


<b>EREM 74/4</b> Journal of Environmental Research, Engineering and Management Vol. 74 / No. 4 / 2018 pp. 53-59 DOI 10.5755/j01.erem.74.4.21073 © Kaunas University of Technology	<b>Changes in Soil Properties and Heavy Metals Concentration in Soil of          Military Shooting Range in Central Lithuania</b>	
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# Changes in Soil Properties and Heavy Metals Concentration in Soil of Military Shooting Range in Central Lithuania

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The aim of the study was to investigate the changes in physical properties and contamination with heavy metals of military shooting range soil. Field soil was collected from outdoor shooting range soils in central Lithuania. The shooting range is located in Alytus city. Physico-chemical examination showed that the pH value of the shooting range soil was described as alkaline (7.91–8.30). A decrease in organic matter content was established in soil samples taken from the backstop berm of a shooting range; moreover, increased soil density was discovered in all soil samples. The soil was heavily contaminated with Pb, Ni, Cd and allowable quantities of Cu. The backstop berm soil was heavily contaminated with lead (max. 653.33 mg/kg); nonetheless, the limit concentration of lead was exceeded in the backstop berm soil. The concentration of cadmium found in the shooting range area (0–400 meters) varied from 17.42 mg/kg to 39.07 mg/kg and was higher than the concentration in the backstop berm ( $p < 0.05$ ). The limit concentration of cadmium, which is 3 mg/kg, was exceeded in all soil samples. Large amounts of nickel were found closer to the beginning of the firing line and decreased with an increasing distance from the firing line ( $r = 0.90$ ,  $p < 0.05$ ). The limit concentration of nickel in the soil (75 mg/kg) was exceeded at 100 m, 200 m and 300 m distances.

**Keywords:** contamination, heavy metals, soil pollution, shooting range.

## Introduction

Soil is a unique part of the ecosystem; however, pollution with heavy metals is the problem of increasing concern (Chibuike and Obiora, 2014). Naturally occurring heavy metals are often not available for biota, while metals from anthropogenic sources have high bioavailability (Khalilova and Mammadov, 2016). At high doses, all heavy metals become toxic and carcinogenic (Tchounwou et al., 2012). Heavy metals remain in ecosystems for long periods of time. Metals can be absorbed and accumulated in various parts of the plant. Soil organisms are directly exposed to soil and heavy metals. Therefore, heavy metals can lead to changes in soil microorganisms, for example, their size, composition, and activity. From the soil, metals can be washed into lakes, rivers, bays and consequently can easily enter the food chain and pose a serious threat (Khalilova and Mammadov, 2016; Sanderson et al., 2014). In general, mobility of heavy metals depends on the physicochemical properties of the soil (ph, organic matter, density, etc.) and properties of a heavy metal itself (Zeng et al., 2011).

The contamination of outdoor shooting range soil is a major environmental problem (Sanderson et al., 2012; Sanderson et al., 2014; Fayiga and Saha, 2016; Rodríguez-Seijo et al., 2017). After the battery industry, shooting activity is the second most important factor contributing to soil pollution with lead (Sorvari et al., 2006; Sanderson et al., 2012). Bullets consist of various amounts of heavy metal alloys (Pb, St, As, Sn, Se, Mn, Cd, Cr, Cu, and Ni) (Fayiga and Saha, 2016). High pollution by heavy metals is seen in the soil of military shooting ranges (Hardison et al., 2004; Ahmad et al., 2012; Perroy et al., 2014; Fayiga et al., 2016; Mariussen et al., 2016). The intensity of the shooting activity is a key factor determining the extent of pollution in the shooting range. Lead is the main component of bullets (> 90%), but various amounts of other heavy metals are also found in bullet mass (antimony, arsenic, bismuth, silver, copper, and nickel). It is clear that the risk assessment and management of these contaminated sites are required to ensure that contamination does not negatively affect the environment (Spuller et al., 2007; Conesa et al., 2010; Sanderson et al. 2014; Fayiga, Saha, 2016).

