



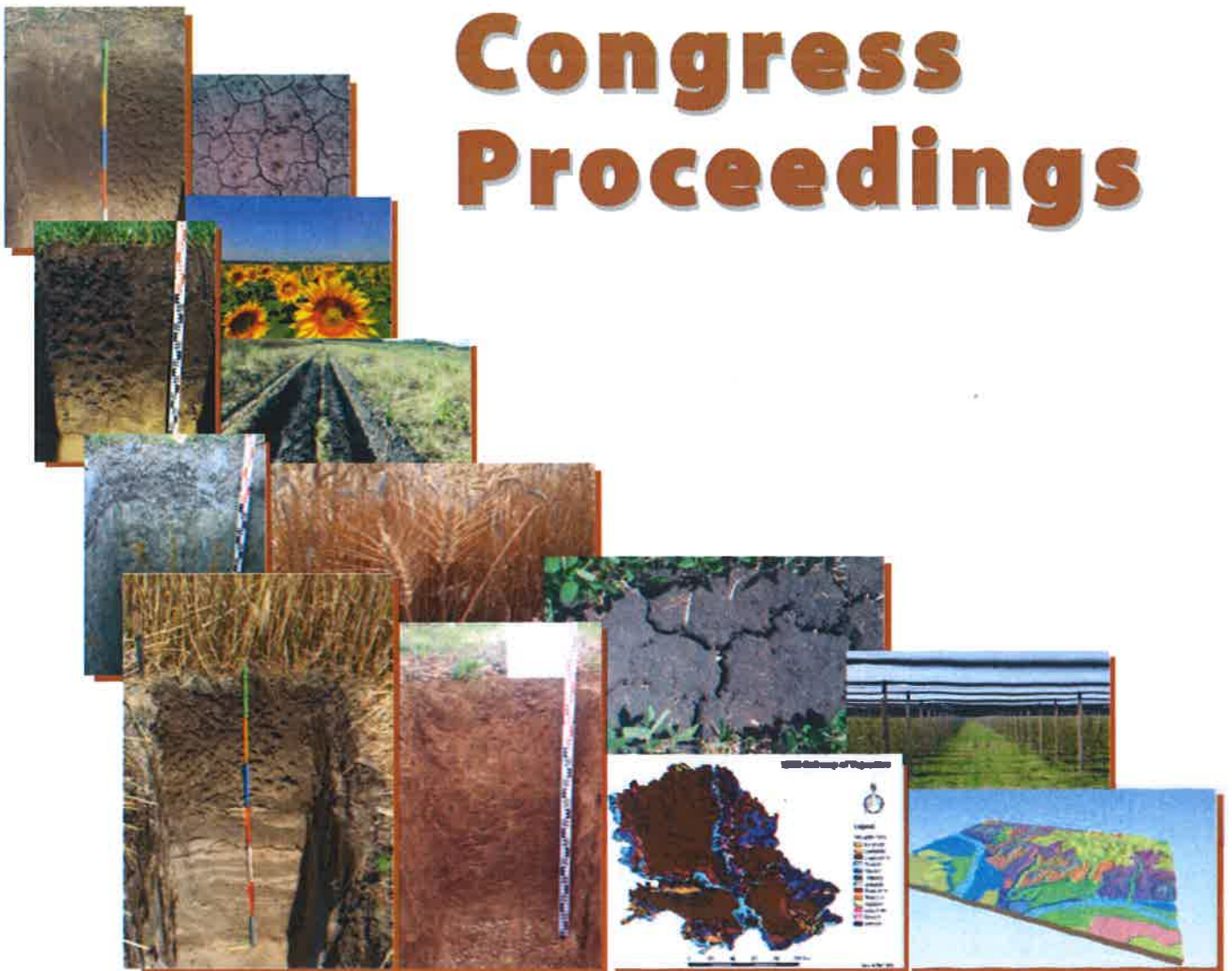
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*2<sup>nd</sup> International and 14<sup>th</sup> National Congress of Soil Science Society of Serbia*

**Solutions and Projections for Sustainable Soil Management**

**NSoil2017**

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Novi Sad, Serbia

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## Mineralogical and geochemical properties of soils around Kuti Lake

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### ABSTRACT

The subject of this study are the soils (calcomelanosol, calcocambisol and regosol) in the area of the Neretva River Delta around the Kuti Lake. The objective of this work was to determine geochemical and mineralogical properties of calcomelanosol, calcocambisol and regosol for better understanding weathering processes of source materials.

