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SOIL POLLUTION WITH TRACE ELEMENTS IN TERRITORIES OF MILITARY GROUNDS IN LATVIA

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Contamination of land used for military activities can significantly differ from that of municipal and industrial land, both in the intensity and type. Largely this is due to the intensity of activities even in a comparatively large surface area, and also by use of substances and materials not common in civil practice. Pollution from military grounds can affect not only soldiers, but also adjacent territories and water resources. In this study, concentrations of trace elements in the soil, water and higher vegetation in former Soviet army military territories were surveyed. The presence of point sources was found, and in a few cases the pollution is intensively spreading into deeper soil horizons and groundwater.

Key words: *military grounds, soil, pollution, heavy metals, trace elements.*

INTRODUCTION

Contamination of territories used for military activities (military grounds, polygons, training sites for development of new types of weapons) can significantly differ from domestic or industrially used territories, waste depositories, brownfields, both in intensity and type. This is largely due to the intensity of activities even in a comparatively large area, and also by use of substances and materials not common in civil practice. During military activities and training, intensive use of commonly rare substances e.g. trace elements such as additives, explosives and ingredients of chemical weapons (Clausen *et al*., 2004) or radioactive elements, for example, depleted uranium can take place (Larson *et al*., 2005). Pollution in military grounds can affect not only soldiers during training activities, but the leakage can affect also adjacent territories and water resources (Raukas, 2004). While the contamination of military areas can be considered as a serious problem, it has not been much studied (probably due to reasons of secrecy). Studies of pollution of former Soviet army military sites have been made in the former German Democratic Republic (GDR) (Renner, 1991; Anonymous, 1997; Pitten *et al*., 1999), and Lithuania (Baltrenas *et al*., 2005; Vasarevicius and Greiciuté, 2004). Several studies (Whitecotton *et al*., 2000; Quist *et al*., 2003; Idzelis *et al*., 2005; Maloney *et al*., 2006; Greičiūté *et al*., 2007) have shown adverse impact of military activities also on landscapes, biodiversity and soil properties.

The aim of this study was to evaluate soil pollution with trace elements and heavy metals of presently used former Soviet army military territories in Latvia.

MATERIALS AND METHODS

Study sites and sampling. Two military training areas in Latvia were studied—Šķēde in the western part of the country and Strautiņi in the north-east (Fig. 1). A total of 56 soil samples in 28 sites were collected in the Šķēde military site and 72 samples in 36 sites in the “Strautiņi” military base. Two soil samples were taken in each site—in the upper layer of the soil profile, mainly corresponding to the O or Ao horizons, and in a deeper layer, which in most cases corresponded to the B horizon. These samples represent not only recent deposition of pollutants, but also contamination left by the Soviet Army. Šķēde was used as a radar site and training base for border guards and Strautiņi as a nuclear missile site (Upmalis *et al*., 2006). The Šķēde military site is located in the dune zone of the Baltic Sea. In this area sod-podzolic soils as well as immature soils dominate (Kasparinskis, 2007), but in some locations technogenic and buried soils are found. The area is partly covered with forest, but lowlands are mostly grasslands, occasionally suffering from erosion due to human activities. The Strautiņi site lies in the hilly part of the Tālava lowland. In the Strautiņi military ground, soils are represented mainly by technogenic and buried soils, typical podzols are infrequent. The area is covered with spruce and pine forest. The site has a dense network of paved roads and squares; with eight large partly underground hangars and a number of ruined buildings and other structures. Presently, both military sites are used for the training of the military personnel, there are shooting ranges, as well as in areas, where trench digging is practiced. The main sources of the soil pollution with metals in both territories can be bullets and their casings used in