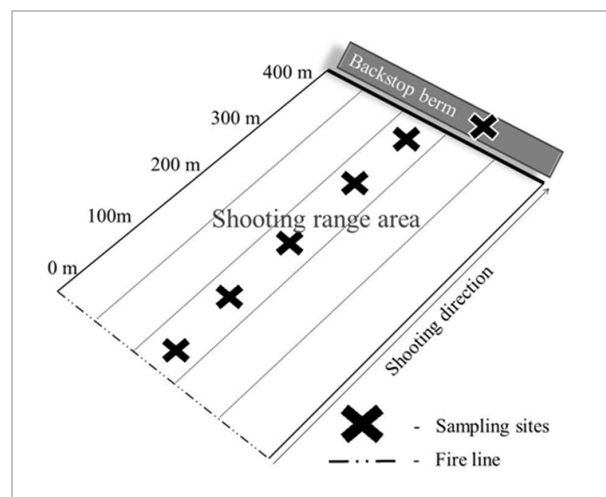
The aim of the study was to investigate the changes in physical properties and contamination with heavy metals of military shooting range soil in central Lithuania. It is crucial to investigate the contamination of active shooting ranges because of threat of harming effects that may occur to humans who are exposed to heavy metals, especially lead.

## Methods

### Study sites and soil sampling

Field soil was collected from outdoor shooting range soils in central Lithuania. The shooting range is located in Alytus city (N 54.373825, E 24.072171). The shooting range structure consists of three main elements: a fire line, a target line and a backstop berm. The shooting range is 400 m long and has target lines at different distances (100 m, 200 m, 300 m, and 400 m). In the range, shooters practice and improve their skills by shooting from different distances with various caliber weapons. Samples were taken from seven plots (Fig. 1). Five samples were taken from the shooting range area in accordance with target lines, one sample was taken from the beginning of the firing line (at a 0 m distance), four samples were taken

**Fig. 1**  
Structure of the shooting range



from target lines (100 m, 200 m, 300 m, 400 m distances) and two samples were taken from the backstop berm (from the bottom of the berm and from 1 m height of the berm). At each distance, from a square plot (0.5 × 0.5 m), five subsamples of the soil were collected from the corners and the centre of the plot using a cylindrical soil corer to a depth of 10 cm. The samples from each plot were pooled and mixed thoroughly to get one representative composite sample at each studied plot. Grassland soil was collected in an unpolluted area of southern Lithuania (54°25'42.8"N 24°14'07.5"E, Pivašiūnai) and was used as reference.

### Physico-chemical analysis

The soil samples were air dried, homogenised and sieved to less than a 2 mm grain size. The samples were stored in plastic bags prior to laboratory analysis. The pH was measured by potentiometric method, water ratio of 1:5 (pH meter - inoLab 720, WTW). Organic matter content was determined by loss on the ignition method. Soil density was determined by pouring air-dry soil samples in a measured cylinder.

To analyse the contamination of the shooting range, lead as the main component of bullet mass was determined; copper, zinc, nickel, and cadmium as minor were components of bullet mass. To determine heavy metals (Pb, Zn, Cu, Ni, and Cd) concentrations, approximately 0.5 g oven-dried soil samples were digested in 8 mL of HCL, 5 mL of HNO<sub>3</sub>, 5 mL of HBr, and 3 mL of HF in a Teflon vessel using a microwave digestion system (Milestone Ethos One). Concentrations of heavy metals were determined by an atomic absorption spectrometer (Shimadzu AA-6800, Japan) with a graphite furnace atomiser (GFAAS). The elemental standard solutions were prepared by diluting a stock solution of 1,000 mg L<sup>-1</sup> (Pb, Zn, Cu, Ni, and Cd).

### Data analysis

Analysis of variance (ANOVA) described the influence of distance from the firing line on the concentration of heavy metals. The t test was used for comparison of physical and chemical soil properties. Differences were considered significant when *p* value was less than 0.05. The Pearson correlation was used to determine the dependence of soil variables and the distance from the firing line. Programme STATISTICA 7 and MS Excel were used for the statistical analysis.

