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# Investigation of Cl⁻ and SO₄²⁻ anion absorption in natural soils

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## Abstract

*In this paper, the results of vertical migration of chloride and sulphate anions in soil are presented. The soil was contaminated with NaCl and CuSO₄. Anions migration were monitored during one hydrological year (425 days). The first sample was taken after 150 days and afterwards samples were taken every 50 days. Before the profile contamination physical and chemical analyses of soil have been done. The obtained results show that chloride concentration in soil was in the range from 0.67 mg/kg up to 11.92 mg/kg, while sulphate concentration was in the range from 0.65 mg/kg up to 9.79 mg/kg.*

*Keywords: natural soil, characterization, anion absorption*

## I. Introduction

The surface charge of soil particles may significantly affect the distribution of cations and anions between soil and water. If the soil particle is negatively charged, then the concentration of anions near the surface decreases. Consequence of this phenomenon is formation of anion-depleted or anion-free water layers, i.e. anion exclusion volume in soils [1,2].

Bower and Goertzen [3] showed that concentration of chloride near the particle surfaces of arid low-organic matter soils is less than in some distances from the surfaces, and the volume of such an anion-depleted water layer decreased with the increasing in chloride concentration. Exclusion of anions (such as nitrate, sulphate and carbonate) was shown to be a dominant electrostatic interaction of anions with charged inorganic surfaces in the natural mixtures containing soils [4–6]. Similarly to clays, a negative absorption of anions may occur in humic substances [7].

Some researchers [7,8] consider that sulphate absorption is simply electrostatic in nature but the most authors [9–11] think that the absorption is a ligand exchange reaction between sulphate ions and hydroxyl groups or water molecules, coordinately absorbed by the soil. In order to describe the absorption, many models have been proposed [12–15].

In soil systems there are a lot of cations and anions present together with sulphate. It has been found that cations such as $Ca^{2+}$, $K^+$ and $Na^+$, affected the absorption of sulphate differently [16,17]. Barrow [18] studied reaction of anions and cations with soils. He concluded that selective absorption caused a stronger affinity of soils surface or soil components for anions than for cations.

The aim of this work is to study the dispersion of chloride and sulphate anions in the first and second soil horizon.

## II. Experimental

The study area selected for the investigation is a small agricultural valley located at Rudovci tableland near Lazarevac, Serbia (44°22' N, 20°24' E). The average inclination of the slopes of the study area is 4–5° and the study area is 4 km². The average annual rainfall of the study area is 675 mm per year.

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The soil was contaminated with NaCl and $CuSO_4$. Anions migration were monitored during one hydrological year (425 days). The first sample was taken after 150 days and afterwards samples were taken every 50 days (the last one after 425 days). The samples in the undisturbed condition are used for the determination of chemical characteristics of the soil. The samples in their natural state were taken from site in the undisturbed area. All those samples were taken with special cylinder with strictly defined volume of 100 $cm^3$, called Kopecky's cylinder. The cylinders have one sharp side for easier indenting the ground surface. The samples were taken from the surface to the horizon depth. The ground surface needs to be prepared for taking samples [19]. It means that it needs to be clean and smooth, without roots and grass. The bulk density of the soil was determined. Bulk density presents the ratio of soil mass dried at 105°C and its volume in natural state defined by the Kopecky's cylinder. Data for 24 soil samples were taken into account in this research.

The organic matter content was determined by the wet digestion method described by Mebius [20]. The wet oxidation procedure included potassium dichromate with external heat and back titration to measure the amount of unreacted dichromate. Soil pH is a measure of the soil acidity. pH value was measured on a Cyber-Scan 510 pH-meter.

The soil specimens were taken by horizons and for this investigation the sample from the first horizon was used. The mechanical composition is determined using sedimentation method [21]. After drying the sample was sifted through 0.2 mm sift and it was ready for characterization.

The crystal structure of soil before and after mechanical milling was examined by X-ray diffractometer Siemens D-500, with Cu $K_\alpha$ radiation. The diffracted X-rays were collected over $2\theta$ range 20–80° using a step width of 0.02° and measuring for 1 s per step.

Anion concentrations were determined by standard analytical titration.

### III. Results and discussion

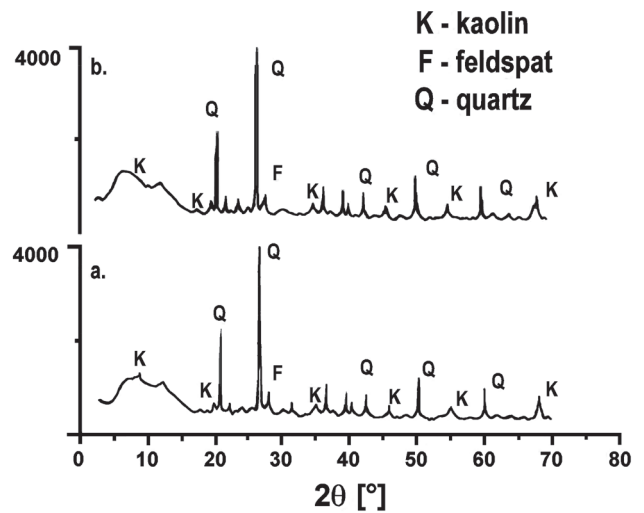Mechanical composition influences physical and chemical properties of the soil and their processing. Me-