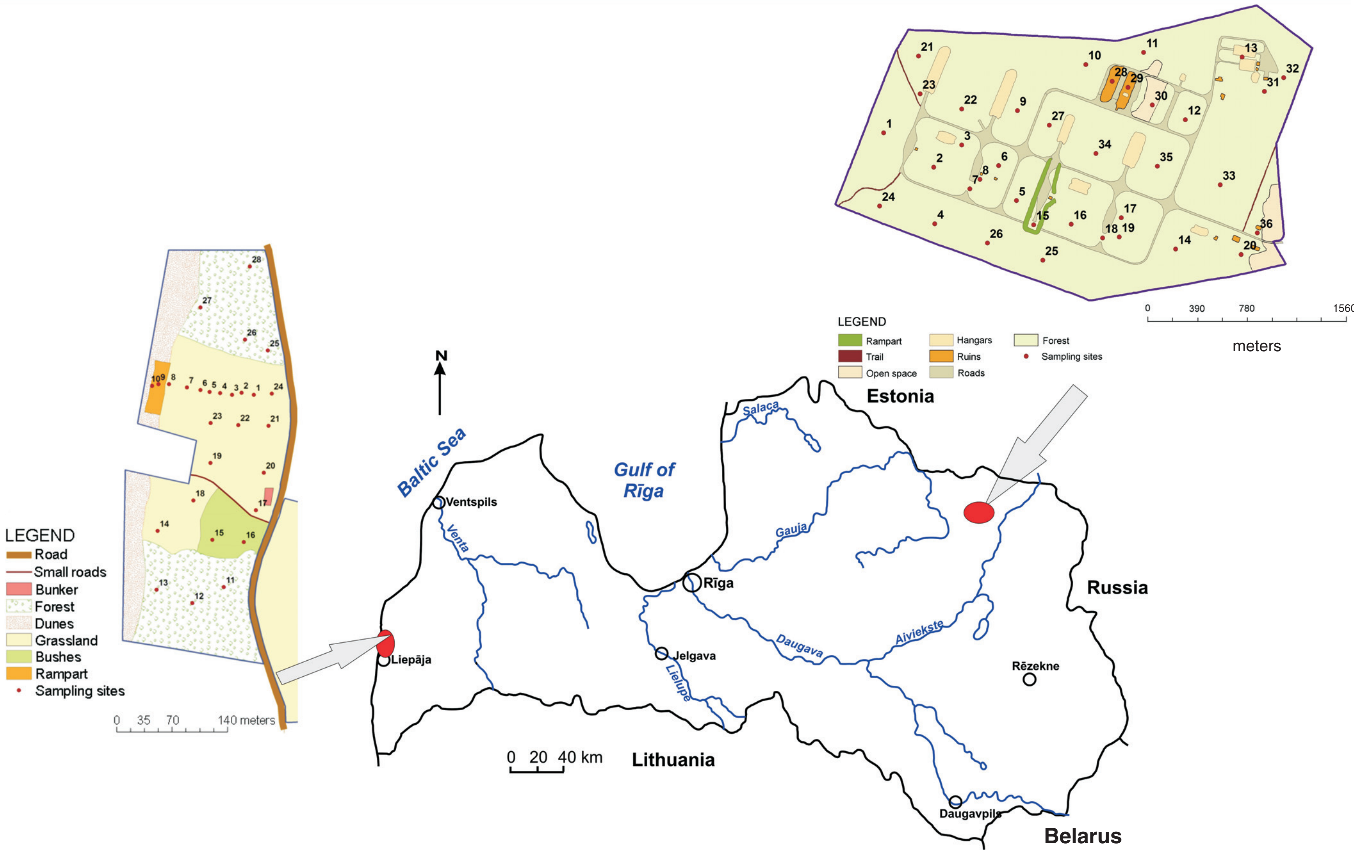

Fig. 1. Location of the studied military training grounds Šķēde and Strautiņi.

shooting exercises, and from demolition of old structures containing pollutants built by Soviet army. In Šķēde the bank rampart for bullet capture of the shooting range lies right in the seacoast, thereby subjecting the Baltic Sea to an increased risk of pollution with lead from deflected bullets. In this territory oil was stored in a large cistern and spills have polluted the soil not only with oil products, but also with heavy metals.