## Results and Discussion

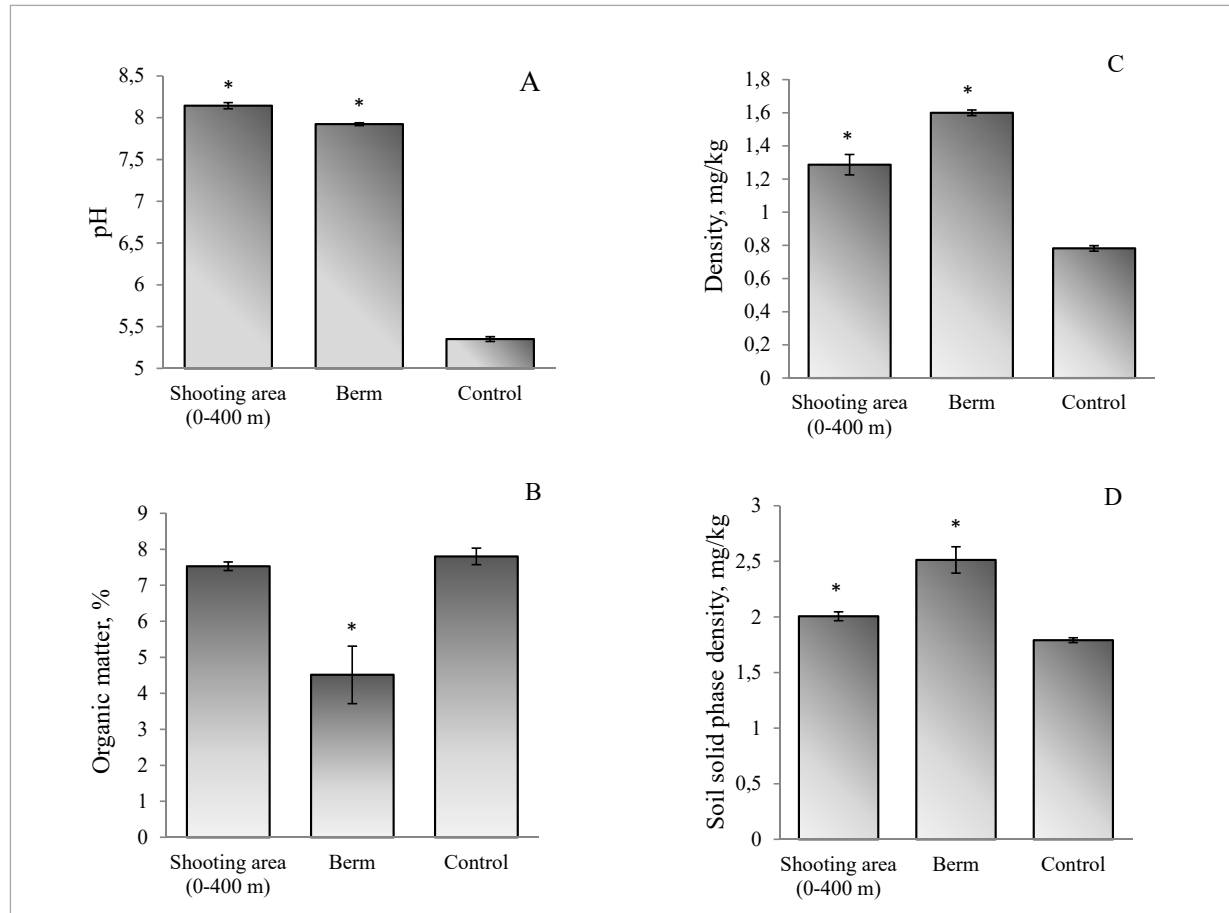
The pH values of the shooting range soil varied from 7.91 to 8.30. The soil of shooting ranges was more alkaline compared with the control. The dispersion analysis revealed that the pH of shooting range soils was significantly higher than that of the control soil ( $p < 0.05$ , Fig. 2A). A strong positive correlation between the distance of the shooting area (0–400 meters) and pH value was observed ( $r = 0.83$ ,  $p < 0.05$ ). These results are in accordance with those of Kelebemang et al. (2017) who showed that in different shooting ranges pH value varied from 6.81 to 8.69. Similar results were observed by Sanderson et al. (2012): the pH of shooting range soil was from 5.3 to 9.3. It is known that the pH can affect solubility and mobility of heavy metals in soil (Kelebemang et al., 2017).

The higher organic matter content (mean 7.53%) was at the shooting area of the range (from 0 to 400 meters) compared with the backstop berm (mean 4.51%) (Fig. 2B). The analysis showed that the soil of the backstop berm was significantly lower in organic matter content compared with the control soil ( $p < 0.05$ ). The mean density of the soil taken from the shooting area of the range was 1.29 g/cm<sup>3</sup> and the density of the backstop berm soil was 1.60 g/cm<sup>3</sup>. The density of all soil samples was significantly higher than that of the control ( $p < 0.05$ , Fig. 2C). It was determined that the density of the soil taken from the backstop berm was significantly higher than in the samples of the shooting area of the range ( $p < 0.05$ ). The density of soil particles varied from 1.84 g/cm<sup>3</sup> to 2.37 g/cm<sup>3</sup>, and significant differences between the soil samples and the control were observed ( $p < 0.05$ ) (Fig. 2D). The particle density of the soil taken from the backstop berm was significantly higher than in the samples of the shooting area ( $p < 0.05$ ).

