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Effect of addition of sewage sludge and coal sludge on bioavailability of selected metals in the waste from the zinc and lead industry

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ABSTRACT

This study evaluated the content of bioavailable forms of selected heavy metals present in the waste from Zn and Pb processing that can potentially have an effect on the observed difficulties in reclamation of landfills with this waste. The particular focus of the study was on iron because its potential excess or deficiency may be one of the causes of the failure in biological reclamation. The study confirmed that despite high content of total iron in waste (mean value of 200.975 g kg^{-1}), this metal is present in the forms not available to plants (mean: 0.00009 g kg^{-1}). The study attempted to increase its potential bioavailability through preparation of the mixtures of this waste with additions in the form of sewage sludge and coal sludge in different proportions. Combination of waste with 10% of coal sludge and sewage sludge using the contents of 10%, 20% and 30% increased the amounts of bioavailable iron forms to the level defined as sufficient for adequate plant growth. The *Lepidum sativum* test was used to evaluate phytotoxicity of waste and the mixtures prepared based on this waste. The results did not show unambiguously that the presence of heavy metals in the waste had a negative effect on the growth of test plant roots.

1. Introduction

One of the negative effects of the zinc and lead industry is the collection of waste which is harmful to the environment. The fine structure of this waste, insufficient amount of nutrients and phytotoxicity connected with the presence of heavy metals are the major causes of difficulties in biological reclamation of soil where such waste is deposited (Kucharski et al., 2005; Turnau et al., 2001). Furthermore, the alkaline character of this waste can prevent trace elements necessary for the development of most plants from being absorbed while their excess can make it difficult to introduce a biological cover (Porębska and Ostrowska, 1999; Skubała, 2011). Limitation of plant growth on waste may also result from insufficient amounts of nitrogen and phosphorus and the lack of organic matter (Tordoff et al., 2000; Ye et al., 2002; Wong, 2003). Other unfavourable characteristics include variability of chemical composition with regard to the horizontal and vertical profile, the presence of heavy metals that disturb microbiological processes that occur in soil and plants (Tchounwou et al., 2012, Gutiérrez et al., 2016) and unfavourable soil structure (Krzaklewski and Pietrzykowski, 2002). Despite a plethora of methodologies which have been proposed, the percentage of reclaimed lands after deposition of the industrial waste from Zn-Pb industry remains insignificant (Gozzard et al., 2011, Galende et al., 2014). The characteristics of waste are the causes of difficulties with obtaining a stable ground cover and the spontaneously growing plants represent a specific and unique composition of various species (Szarek-Łukaszewska and Grodzińska, 2007; Skubała, 2011).

The characteristic feature of waste obtained during processing of Zn-Pb ores extracted in the region of Bytom (southern part of Poland) is high iron content that results from petrography of rocks that form the ores deposit. The ore-rich rocks include dolomites, often defined as iron formations due to high amounts of iron minerals that form pockets in Triassic carbonate deposits. Iron is one of bioelements necessary for plant growth, but it is also very difficult for them to absorb. Its deficiency in plants results mainly from unfavourable conditions, such as improper pH of the soil environment or the presence of high contents of other competitive macro- and microelements since the excess of one element in the soil may have a negative effect on the absorption of the other (Briat et al., 2007, Chen and Barak, 1982, Asad and Rafique, 2000). Due to its low solubility, poor iron availability, despite its relatively high content in soils, represents one of the major limitations to vegetation growth (Pii et al., 2016). As demonstrated in numerous studies (Bartakova et al., 2001; Batty and Younger, 2003; Dhiman and Bhargava, 2008), too high iron content in soil may have a negative effect on the growth and development of germs of certain plants, causing inhibition or even entirely preventing germination.

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The beneficial effect on growth and crop yielding and biological, physical and chemical properties of the soil can be obtained using the addition of sewage sludge in the soil reclamation process (Rehab et al., 2003; Vaca et al., 2011, Ailincăi et al., 2012). Organic matter that can be found in the soil, both of autochthonic origin as well as introduced with fertilizer (e.g. sewage sludge) reduces the presence of metals in forms potentially bioavailable to plants. Another important factor affecting the above process is soil reaction type (Ociepa et al., 2013). This method was used for reclamation of Zn-Pb industry landfills. An improvement in surface water retention in the layer of the landfill was found. Solubility of trace elements declined result of precipitation of insoluble metal compounds to the presence of phosphorus contained in the sludge (Stuczyński et al., 2007). A stabilizing effect of sewage sludge on soil reaction was found, translating directly into bioavailability of micro- and macroelements, including heavy metals. It was also found that fertilization with sewage sludge caused an increase in plant resistance to unfavourable environmental conditions such as drought, salinity and low temperature (Antolín et al., 2005, 2010). Using sewage sludge for fertilization causes an increase in heavy metals content in the soil, but it is not unequivocal with the increase in their content in plants that causes a negative effect (Nogueira et al., 2013; Latare et al., 2014; Bourioug et al., 2014).