To estimate the uptake of the pollutants by vegetation in the areas, samples of plants were taken (six in Šķēde and nine in Strautiņi). In samples from the Šķēde military ground the dominant plants were cleavers (*Galium verum, Galium boreale*), small-reed (*Calamagrostis epigeios*), meadow grasses (*Artemisia campestris, Poa angustifolia*), milfoil *(Achillea millefolium),* hoary alison (*Berteroa incana*), hawkbit (*Leontodon autumnale*), speedwell (*Veronica chamaedrys*), and sand grass (*Leymus arenarius*), and plant samples taken in the Strautiņi site contained mostly small-reed (*Calamagrostis epigeios*), cocksfoot grass (*Dactylis glomerata*), horsetail (*Aegopodium podagraria*), clover (*Trifolium pratense*), and couch-grass (*Elytrigia repens*).

Trace element analysis using atomic absorption spectrometry. 1 gram of dried soil sample was acid digested with 25 ml of 50% HNO_3 and 5 ml H_2O_2 and heated in a steam bath until the mixture volume was halved. Then additional 25 ml of 50% HNO_3 were added and the sample was heated until boiling. Thereafter, the solution was cooled and filtered and the filtrate was diluted to 50 ml with distilled water. Samples (2 g) of dried plants were ashed in a muffle furnace at 550 ^{o}C. The ash was digested by concentrated HNO_3 and heated. The solution was filtered and diluted to 15 ml with distilled water. The analysis of heavy metals (Mn, Fe, Ni, Cu, Cr, Zn, Cd, and Pb) and macroelements (Na, K, Ca, and Mg) metals in both soil and plants was conducted using a flame atomic absorption spectrometer (Perkin-Elmer AAnalyst 200).

Additionally, six soil samples (100 g) from the Šķēde military ground were sieved through 1000 μm, 710 μm, 500 μm, 250 μm, and 50 μm sieves. Concentrations of macro- and trace elements were determined also in each of the obtained soil fractions.

Metal concentrations were measured by flame atomic absorption (Perkin-Elmer AAnalyst 200). Identification limits were (mg/l in 100 ml measuring solution): Cd-0.003; Co-0.02; Cu-0.02; Mn-0.01; Zn-0.001; Pb-0.05. For analytical quality control of total metal concentrations, the following standard reference materials (SRMs) were used: Marine Sediment Reference Materials (BCSS-1, MESS-1) from the National Research Council (Canada). The results from the analysis of SRM were all within the 95% confidence level of the SRMs.

Trace element analysis using total reflection X ray fluorescence spectrometry. Total reflection X ray fluorescence spectrometry (TXRF) analysis was carried out using Röntec PicoTAX TXRF spectrometer supplied with a 50 kV fine focus X-ray tube (Mo anode), Be detector with an active area 10 mm^2 and thickness 7.5 μm. Ga (as $GaCl_3$) was used as an internal standard and samples were placed on the glass sample window (30 mm). A multi-channel analyser coupled to a computer allowed the storage and analysis of the data. The acquisition mode supported analysis of 76 elements.

Data treatment methods. Treatment of the analytical results was made using SPSS. For preparation of maps ArcMap 9.2 was used.