The highest concentration of lead in the shooting range was determined at the bottom of the backstop berm (Fig. 3A "Berm 0"), i.e., 653.33 mg/kg, and in the samples taken from 1 m height of the backstop berm (230.58 mg/kg). At the distance of 200 to 400 m, the lead concentration ranged from 20.48 to 38.94 mg/kg; and from the firing line to 100 meters, it ranged from 2.01 to 2.94 mg/kg. The limit lead concentration (100 mg/kg, HN 60: 2004) in the soil was exceeded

**Fig. 2**

Physical and chemical soil properties of the soil samples at the shooting area and the backstop berm (\* indicates significant changes compared with the control soil)



only in the backstop berm of the shooting range. It was determined that the concentration of lead in the backstop berm was significantly higher than in the shooting area (0–400 m) ( $p < 0.05$ ).

The maximum concentration of copper was also found at the bottom of the backstop berm (23.49 mg/kg). In the shooting area, the concentration of Cu varied from 0.75 to 9.59 mg/kg (Fig. 3B). The concentrations of copper in the backstop berm were significantly higher in comparison with the shooting area (0–400 m) ( $p < 0.05$ ). The concentration of cadmium found in the shooting area of the range was higher than the concentration in the backstop berm ( $p < 0.05$ ). At a distance of 0–400 m, cadmium concentration varied from 17.42 mg/kg to 39.07 mg/kg; however, in the

backstop berm, the concentrations of cadmium were 6.16 mg/kg (berm 0) and 5.73 mg/kg (berm 1) (Fig. 3C). The limit concentration of cadmium (3 mg/kg) was exceeded in all soil samples.

Large amounts of nickel were found closer to the beginning of the firing line and decreased with an increasing distance from the firing line ( $r = 0.90$ ,  $p < 0.05$ ). In general, the concentration of nickel ranged from 3.12 mg/kg to 152.15 mg/kg (Fig. 3D). The limit concentration of nickel in the soil (75 mg/kg) was exceeded at 100 m, 200 m and 300 m distances from the firing line.

Physicochemical analysis revealed that the shooting range soil was affected by shooting activity. It is important to study soil properties because of different