**Figure 1. XRD analysis of soil: a) frst horizon (depth from 0 to 13 cm) and b) second horizon (depth from 13 to 30 cm)**

chanical elements of the soils have a significant difference in their dimensions, shapes, origin, mineralogical composition and chemical and physical properties. Particles dimensions are in the range from several millimetres to several nanometres [22]. According to soil classification of Wiegner [23] by its texture and percentage composition of physical clay, those samples are classified as a light clay. In Table 1 the chemical composition for each horizon is presented and their size detected by XRF analysis. By decreasing the particle size amount of $SiO_2$ decreases and amount of $Al_2O_3$ increases [22]. These results in different oxide ratio affect chemical and physical properties.

The recent investigation shows that all types of soils have more or less complex mineralogical composition [25]. X-ray analysis of soil, shown in Fig. 1, gave basic data of qualitative composition of soil samples. Soil powder consists of different minerals and the most frequent components are kaolin, quartz and feldspate. Mineralogical composition of the specified fraction of particles is different and depends on their chemical composition. Quartz in the soils has primary volcanic origin and it is the most frequent in acid soils.

**Table 1. The chemical composition of the first and second soil horizon**

| Depth [cm] | $SiO_2$ [wt.%] | $Al_2O_3$ [wt.%] | CaO [wt.%] | $K_2O$ [wt.%] | $Fe_2O_3$ [wt.%] | $ZrO_2$ [wt.%] | $TiO_2$ [wt.%] |
|---|---|---|---|---|---|---|---|
| 0–13 | 74.93 | 4.89 | 1.72 | 3.65 | 3.27 | 0.047 | 1.22 |
| 13–30 | 74.95 | 4.85 | 1.502 | 3.68 | 3.33 | 0.05 | 1.15 |

**Table 2. Determination of texture and soil moisture ($W_{H2O}$)**

| Depth [cm] | Sand [wt.%] | Silt [wt.%] | Clay [wt.%] | $W_{H2O}$ [wt.%] |
|---|---|---|---|---|
| 0–13 | 3.2 | 2.7 | 55.48 | 3.52 |
| 13–30 | 2.0 | 1.6 | 59.19 | 4.54 |

In order to better explain the dispersion of pollutants in soil, the soil texture and moisture were investigated (Table 2). The amount of moisture depends on the mechanical, mineralogical and chemical composition of the soil. Clay-rich humus soils show higher moisture content, $W_{H_2O}$, than sands and sandy soils. Soil moisture is strongly affected by the amount of water, and the porosity of soil, primarily on the size and pores shape, as well as the presence of cracks and a capillary behaviour of land fauna [22].

One of the investigations conducted in the soil analysis was determination of soil bulk density. According to the SEM image analysis, increasing the sampling depth, size of pores decrease, because the interstitial space is filled with clay [22]. By depth increasing, percentage of clay increases (Table 2), therefore increasing size of pores in the soil have an influence on bulk density lowering it and vice versa.

Table 3 presents the results of bulk density and filtration coefficient of soil. The filtration coefficient $K$ was determined by the following equation:

$$K = \frac{al}{A\Delta t} \ln \frac{H_1}{H_2} \qquad (1)$$

where $a$ is the diameter of the pressure pipe, $l$ height of the soil sample, $A$ is the vertical section of the experimental body, across the stream direction, $H_1$ pressure height at the moment $t_1$, $H_2$ pressure height at the moment $t_2$ and $\Delta t$ is $t_2 - t_1$. In order to avoid the random error due to inhomogeneous of soil, three samples from each sampling depth were investigated and the average value was calculated. Analysing the obtained results, it is clear that the filtration coefficient of the first horison has a greater value. The obtained results confirmed the previously stated conclusion which presented in Table 2.

Table 4 presents the pH values for samples in the first profile. Obtained values are in the range from 5.1 to 6.9, what confirm some of these soil profiles have a great acidity (5.1). The greatest pH value was detected in the second horizon, during the second and eighth sampling (6.9), what confirm almost neutral behaviour. Those significant differences between pH values can be a consequence of the hydrological periods of rain and dry seasons.

In order to determine the physical and chemical properties of soil profiles, the anions concentration in natural state were determined. The values of the natural ions concentration were subtracted from absorbed values in order to determinate of $Cl^-$ and $SO_4^{2-}$ anion absorptions in natural soils. Chloride concentration was very small because of its volatility and solubility. Chlorides are negatively absorbed in the soil and their concentration decreases up the horizon (Fig. 2a). Concentrations of chlorides in the profiles also decrease by horizons and they are in the range from 0.67 mg/kg to 11.92 mg/kg. From the physical and chemical analysis of horizons in the profiles, information about the chemical composition of the soil was obtained. The movement of contaminants through the soil will be determined with the amount of rainfall and with the interaction between pollutants and soil. In the first profile after all nine sampling, the concentrations of migrating species change in a similar way. The highest concentration in the surface layer 150 days after contamination was 11.92 mg/kg. The lowest chloride concentrations were recorded after the hydrological year, or after 425 days of sampling, in the surface layer that is the most porous layer in the soil (Fig. 2b).