RESULTS

The composition of major and trace elements in the studied soils differ significantly depending on the origin, sources and behaviour of elements in the soils: the lowest are common for elements usually found only at trace level (Cr, Ni, Cu, Pb, and others) and highest for elements of natural origin (Na, K, Mg, Fe, and Ca) (Tables 1 and 2). As indicated

Table 1

MEAN, MAXIMUM AND MINIMUM CONCENTRATIONS OF CHEMICAL ELEMENTS IN SOILS OF THE STUDIED MILITARY BASES

Element	Strautiņi military ground			Šķēde military ground			Target value[1]	Average concentration in Latvia[2]
	mean	max	min	mean	max	min		
Soil upper layer								
Ni, mg/kg	2.6	6.4	0.4	1.3	3.7	0.7	3	1.2
Cr, mg/kg	2.8	10.9	0.4	0.9	1.3	0.6	4	2.5
Cu, mg/kg	7.7	142.6	0.1	1.7	6.9	0.2	4	1.65
Pb, mg/kg	27.6	428.8	2.1	7.1	16.5	3.8	13	9.5
Zn, mg/kg	26.2	102	2.3	16.9	56	7.9	16	6.8
Mn, mg/kg	77.0	256	5	35.1	148.6	5.9		29.0
Na, mg/kg	50.2	74	26	59.6	153	18		
K, mg/kg	224.5	545	74	134.5	234	95		0.04
Mg, mg/kg	1015.9	4430	64	279.5	1229	110		
Fe, mg/kg	1981.1	4342	423	924.4	1520	400		
Ca, mg/kg	3038.1	17012	154	1372.9	8287	344		
Soil deeper layer								
Ni, mg/kg	2.0	3.8	0.7	1.0	1.6	0.7	3	
Cr, mg/kg	2.0	4.3	0.6	0.9	1.4	0.6	4	
Cu, mg/kg	1.7	8.1	0.3	0.8	3.9	0.2	4	
Pb, mg/kg	5.9	60.8	2.1	2.5	6	1	13	
Zn, mg/kg	12.2	116.9	3.8	10.8	25.9	4.6	16	
Mn, mg/kg	78.1	238	9	15.7	51.8	3.4		
Na, mg/kg	47.2	100	18	60.5	133	22		
K, mg/kg	202.5	537	67	110.1	388	79		
Mg, mg/kg	805.5	7028	88	188.3	887	114		
Fe, mg/kg	2374.7	4172	1156	761.9	2012	347		
Ca, mg/kg	2191.6	23891	79	777.0	5211	347		

[1] Republic of Latvia Cabinet of Ministers Regulations No. 804 (2005), target value for sandy soils

[2] Values for sandy soils (from Gilucis, 2007)

Table 2

TRACE ELEMENT CONCENTRATIONS IN SOILS OF STRAUTIŅI MILITARY BASE DEPENDING ON THE SAMPLING DEPTH (AS DETERMINED BY TOTAL REFLECTION X-RAY FLUORESCENCE

Element	Concentration, mg/kg									
	1*		4		10		13		14	
	upper layer	deeper layer	upper layer	deeper layer	upper layer	deeper layer	upper layer	deeper layer	upper layer	deeper layer
Ti	0.193	0.812	0.139	0.288	0.594	0.671	0.395	0.393	0.481	0.479
V	0.009	0.026	0.011	0.012	0.022	0.023	0.039	0.035	0.024	0.034
As	0.006	0.007	0.012	0.004	0.006	0.007	0.008	0.016	0.010	0.006
Br	0.039	0.006	0.007	0.007	0.011	0.009	0.005	0.006	0.005	0.006
Rb	0.009	0.025	0.005	0.010	0.036	0.025	0.024	0.020	0.026	0.020
Sr	0.031	0.020	0.018	0.007	0.032	0.011	0.088	0.028	0.032	0.019
Y	0.342	0.626	0.224	0.245	0.976	0.372	0.897	0.536	0.790	0.350
Zr	0.155	0.149	0.075	0.096	0.208	0.223	0.186	0.112	0.074	0.085
Ba	0.381	0.570	0.247	0.305	0.669	0.573	0.614	0.404	0.596	0.579
Th	0.014	0.024	0.007	0.012	0.018	0.017	0.012	0.015	0.023	0.029