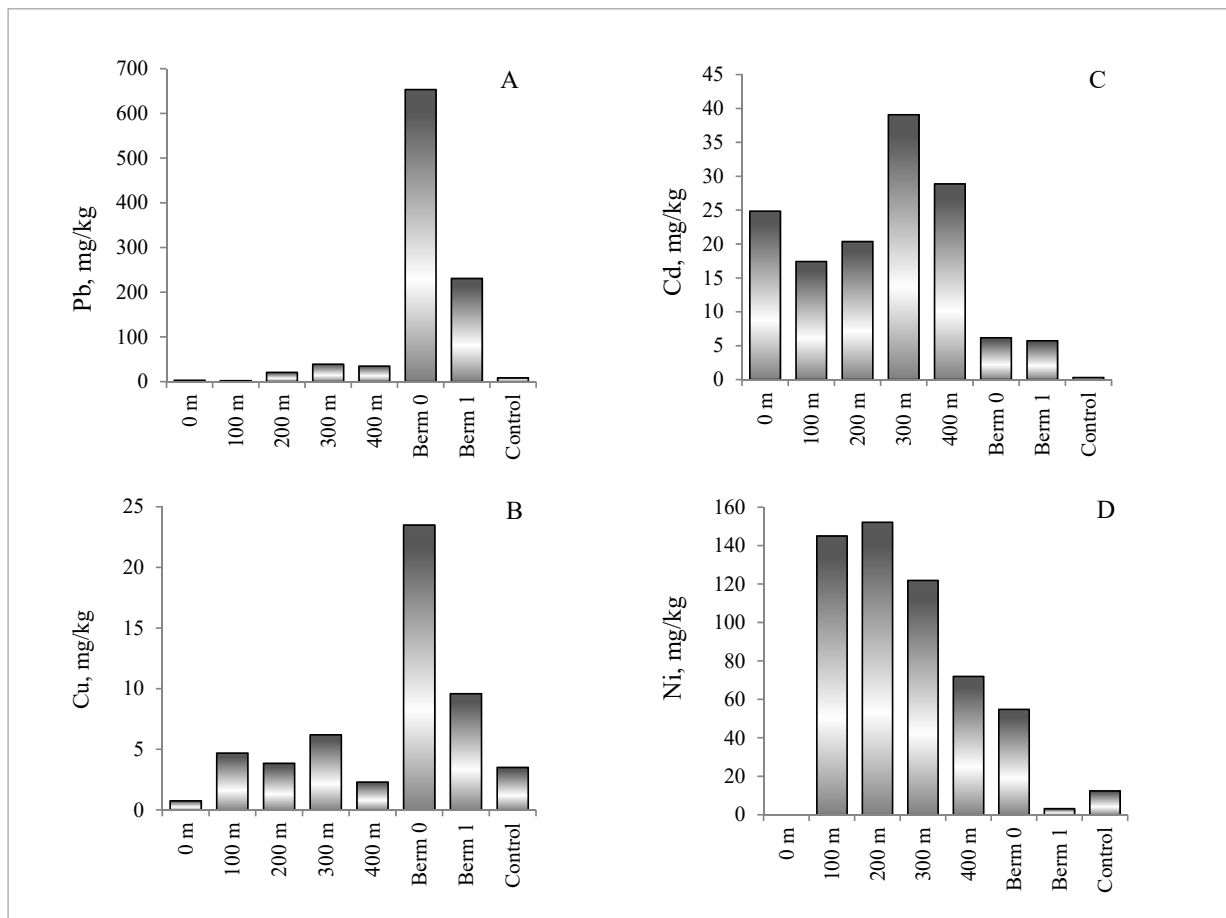
solubility of heavy metals at various conditions. For example, under the neutral soil pH,  $Pb^{2+}$  is bound to clays, organic matter and iron (Fe) hydroxides (Tandy et al., 2017). In addition, cadmium seems to be less stable in soils compared with lead (Ahmadipour et al., 2015). Our study showed that organic matter content was lower in the area where bullets dropped (back-stop berm), which is in accordance with the results observed by Murray et al. (1997). It is clear that organic matter content is one of the most important properties that determines quality, productivity and ecological functioning of soil (Kučerík et al., 2018). Therefore, our results clearly show that soil is adversely affected by shooting activity. Physico-chemical properties not only affect bullet weathering and availability of heavy

metals, but also can increase chemical stabilisation and phytoremediation of these contaminants and can improve contamination management approaches (Seshadri et al., 2017).

A high concentration of lead was found in the back-stop berm of the range. The shooting area contains back ground levels of lead. Similar results have been found by Kelebemang et al. (2017) and Sanderson et al. (2012). The study shows that the majority of lead is concentrated in the backstop berm soil as it collects used bullets. Interestingly, high concentrations of cadmium and nickel were found in the shooting range area. Although, the limit concentrations of Pb, Cd and Ni were exceeded at several samples, in comparison with other research this shooting range

**Fig. 3**

Heavy metal concentrations of the samples taken from different sites of the shooting range (A – Pb, B – Cu, C – Cd, and D – Ni)



was not highly contaminated. Islam and Park (2017) found 3436 mg/kg lead; the maximum concentration of lead that Kelebemang et al. (2017) found in the soil of the shooting range was over 10,000 mg/kg. Even abandoned shooting range soil is contaminated with lead from 160 to 720 mg/kg (Rodriguez-Seijo et al. 2016). Nevertheless, the contamination of the shooting range is serious and further investigations should be considered. However, differences of properties and contamination of heavy metals in soil of various shooting ranges suggest that overall contamination of shooting ranges is based on site-specific conditions. Therefore, a unique approach to contamination management should be applied.

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## Conclusions

The study highlighted changes in soil characteristics (pH, organic matter, and soil density) and the contamination with heavy metals of the shooting range soil. The pH value of the shooting range soil was more alkaline, lower in organic matter content (especially in the backstop berm soil), and higher in soil density. The shooting range soil contained elevated Pb and Cu concentrations, which are mostly concentrated in the backstop berm; Ni and Cd were mostly concentrated in the area of the shooting range (0–400 meters). The limit concentrations of Pb, Cd, Ni were exceeded in soil samples of the shooting range. Further studies describing contamination mitigation techniques are required.

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