The aim of the study was to evaluate the amount of bioavailable forms of selected heavy metals present in the waste that can have an effect on the observed difficulties in biological reclamation of landfills of this waste. The particular focus of the study was on iron, with the assumption that its potential excess or deficiency may be one of the causes of the unsuccessful biological reclamation process. Therefore, another stage of the study was the attempt to modify the potentially bioavailable pool of iron and other metals through the addition of sewage sludge and coal sludge to the waste. The use of coal sludge as an addition for the mixtures resulted from its high content of the carbonaceous substance and clay minerals which improve sorption properties of the material in regard to heavy metals.

2. Materials and methods

2.1. Location of the study area

The examination site was a landfill of waste from the Zn-Pb industry located in Piekary Śląskie, city district Brzeziny Śląskie (southern part of Poland). The waste originates from the gravity separation process of Zn-Pb ores, and is conventionally termed washery waste. This landfill was established in 1915–1930 and its location is unfavourable since it is adjacent to both residential buildings and agricultural fields (Wójcik et al., 2014). The surface of the landfill does not have a full ground cover, because apart from the areas of vegetation, there are also places without plants. This increases the risk of the spread of metal-containing dusts. Based on the evaluation of the degree of covering of the landfill surface with vegetation, we determined 12 locations of waste sampling (Fig. 1), including those with (points 3–5,7,9,11) and without vegetation (points 1,2,6,8, 10,12).

The samples were collected after removing 5 cm of the surface layer and consisted of the soil profile between 5 cm and 30 cm. After transportation to the laboratory samples were averaged using the quartering method, dried and subjected to further test procedures.

2.2. Research procedures

The following characteristics were evaluated: total metal content (Fe, Zn, Pb and Cd) and content of organic carbon, nitrogen and phosphorus. Extraction by the DTPA (diethylene triamine penta-acetic acid) was used to evaluate the contents of metals which are potentially available for plants (potentially bioavailable).

Another stage of the study was the modification of the potentially bioavailable pool of the studied metals using the addition of sewage sludge and coal sludge in varying proportions. The tested combinations were presented in Table 1. The mixtures were prepared using the waste sampled from the site lacking vegetation (point 1).

These mixtures were subjected to DTPA extraction in order to determine the contents of potentially bioavailable forms of the analysed metals. Phosphorus content was also determined. The *Lepidium sativum* test was used to evaluate the toxicity of the waste and its mixtures with additions.

2.3. Analysis of substrates for the examinations

The samples of washery waste from 12 locations were used to prepare the averaged sample which was subjected to the powder X-ray analysis using the X-ray diffractometer (Philips PW 3710) with the following measurement conditions: Cu kα_1 lamp, pulse integration time of 2 s, recording rate of 0.02^0 for 2Θ. Using analogous conditions, the X-ray analysis was employed for the examination of the coal sludge sample from the process of dewatering of the products of hard coal processing sampled from one of the coal mines located in the southern part of Poland. Sewage sludge was obtained from a municipal wastewater treatment plant. Selected physical and chemical parameters were determined for this sludge.

2.4. Analytical procedure

Prior to analysis all samples were dried and ground in a mortar until particle size below 0.063 mm was reached. In order to determine the total content of metals, mineralization in a microwave mineraliser of the solid samples was performed and then in the obtained extracts selected metals were determined using the emission spectrometers with ICP-OES Thermo Elemental IRIS INTREPID II XSP DUO plasma induction. The analysis was performed using the internal standard and the obtained results were verified using the reference material BL 12-1-12. The solvent used for the mineralization of the samples was *aqua regia* (Stuczyński et al., 2007).

The pH values were determined in water extracts (sample/H_2O ratio of 1:10) using a multifunctional meter HANNA INSTRUMENTS HI 9828. Total nitrogen was determined by the Kjeldhal method (Hornec and Miller, 1998). Available phosphorus was extracted via the Egner-Riehm method and analysed using a spectrophotometer (Riehm, 1958). Organic carbon content was done in accord to the Tiurin method.

Due to the alkaline character of the waste, the content of the bioavailable metals in the samples was evaluated using the DTPA test (Lindsay and Norvell, 1978), which allows for the determination of the metals content in organic and carbonate forms. Metal contents obtained from the ICP analysis were converted from mg L^{-1} to mg kg^{-1} according to the recommendations of the authors of the test.

2.5. Toxicity test

The washery waste and the mixtures were evaluated with regards to their phytotoxicity using a standard test with *Lepidium sativum*. The test is useful for evaluation of phytotoxicity of soils contaminated with heavy metals (Płaza et al., 2009). It was found (Pavel et al., 2013) that heavy metal ions tend to hinder germination of *Lepidium sativum* seeds and root development is influenced by both the type of ion as well as its concentration.The test was performed for water extracts obtained from waste and mixtures as well as for the control sample consisting of distilled water. The extracts were obtained through shaking of 10*g* of the sample in 100 ml of distilled water for 24 h in room temperature in the darkness. Flasks were centrifuged and the obtained supernatant was filtered through a paper filter. Twenty seeds of *L. sativum* were placed on Petri dishes covered with filter paper (Whatman No. 3) infused with 5 ml of each extract. A Petri dish covered with filter paper infused with 5 ml of distilled water served as the control sample. The dishes were stored in an incubator at a constant temperature and air humidity set to