* sampling stations as in Fig. 1

Table 3

TRACE ELEMENT CONCENTRATIONS IN SOILS OF ŠĶĒDE MILITARY BASE (SAMPLING STATION NR 7) DEPENDING ON THE SAMPLING DEPTH (AS DETERMINED BY TOTAL REFLECTION X-RAY FLUORESCENCE)

Element	Concentration, mg/kg				
	0–20 cm	20–40 cm	40–60 cm	60–80 cm	80–100 cm
Ti	0.258	0.408	0.409	0.577	0.689
V	0.014	0.022	0.016	0.144	0.055
As	0.003	0.003	0.006	0.012	0.045
Br	0.003	0.002	0.003	0.055	0.060
Rb	0.018	0.030	0.023	0.028	0.106
Sr	0.092	0.108	0.091	0.123	0.205
Y	0.870	2.192	0.982	26.181	4.233
Zr	0.085	0.125	0.219	2.772	2.225
Ba	0.466	0.640	0.416	0.550	0.723
Th	0.016	0.013	0.027	0.015	0.032
Cd	0.105	2.102	0.357	3.814	0.675

by TXRF analysis, in the territories of military grounds trace levels can be found also for elements such as Th, Zr, V, Sr, Rb, V, and As. For the studied sites the element concentrations in the upper soil layer are significantly higher than in the deeper layer indicating comparatively recent contamination (Tables 2 and 3). Also the variability, especially of trace elements in the upper layers, is significantly higher than in deeper layers.

The studied military territories are characterised by high spatial variability of the element concentrations (Figs. 2 and 3). The distribution of concentrations of elements of evidently natural origin (Ca, K, Fe, etc.) is quite even and their concentrations can be high also in deeper horizons. Elements associated with human activities (Cu, Cr, Ni, Pb, etc.) suggest point-source pollution, possibly associated with military activities (Figs. 2 and 3) while the mean concentrations of the pollutants are slightly elevated above concentrations common for the territory of Latvia, in the contaminated territories their concentrations are high.

