Cation exchange capacity of loess and overlying soil in the non-carbonate loess sections, North-Western Croatia

Nenad Tomašić1, Štefica Kampić1, Iva Juranić Cindrić2, Kristina Pikelj3, Mavro Lućić1, Danijela Mavrić1, Tajana Vučetić1

1 Institute of Mineralogy and Petrology, Faculty of Science, University of Zagreb, Horvatovac 95, HR-10000 Zagreb, Croatia
2 Laborator of Analytical Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia
3 Institute of Geology and Paleontology, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia

Received 30 July 2013; accepted 7 October 2013

Abstract: The adsorption properties in terms of cation exchange capacity and their relation to the soil and sediment constituents (clay minerals, Fe-, Mn-, and Al-oxyhydroxides, organic matter) were investigated in loess, soil-loess transition zone, and soil at four loess-soil sections in North-Western Croatia. Cation exchange capacity of the bulk samples, the samples after oxalate extraction of Fe, Mn and Al, and after removal of organic matter, as well as of the separated clay fraction, was determined using copper ethylenediamine. Cation exchange capacity (pH~7) of the bulk samples ranges from 5 to 12 cmol/kg in soil, from 7 to 15 cmol/kg in the soil-loess transition zone, and from 12 to 20 cmol/kg in loess. Generally, CEC values increase with depth. Oxalate extraction of Fe, Mn, and Al, and removal of organic matter cause a CEC decrease of 3-38% and 8-55%, respectively, proving a considerable influence of these constituents to the bulk CEC values. In the separated clay fraction (<2 µm) CEC values are up to several times higher relative to those in the bulk samples. The measured CEC values of the bulk samples generally correspond to the clay mineral content identified. Also, a slight increase in muscovite/illite content with depth and the vermiculite occurrence in the loess horizon are concomitant with the CEC increase in deeper horizons, irrespective of the sample pretreatment.

Keywords: loess • topsoil • cation exchange capacity • clay minerals

© Versita sp. z o.o.

1. Introduction

Loess is an aeolian deposit which covers significant continental areas. It has been extensively investigated as it contains a record of quaternary climate changes. Generally, loess has been deposited in periglacial areas during glacial periods, and it is a good material to probe climate variations. Many mineral proxies in loess have been utilized in that respect, especially when temperature changes and precipitation variations are concerned. Mineral composition, particularly changes in clay mineralogy throughout loess sections and paleosol horizons [1–6], magnetic susceptibility and iron oxide mineralogy [7] as well as grain size of the sediment [8] are among those...
most frequently examined in the Quaternary climate research. Soil development upon loess horizons has been promoted in the interglacial stages during warm climate periods. This soil represents valuable arable areas due to its fertility and spreading in moderate climate regions.

In inland areas of Croatia loess deposits stretch from the northwestern to eastern regions. Especially, well-exposed loess-paleosol sections in the eastern part of the country have been extensively investigated, and they are situated along the right bank of the Danube River [9–11]. Here, granulometry, calcium carbonate content, mineralogical properties, mollusc record, total organic carbon, luminescence dating, magnetic susceptibility and geochemical studies have been used as proxies for climate and environmental changes during the Middle and Late Pleistocene. This loess area continues eastwards to neighboring Vojvodina, Serbia, with the well documented paleoclimatic periods. This soil represents valuable arable areas due to its fertility and spreading in moderate climate regions.

Inland areas of Croatia loess deposits stretch from the northwestern to eastern regions. Especially, well-exposed loess-paleosol sections in the eastern part of the country have been extensively investigated, and they are situated along the right bank of the Danube River [9–11]. Here, granulometry, calcium carbonate content, mineralogical properties, mollusc record, total organic carbon, luminescence dating, magnetic susceptibility and geochemical studies have been used as proxies for climate and environmental changes during the Middle and Late Pleistocene. This loess area continues eastwards to neighboring Vojvodina, Serbia, with the well documented paleoclimatic record of the Batajnica loess sequences [12, 13] as one of the most complete records of the Middle and Late Pleistocene climate variations in the region. The loess deposits have been described in the Carpathian area (Romania, Ukraine) [13, 14], as well as in Hungary, where chemical weathering in the last 800 ka was investigated [15] but also the rate of the atmospheric dust deposition in the Pleistocene was calculated [16].

Adsorption properties of a sediment and overlying soil are an important feature of environmental significance: it helps modern agriculture plan an intensive but sustainable production. Also, it can be helpful in the assessment and evaluation of environmental hazards due to agricultural and industrial activity, urban pollution, and any accidental threat to environment. This particularly deserves attention in loess areas which are extensively populated.

Since adsorption properties of a sediment and soil are dependent on their composition, it is of interest to relate them to the main sediment and soil constituents. Adsorption in sediments and soils is mostly influenced by clay mineralogy, iron, manganese and aluminum oxyhydroxides, and organic matter. Clay minerals can significantly influence this property depending on the prevailing clay minerals in a sediment and soil. Their cation exchange capacity can be as low as 5-15 cmol./kg for kaolinite and up to more than 100 cmol./kg for vermiculite [17, 18]. Organic matter largely contributes to the overall adsorption score of certain soils. For instance, in some types ofoxic soils in tropical climate regimes organic matter proved to have a prevailing role as much as copper was concerned [19, 20]. Adsorption of copper in soil has been frequently studied due to the role of copper in bio-ecological cycles and its importance for plant nutrition. Also, its presence in some fertilizers, different kinds of residue and various agrochemicals applied in agricultural production can cause possible toxic effects. Organic matter strongly effects copper adsorption in soil when pH is around neutral [21]. In acidic environments metal oxides are more important, although less than is the case for organic matter in pH neutral soils. In this paper, adsorption properties in terms of cation exchange capacity (CEC) were investigated in loess and overlying soil of four loess–soil sections in the north-western part of Croatia. Adsorption properties of bulk samples as well as those upon removal of Fe-, Mn-, Al-oxyhydroxides (oxalate extraction), organic matter, and the one of the clay fraction alone (<2 µm) were mutually compared. A contribution of certain soil and sediment constituents to CEC was assessed throughout the investigated loess–soil sections. Contrary to most of the loess spread around the world, the investigated loess and accompanying soil are carbonate-free, and in this respect the adsorption properties could slightly diverge throughout the soil–loess sections. This is especially true for the distribution of clay minerals since carbonate leaching supports eluviation of clays [6]. The application of the copper ethylenediamine method for determination of CEC in this study could be considered advantageous due to a general interest in copper adsorption behavior in different soil types, especially when arable land is concerned. Also, this is not a commonly used method for CEC determination, especially not in the loess studies, and the data obtained could be a reference for comparisons to other CEC methods frequently applied.

2. Materials and methods

2.1. Sampling area and geological background

The investigated area stretches up to 60 km eastwards and northeastwards from the Croatian capital Zagreb (Figure 1). The loess and soil samples were collected at the sites of the abandoned quarries where loess material with appropriate clay content was exploited for brick production industry. Open loess-soil sections down to 3-12 m in depth were chosen as sampling sites. The samples were collected at three horizons in the loess-soil sections (depth): loess horizon (C-horizon) (3-12 m), transition horizon (B-horizon) between loess and topsoil (40-50 cm), and topsoil horizon (A-horizon) excluding upper 15 cm of the soil organic/humic layer (15 cm). The sampling was done by using a sampling shovel, and approximately a kilogram of each sample was collected. The horizons could be mutually distinguished by color: the loess horizon was yellowish brown to ochre, the topsoil was