Chemical, mineralogical and geochemical analysis of the collected soils were carried out in order to determine their properties, such as soil reaction (pH), electrical conductivity, content of carbonates. Organic material was removed from the fraction <2 mm using two methods, H<sub>2</sub>O<sub>2</sub>, and NaOCl. Following that, the content of TOC was measured in order to determine the effectiveness of these two methods. The presence and importance of Fe-oxide was measured using the dithionite and oxalate treatment. Mineralogical characteristics were determined by the help of XRD. Sequential extraction analysis was made to determine the main binding site of trace metals in the soil, and evaluate their ability to evaluate the bioavailability and remobilisation. The analyses were performed according to the BCR procedure and proportions of elements were determined in four fractions: (1) carbonate, (2) the fraction of Fe-Mn oxide and hydroxide, (3) organic-sulphide, and (4) residual fraction. The following elements were measured: Cu, Mn, Zn, Co, Cd, Ni, Cr, Pb. The extracts obtained by dithionite treatment, oxalate and the sequential extraction analysis were measured by atomic absorption spectrometry.

Calcomelanosol and calcocambisol soils have slightly acid pH, while in regosol is slightly alkaline. Proportion of well crystallized is higher than poor crystallized Fe oxides. Phyllosilicates are dominant mineral phase in calcomelanosol and calcocambisol. Beside this mineral, quartz and mica minerals are also present in analysed soils. Most of analysed elements are bound to residual fraction. Cadmium has higher concentration in organic sulphide fraction.

**KEY WORDS:** calcomelanosol; calcocambisol; regosol; mineralogical and geochemical properties; Kuti Lake

### INTRODUCTION

Geochemical and mineralogical properties of soils may give an insight into the influence of factors determining weathering rates. The investigate area is built of carbonate and dolomite rocks and flysch sediments. Regosol are formed mainly on unconsolidated parent substrate and marl, limestone and flysch. Regosol on flysch is widespread throughout the Adriatic region and islands (Bašić, 2013). Regosol development is totally influenced by the properties of parent material (Hristov, 2016). The main component that determine the soil reaction in these soils are carbonates (Hristov, 2014). Calcomelanosol occurs only on limestone or dolomite rocks. The dominant process of Calcomelanosol genesis is dissolution and leaching of calcium and magnesium. Calcocambisol is formed by dissolving calcite and/or dolomite and by accumulation of insoluble residue on stable relief positions protected from water and wind erosion (Bašić, 2013). Heavy metal retention by soils can be evaluated by investigating their partitioning among the various geochemical phases (Navas and Lindhorfer, 2005). The partitioning of metals in soils is element specific and depends on soil properties such as soil pH, organic matter, clay, and oxide concentrations (Brümmer et al., 1986). The subject of this study are the soils (Calcomelanosol, Calcocambisol and Regosol) in the area of the Neretva River Delta around the Kuti Lake. The objects of this research was: a) to determinate geochemical and mineralogical properties of Calcomelanosol, Calcocambisol and Regosol for better understanding weathering processes of parent materials and b) to study the mobility of selected heavy metals in investigated soils.

## MATERIALS and METHODS

Field research was conducted in the area of Kuti Lake, which is located near Metković town in Croatia. The field research consisted of sampling and description of soils.

Three disturbed soil samples (0-25 cm) for laboratory analysis were collected from Calcomelanosol, Calcocambisol and Regosol soils. Soil samples were air-dried and passed through a 2 mm sieve for laboratory analysis.

Chemical, mineralogical and geochemical analysis of the collected soils were carried out in order to determine their properties, such as soil reaction (pH), electrical conductivity and content of carbonates. The presence of Fe-oxides was determined based on iron extractable with Na-dithionite-citrate bicarbonate (both well and poorly crystallized Fe-oxide phases; Fe<sub>d</sub>) and iron extractable with ammonium oxalate (poorly crystallized Fe-oxide phases; Fe<sub>o</sub>) after the method of Mehra and Jackson (1960). Mineral composition was determined using XRD analyses. Sequential extraction analysis of heavy metals was made to evaluate their bioavailability and remobilisation. The analyses were performed according to Rauret et al. (2001) and proportions of elements were determined in four fractions: (1) carbonate, (2) the fraction of Fe-Mn oxide and hydroxide, (3) organic-sulphide, and (4) residual fraction. The following elements were measured: Cu, Mn, Zn, Co, Cd, Ni and Cr. The extracts obtained by dithionite treatment, oxalate and the sequential extraction analysis were measured by atomic absorption spectrometry (AAnalyst 700, Perkin Elmer).

## RESULTS and DISCUSSION

Table 1 present physical and chemical characteristics of Calcomelanosol, Calcocambisol and Regosol type of soils. Values of pH vary from 6.41 to 7.18. Calcocambisol and Calcomelanosols belongs to slightly acid while Regosol to slightly alkaline to neutral soil. Hamidovic et al. (2013) and Miloš and Bensa (2014) also reported similar pH values for Calcocambisol soils. Electrical conductivity is the highest in Calcomelanosol, and the smallest in Regosol, due to their geochemical and mineralogical properties. Carbonate content of investigated soils vary. Miloš and Bensa (2014) reported similar carbonate content for Calcocambisol soils. The highest proportion is determined in Regosol due to their source material. Fe<sub>o</sub>/Fe<sub>d</sub> ratio is low indicating prevalence of well crystallized iron oxides (Table 1). Merkli et al. (2009) found similar proportion of Fe oxides in Calcomelanosol and Calcocambisol soils. On the contrary, Mn<sub>o</sub>/Mn<sub>d</sub> ratio indicate prevalence of poorly crystallized Mn-oxides (Table 1).