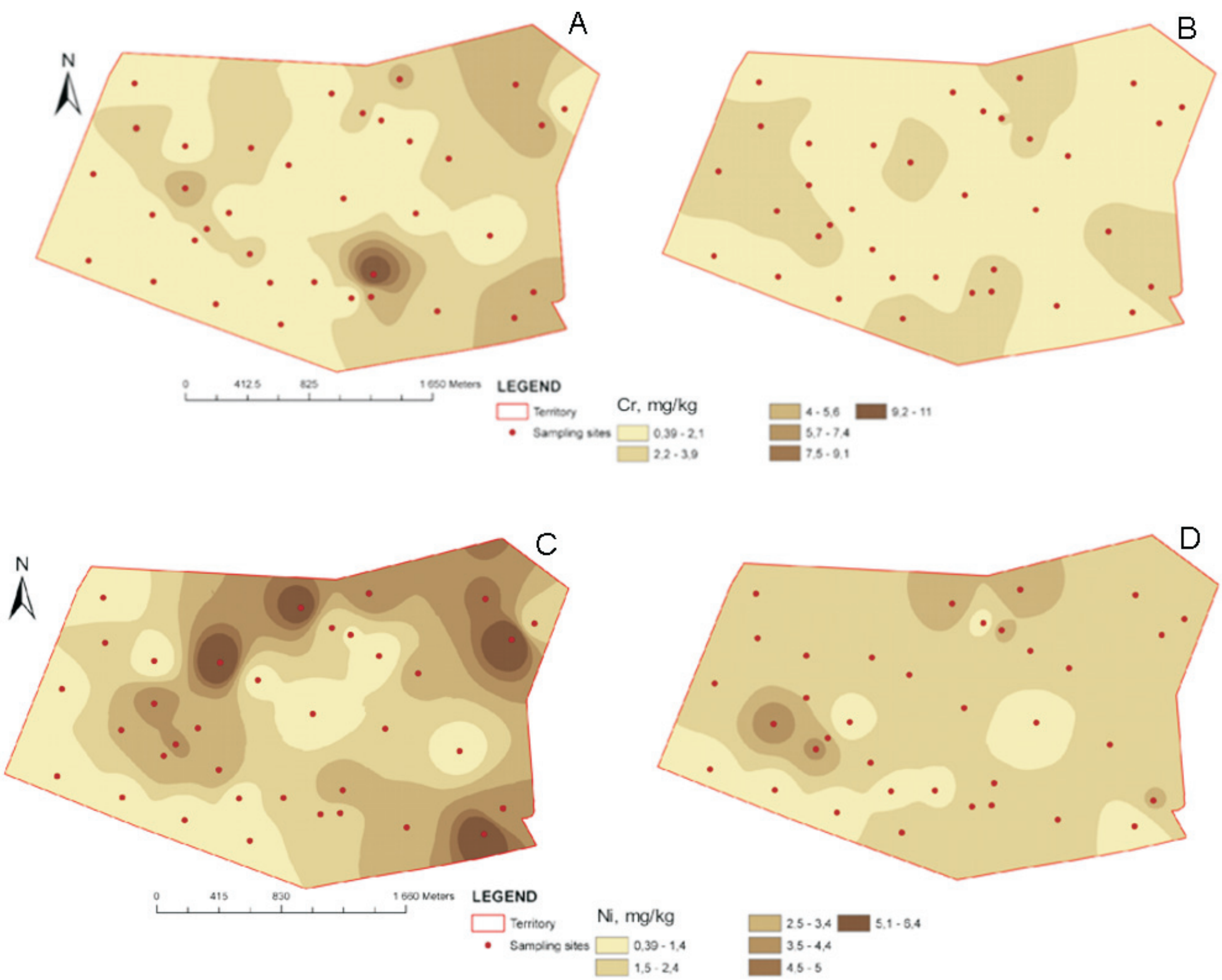

Fig. 2. Concentrations of heavy metals in soils of Strautiņi military base: **A** – Cr in soil upper layer; **B** – Cr in soil deeper layer; **C** – Ni in soil upper layer; **D** – Ni in soil deeper layer.

