
<td>Sludge lagoon №25</td>
<td>287</td>
<td>326</td>
<td>563</td>
<td>0</td>
<td>64</td>
<td>435</td>
<td>377</td>
<td>346</td>
<td>14440</td>
<td>1364</td>
</tr>
</tbody>
</table>

Discussion and future research

Various factors cause fluctuations in the trace element composition of the sewage sludge at different depths. One significant factor is the leaching of chemical compounds from the upper layer of the sewage sludge, which then are accumulated in the lower layers. The leaching process is also influenced by meteorological and seasonal conditions, such as rainfall and temperature fluctuations. Additionally, the intensity of biochemical processes occurring in the sewage sludge can also contribute to the variations in trace element composition. These processes involve the activities of microorganisms, plants, and other biological agents, which can alter the concentration of trace elements over time. Furthermore, the wastewater components can impact the trace element composition of the sewage sludge.

The samples obtained from the old and new storage platforms, as well as from sludge lagoon №21 with a storage period of 2 years, have demonstrated the highest levels of bacterial contamination. This finding emphasises the importance of careful control and treatment of these sludge samples before their utilisation or disposal. It’s worth noting that the titers of coliform bacteria in all samples were less than 0.1, except for one sample where it was greater than 0.1. Although the exact unit of measurement is not specified, the low titers generally suggest a relatively low level of contamination by coliform bacteria. However, it is important to assess the sanitary and biological aspects of the sewage sludge comprehensively, taking into account other parameters such as the presence of helminth eggs and Titre Cl. perfringes, as
presented in the Table 1. These additional parameters provide insights into the potential health risks associated with the sludge. Overall, the findings emphasise the need for proper monitoring, treatment, and management of sewage sludge to ensure its safe handling and minimise potential environmental and health hazards.

The provided information in Table 2 includes the details of the samples collected from different sources, their time of collection, and various parameters related to the sludge's physical and chemical composition. The table consists of six samples collected in March and May 2021. The first two samples were obtained from storage platforms, one from the old storage platform and the other from the new storage platform. The third sample was collected from Sludge Lagoon №21. There were others, the Storage platform (new), Sludge Lagoon №1 – V.Myshkovychi, and Sludge Lagoon № 25.

Based on the provided information in Table 2, the possibility of the sewage sludge being used as a soil fertiliser can be assessed. The sludge samples exhibit various characteristics that are desirable in a fertiliser, such as significant nutrient content. The nitrogen (N), phosphorus (P₂O₅), and potassium (K₂O) concentrations are present in measurable amounts, indicating that the sludge contains essential nutrients that can contribute to plant growth and development. Additionally, the carbon (C) content suggests the presence of organic matter, which can enhance soil fertility and improve its overall structure and water-holding capacity. However, certain factors need to be considered when evaluating sewage sludge use as a fertiliser. The pH values of the sludge samples range from slightly acidic to neutral, which may require additional adjustments depending on the specific soil conditions and crop requirements. Furthermore, the ash content indicates the mineral composition of the sludge. Higher ash content may indicate a higher concentration of inorganic compounds, which can be beneficial for certain crops but may require careful consideration to prevent excessive buildup of specific elements in the soil. When comparing the heavy metal content in the Ternopil city sewage sludge samples (Table 3) with permissible limits and analysing the data, several observations can be made:

1. The concentrations of Cd in all samples are noticeable, with values ranging from 36 mg/kg to 64 mg/kg. These values exceed the maximum permissible concentration for sludge application in agriculture, indicating potential environmental and health risks associated with Cd contamination.

2. The sludge samples also demonstrate elevated Pb concentrations, ranging from 118 mg/kg to 520 mg/kg. Similar to Cd, these values exceed the permissible limits for agricultural use, suggesting the presence of potentially harmful levels of Pb in the sludge.
3. Chromium concentrations vary across the samples, ranging from 24 mg/kg to 326 mg/kg. Although these values do not exceed the maximum permissible concentration, they indicate the presence of Cr³⁺ in the sludge, which may require careful monitoring and management to prevent further accumulation.

4. The concentrations of other heavy metals such as strontium (Sr), nickel (Ni), cobalt (Co), manganese (Mn), copper (Cu), iron (Fe), and zinc (Zn) also vary among the samples. While some values fall within acceptable ranges, others approach or exceed the maximum permissible concentration.

Overall, the results indicate the presence of various heavy metals in the Ternopil city sewage sludge, with several metals exceeding the permissible limits for agricultural use. Landfills and water systems, which consist of old metal pipes, are determined as the main sources of heavy metal pollution in the Ternopil region. Landfills might contain heavy metals, such as lead and mercury, which gradually enter groundwater and surface water sources and contaminate wastewater. In addition, intensive agriculture, the usage of mineral fertilisers, pesticides, and other chemicals can also cause heavy metal pollution in soil and wastewater. According to the above-mentioned indices and existing standards that regulate the content of heavy metals ACs, all identified sludge samples in Ternopil city are of the fourth group (Norm, 1999), i.e. it can be applied only for composting (Kalamdhad & Singh, 2013; Osman et al., 2017; Van Reeuwijk, 2002; J. Zhang et al., 2017; Q. Zhang et al., 2017).

Technological solution:

One of the possible examples of sediments for composting preparation with increased content of heavy metals in bioconvectors may include the following steps: a preliminary analysis of the heavy metals content, which will help to define the level of contamination and determine the necessary measures to prepare material for composting; material sorting with separation of heavy metals and other unwanted impurities; chemical treatment of sediments by using chelating agents, which ensure binding of heavy metals and their removal from the material; composting of sediments in bioconvectors, while observing the optimal temperature, humidity and ventilation to ensure the effective decomposition of organic substances and finished compost formation; analysis of heavy metals content in finished compost to ensure its safe usage (Osman et al., 2017; El-Fadel et al., 1997; Chen et al., 2018; Zhang et al., 2017).
Conclusions

The microelement composition of the sewage sludge of the Ternopil City, located in the Western region of Ukraine, was studied at various depths. It was found that bacterial contamination is observed in samples from both old and new sludge storage platforms, emphasising the importance of proper control and treatment before disposal or utilisation. The possibility of the sewage sludge being used as a fertiliser was assessed based on its nutrient content, carbon levels, pH values, and ash content. It was revealed that significant amounts of nutrients and organic matter are present in the sludge, although adjustments might be necessary depending on specific soil conditions. Furthermore, the permissible limits for agricultural use were exceeded by the concentrations of heavy metals in the sludge samples, particularly cadmium (Cd) and lead (Pb), as well as other elements. The presence of various heavy metals in the sewage sludge indicates pollution sources such as landfills, old metal pipes, and intensive agricultural practices, which have the potential to contaminate groundwater, surface water, soil, and wastewater. Consequently, the identified sludge samples are only suitable for composting following existing standards and regulations. Overall, the importance of proper monitoring, treatment, and management of sewage sludge to ensure safe disposal, minimise environmental risks, and reduce potential health hazards is emphasised by the results. Future research should focus on the development of effective treatment methods to reduce heavy metal concentrations in sewage sludge and the exploration of alternative options for the disposal or utilisation of contaminated sludge.

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The contribution of the authors

T.V. conceived of the presented idea, developed the theory and performed the computations, suggested the research methods, and designed the figures. T.V. wrote the manuscript with support from N.M. and I.K. N.M. prepared the research results analysis. I.K. summarised the research results.

All authors discussed the results, and contributed to the final manuscript.
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