**Table 1**

Physical and chemical properties of the investigated soils. Units for Fe are in mass.%, while for Mn are in mg/kg.

Soil type	pH (KCl)	EC (µS/cm)	CaCO <sub>3</sub> (%)	Fe <sub>d</sub>	Fe <sub>o</sub>	Fe <sub>o</sub> /Fe <sub>d</sub>	Mn <sub>d</sub>	Mn <sub>o</sub>	Mn <sub>o</sub> /Mn <sub>d</sub>
Calcomelanosol	6.67	171.2	0.57	3.80	0.67	0.18	737	591	0.80
Calcocambisol	6.41	124.2	0.78	3.90	0.71	0.18	694	561	0.81
Regosol	7.18	123.5	49.68	0.62	0.11	0.18	210	90	0.43

Phyllosilicates are dominant mineral phases in Calcomelanosol and Calcocambisol (Table 2). Both soil types contain chlorite and/or kaolinite as dominant phyllosilicate mineral phases while mica and mixed-layer clay minerals are subordinate. Regosol is dominated by calcite, while main phyllosilicates are mica, 14 Å phyllosilicates and mixed-layer clay minerals. Raičević et al. (2016) found similar mineral composition of Calcocambisol and Calcomelanosol in their study. The similar mineralogical composition reported by Hristov et al. (2010) in their study of Regosols.

**Table 2**

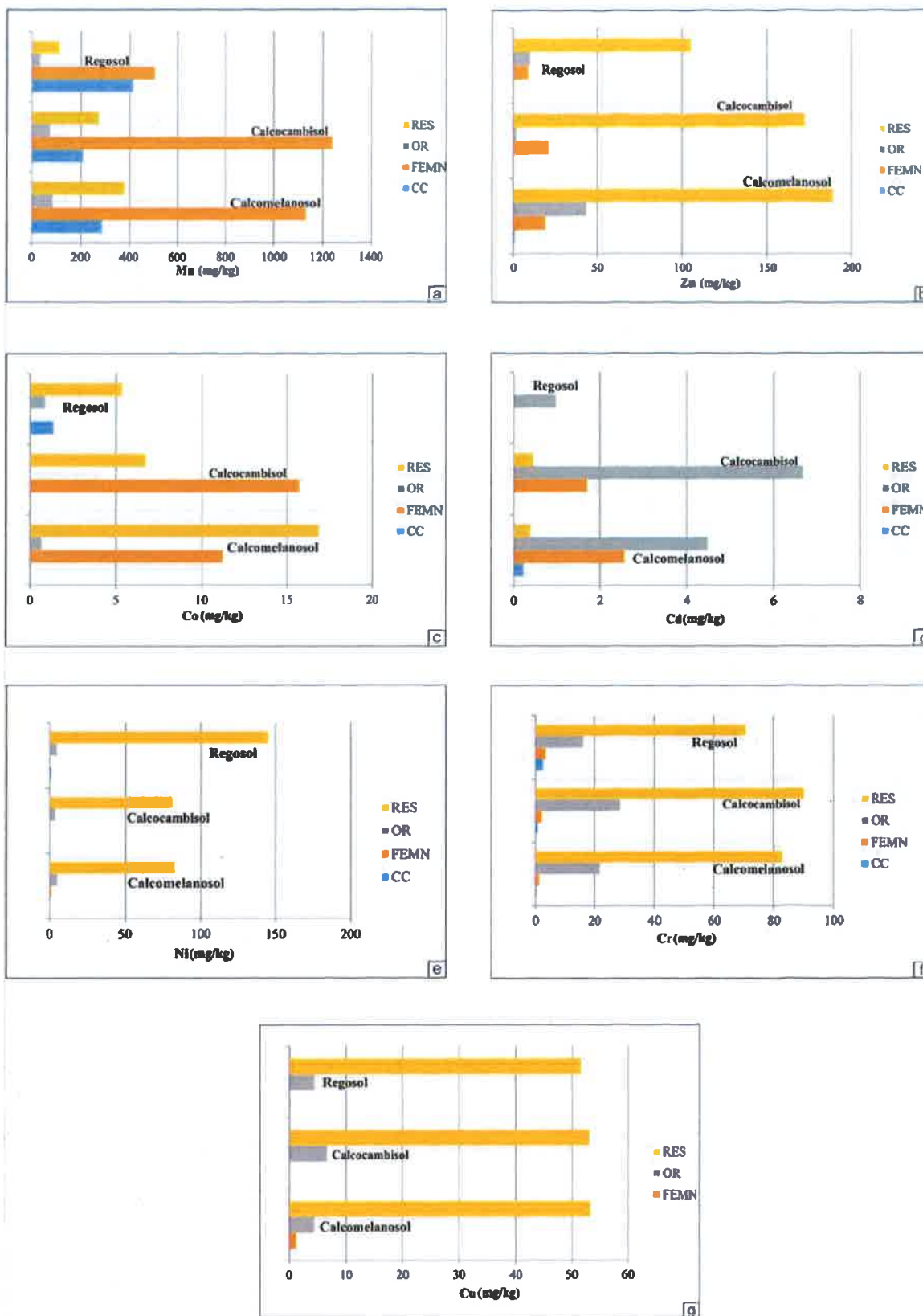
Semi-quantitative mineral composition of the <2 mm fraction of soils. Legend: Q-quartz; Cal-calcite; Dol-dolomite; Pl-plagioclase; Kfs-potassium feldspars; M-mica minerals; Gt-goethite; Hem-hematite; Kln-kaolinite; Chl-chlorite; 14 Å-14 Å phyllosilicates; MM-mixed-layer clay minerals; AM-amorphous matter; + = mineral is present in the sample; ++-major mineral content (10-20 mass. %);+++-dominant mineral content (>20 mass. %);--mineral is not present in sample; ? = mineral is probably present in the sample but due to the low content and/or overlapping of diffraction peaks cannot be confirmed with certainty.