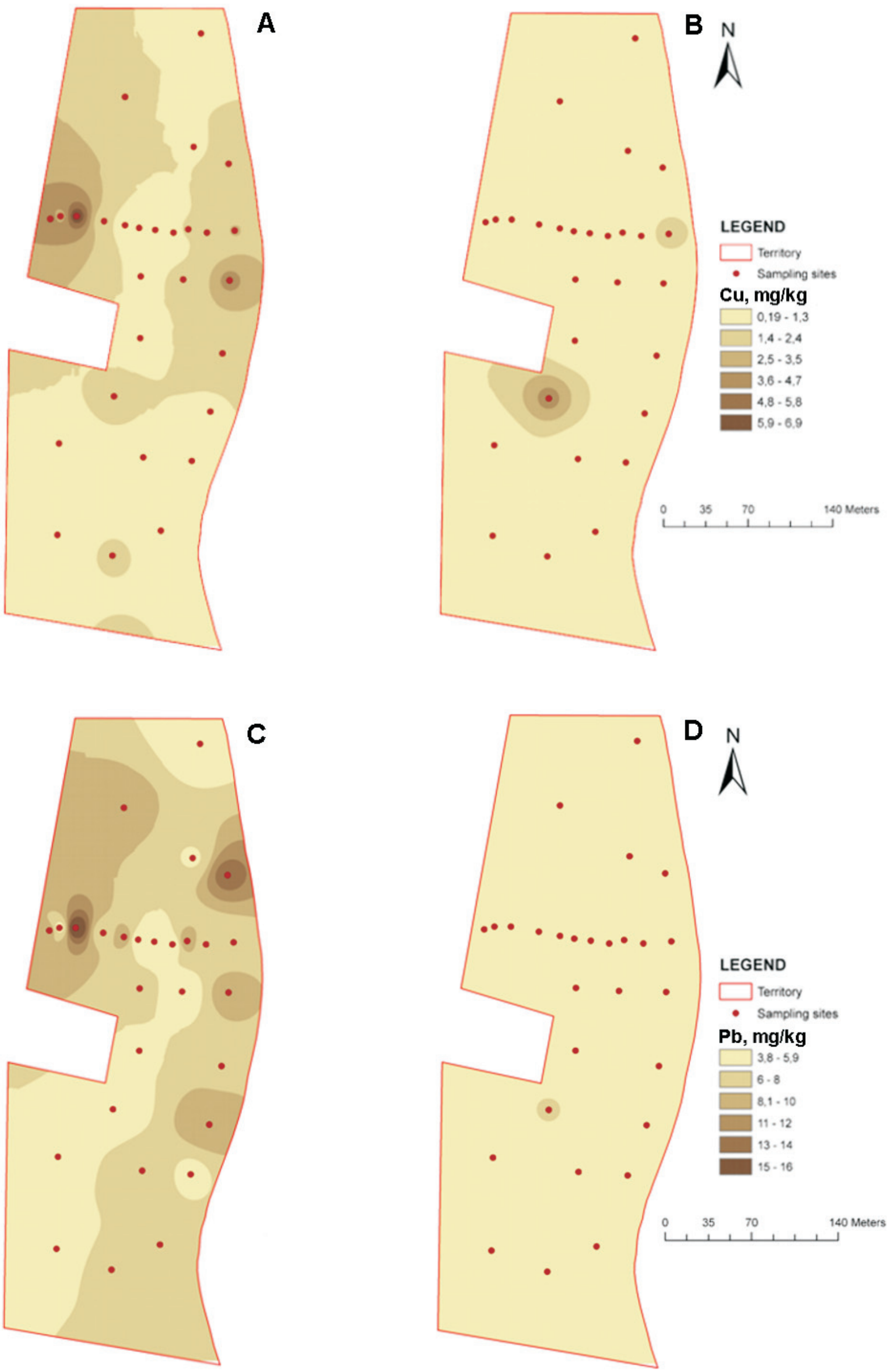

Fig. 3. Concentrations of heavy metals in soils of Šķēde military base: **A** – Cu in soil upper layer; **B** – Cu in soil deeper layer; **C** – Pb in soil upper layer; **D** – Pb in soil deeper layer.

Element and trace element composition much depends on the size of the soil material, as evident from Figures 4 and 5. The greater part of metals and trace elements are associated with smaller size fractions—clay fractions, while elements such as Na, K, Ca, and Mn that are usually associated with clay or carbonatic minerals can be found also in the larger size fraction.

DISCUSSION

Concentrations of trace elements and major elements in soils have been studied worldwide and also in Latvia (Reimann *et al*., 2000; Gilucis, 2007). Geochemical mapping provides information about the mean concentrations of elements, ranges of their variability and associations of ele-

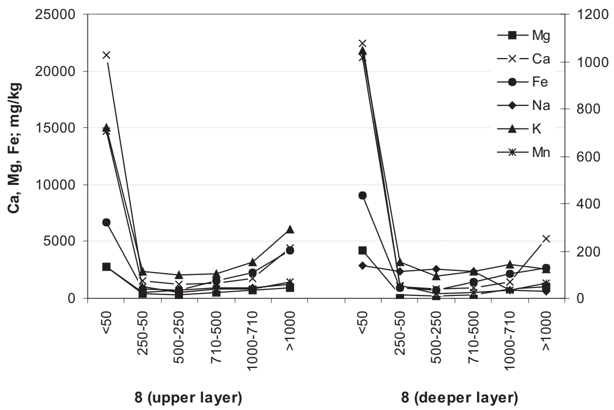

Fig. 4. Concentrations of macroelements in the soils of Šķēde military base depending on the fractional composition.