Sulphate concentration was in the range from 1.78 mg/kg up to 8.68 mg/kg. The greatest value was found in the second horizon just after the contamination, as well as the lowest concentration was found in the same horizon after the 425 days. The obtained results show that the sulphate anions have a greater mobility and dif-

**Table 3. Determination of the filtration coefficient and bulk density**

| Depth [cm] | ln ($H_1/H_2$) | $K$ [cm/s] | Bulk density [g/cm³] |
|---|---|---|---|
| 3–8 | 0.29 | 0.01201 | 1.065 |
| 3–8 | 0.15 | 0.00872 | 1.304 |
| 3–8 | 0.07 | 0.00078 | 1.073 |
| 18–23 | 0.01 | 0.00018 | 1.484 |
| 18–23 | 0.01 | 0.00011 | 1.586 |
| 18–23 | 0.01 | 0.00011 | 1.484 |

**Table 4. pH value after each sampling**

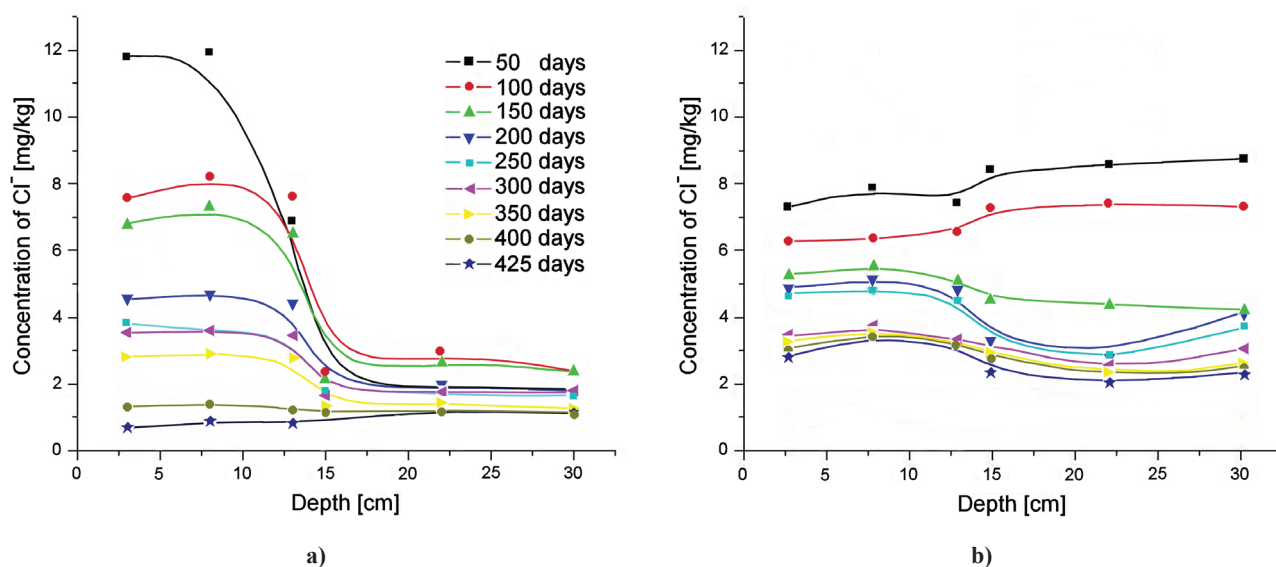| Depth [cm] | pH | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | I (50 days) | II (100 days) | III (150 days) | IV (200 days) | V (250 days) | VI (300 days) | VII (350 days) | VIII (400 days) | IX (425 days) |
| 0–13 | 5.3 | 5.8 | 5.6 | 5.4 | 5.3 | 5.1 | 5.3 | 5.8 | 5.3 |
| 13–30 | 6.1 | 6.9 | 6.2 | 6.1 | 6.2 | 6.1 | 6.1 | 6.9 | 6.2 |

**Figure 2. Anions dispersion in the soil: a) chloride and b) sulphate**

fusivity in the first horizon. In the second horizon the sulphate anions made an accumulation, because their diffusivity decreased.

## IV. Conclusions

Vertical migration of chloride and sulphate anions in soil were investigated. The obtained results have shown that the sulphate anions have a greater mobility and diffusivity than chloride anions. Separated investigation of horizons has shown greater chloride anions concentration in the profile. Anions migration was monitored during the one hydrological year in two horizons, but the unsolved question remains about the behaviour of these anions in the deeper horizons. In deeper horizons mobility and diffusivity of anions are determined by soil properties.

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