Soil	Qtz	Cal	Dol	Pl	Kfs	M	Gt	Hem	Kln	Chl	14 Å	MM	AM
Calcomelanosol	16	3	2	4	2	++	+ Gt and/or Hem		+++ Chl and/or Kln		?	++	++
Calcocambisol	15	-	-	?	?	++	+ Gt and/or Hem		+++ Kln and/or Chl		?	++	+/+ +
Regosol	11	50	-	2	?	++	?		?		++		+

The highest Mn concentration is determined in FEMN fraction of Calcocambisol (Fig. 1a). The similar values of manganese determined by Redžić et al. (2014) in their study of Calcocambisol. Total concentrations of Zn varies between 105.6 to 190.2 mg/kg (Fig. 1b). Total concentrations of 170 mg/kg of zinc is determined. Dvořák et al. (2003) measured similar concentrations of zinc in Calcocambisol. After RES fraction, Zn is bound to OR fraction. Zinc is bound to CARB fraction only in Calcomelanosol. Total concentrations of Co varies between 5.32 to 16.90 mg/kg (Fig. 1c). After RES fraction, Co is bound to FEMN fraction. Cobalt is bound to CARB fraction only in Regosol. The maximum Cd concentrations are determined in OR fraction (Fig. 1d). The Cd distribution for all fractions is same in Calcomelanosol and Calcocambisol. Total concentrations of Ni varies between 81 to 145 mg/kg (Fig. 1e). All samples show same trend of Cr in fractions (Fig. 1f). After residual fraction, chromium is bound to the organic fraction. This agrees with findings by Balasoiu et al. (2001) that reported high retention of Cr in organic fraction in soils.

Total concentrations of Cu varies between 52.27-54.80 mg/kg (Fig. 1g). After RES fraction, Cu is bound to OR fraction. Cu is bound to FEMN fraction only in Calcomelanosol. Pakula and Kalembasa (2013) in Calcocambisol reported the highest concentration of Cu in the residual fraction, and the lowest in the carbonate fraction.





**Figure 1.** a) Distribution of Mn in fractions of soils; b) distribution of Zn in fractions of soils; c) distribution of Co in fractions of soils; d) distribution of Cd in fractions of soils; e) distribution of Ni in fractions of soils; f) distribution of Cr in fractions of soils; g) distribution of Cu in fractions of soils.

## CONCLUSIONS

Calcomelanosol and Calcocambisol soils have slightly acid pH, while in Regosol is slightly alkaline to neutral.  $Fe_0/Fe_d$  ratio is low in all soil typed and indicates prevalence of well crystallized iron oxides. Both Calcomelanosol and Calcocambisol contain chlorite and/or kaolinite as dominant phyllosilicate mineral phases while mica and mixed-layer clay minerals are subordinate. Regosol is dominated by calcite, while main phyllosilicates are mica, 14 Å phyllosilicates and mixed-layer clay minerals. Most of analysed elements are bound to residual fraction. Cadmium has higher concentration in organic sulphide fraction due to its affinity to organic matter which is in line with mineralogical composition. The metal retention in studied soils can be put in the following order: Calcocambisol>Calcomelanosol>Regosol.

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