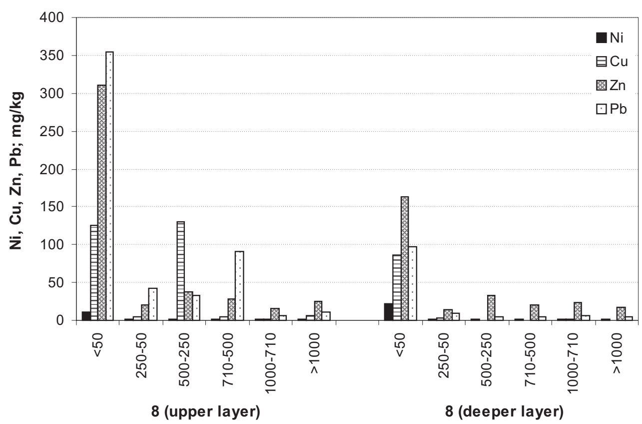

Fig. 5. Concentrations of trace elements in the soils of Šķēde military base depending on the fractional composition.

ments in the studied soils. However, contamination of territories used for military activities (military grounds) can much differ in the type of contamination, compared with pristine, agricultural, domestic or industrial territories, waste depositories, and brownfields.

In this study military sites intensively used for military activities for the last 50 years were surveyed. Multielement analysis performed using TXRF (Tables 1 and 2) showed few "unexpected" trace elements. Also the concentration levels in the most part of the studied territories (Table 1) do not demonstrate significantly higher element concentrations, especially if compared with average values common for the territories of the Baltic countries (Reimann *et al.*, 2000; Gilucis, 2007), while the mean values are well within the range common for Latvia, in some sampling stations high concentrations of toxic trace elements were recorded, for example V, Sr, Y, Th, and Cd in some stations of Šķēde and As, Zr, and Y in the Strautiņi area. While elevated concentrations of these elements have not been found to be common for Latvia, their elevated concentrations can be associated with military activities.

The spatial distribution of pollutants (Figs. 2 and 3) yet more clearly demonstrates the presence of point sources (evidently increased concentrations of trace elements). The pollution can be considered as quite recent, as it is located dominantly in upper soil layers and is associated with a small-sized soil fraction.

In conclusion, the two studied military sites in Latvia do not show extremely high pollution levels, but elevated concentrations of trace elements such as Cr, Pb, Cd, and Cu, as well as the presence of elements usually found only in trace amounts indicates the presence of pollutants posing risk. Considering this, it could be important to begin remediation activities in the studied territories.

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AUGSNES PIESĀRŅOJUMS AR MIKROELEMENTIEM LATVIJAS MILITĀRAJĀS TERITORIJĀS

Militārajās teritorijās var būt vērojama vides mehāniskā degradācija, vides objektu lietojumveida izmaiņas, kā arī ķīmiskais piesārņojums, kas var skart ne tikai pašus militāros poligonus, bet arī blakus esošās teritorijas. Pētījuma ietvaros tika ievākti augsnes un augstākās veģetācijas paraugi Strautiņu un Šķēdes armijas poligonu teritorijās makro- un mikroelementu satura analīzēm. Analīžu rezultāti rāda, ka smago metālu koncentrācija apsekoto poligonu augsnēs, lai arī nav ekstremāli augsta, tomēr pārsniedz 2005. g. LR MK noteikumos Nr. 804 noteiktos mērķlielumus Zn, Pb, Ni, Cu, Cd saturam smilts augsnēs. Atsevišķu mikroelementu, piemēram, V, Sr, Y saturs augsnēs liecina par piesārņojuma avotu klātbūtni. Lai novērstu piesārņojošo vielu iedarbības iespējamās negatīvās sekas un ierobežotu piesārņojuma tālāku migrāciju, būtu nepieciešams veikt poligonu teritorijas rekultivāciju.