

Interaction of Brilliant Blue dye solution with soil and its effect on mobility of compounds around the zones of preferential flows at spruce stand

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Abstract

We performed field experiment with 10 g l⁻¹ concentration of Brilliant Blue solutes in 100 l of water sprinkling on 1 × 1 m surface of the Dystric Cambisol. Consequently, four vertical profiles were exposed at experimental plot after 2 hours (CUT 2), 24 hours (CUT 24), 27 hours (CUT 27) and after 504 hours (CUT 504) in order to analyse spatio-temporal interactions among the BB solution (Na-salts), soil exchangeable complex and fine earth soil (%) samples extracted from both the high and low coloured zones located around the optically visualised macropore preferred flow (PF) zones. The concentration changes were quantifying via soil profiles not affected by BB (termed as REF) located in the close vicinity of experimental plot. Observed changes in pH (H₂O), chemical composition of fineearth soil, as well as in concentration of Na⁺ in soil exchangeable complex to suggest, the BB dye solution didn't represent an inert tracer, but compounds strongly involved in reaction with surrounding soils. Recorded chemical trends seems to be the result both the competitive processes between the Na⁺ of BB dye solution and composition of surrounding soil exchangeable complex, as well and the spatial-temporal controlled mechanism of dye solution transfer in soil.

Key words: preferential flow; compounds migration; spatial-temporal evolution; dye solution- soil interaction; Brilliant Blue dye

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1. Introduction

Bundt et al. (2001a, b) were probably the first to investigated whether preferential flow path (PF) have higher microbial biomass and different microbial community structures than the rest of soil at a forested site. Bogner et al. (2012) showed the different pH values, concentrations of C, N, Fe, Ca and Mg in zones of preferential flow in comparison with rest of soils. The cited authors used Brilliant Blue (BB) dye solution to visualisation of macropore preferential flow path and its research was based on assumption the stained areas of preferential flow paths remain stable down to subsoil (Ritsema & Dekker, 2000) and the BB represents an inert compound not involved into the dye solution-surrounding soil interaction.

On the other hand, Flury & Flühler (1994) noted the BB dye represents Na-salts much more susceptible to sorption processes in soil when compared to anionic forms of the dye and in consequence, its complex reactions with surrounding, soil can alter soil sorption characteristics leading to risk of fatal misinterpretations

by studying chemical processes in soil while using dye solution (Flury & Wai 2003). The properties of BB as Na salts in field condition have not been explored till now, and only the results of laboratory batch sorption studies are available to show, the adsorption of BB on soil particles can be described by the Freundlich isotherm if the dye concentration is low 0.1 – 15 mg l⁻¹ (Flury & Flühler 1995; Perillo et al. 1998), or by the Langmuire isotherm by concentrations 100 – 5000 mg l⁻¹ (Ketelsen Meyer-Windel 1999). Some breakthroughs of these experiments to show relationships among the dye sorption, the pH, the clay content as well as the composition of secondary minerals in soils (Germán-Heins & Flury 2000).

The role on sodium as component of Brilliant Blue FCF (BB) (5.8% of the BB molecule weight) may have essential effect not only on movement and redistribution of chemical elements around the PF paths (Sparks 2003), but also on modification of soil structure and resulting water transport processes on the boundaries between the gravitational pores and the soil matrix themselves (Brady & Weil 2001).

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The information about spatial-temporal controlled process of dye solution movement around the zones of macroscopically visible PF pathways in soils are missing till now, due to the disadvantage of staining experiments during the soil sampling: excavation of pedon is destructive and experimental results cannot be repeated at the same location (Flury et al. 1994), hence the sampling is limited usually per sole vertical dye pattern of soil profile exposed on experimental plot usually 12 or 24 hours after the dye application (Flurry & Flühler 1994; Flurry et al. 1994; Hagedorn & Bundt 2002; Bogner et al. 2012; Bundt et al. 2001; Garrido et al. 2014). On the other hand, the movement of water in soil around the zones of PFs can be extremely dynamic process, different types of PFs: macropore flow, finger flow (Ritsema & Dekker 1995) and funnelled (or heterogeneous) flow (e.g. Kung 1990; Roth 1995) may occur individually, in tandem (Jury & Horton 2004), or over time they can convert to s matrix flow (Jarvis & Dubus 2006).

In order to evaluate the concept of spatial-temporal controlled movement of dye solution in soils, as well as to screening the role of sodium during the BB dye solution movement in soils around the zones of PF, we designed the field experiment based on next working hypothesis:

- the object of study on experimental plot – a soil pedon – represents spatially homogenous body, with identical stratification of soil horizons, identical soil textures, the same chemical and mineralogical composition of fine earth soil and volumetric content of soil skeleton,
- macropore PF pathways visualised by BB dye solution in particular soil profiles (CUTs), exposed on experimental plot in different time will represents 2D cross sections of different PF pathways, but with common history of dye solution movement,
- the observed chemical changes in dye pattern profiles exposed in different time are to be the consequences of dye solution movement and its interaction with surrounding soils,
- the soil profiles labelled as reference (REFs) non affected by dye solution irrigation experiment and excavated in close vicinity of experimental plot, with identical stratification of soil horizons, soil textures, chemical, mineralogical composition and volumetric content of soil skeleton as recorded on the experimental plot, will enable to quantify the effects of chemical changes observed.

The objective of proposed article is:

- (I.) to analyse and to quantify the chemical changes in composition of fine earth soils sampled of soil profiles exposed in different time induced by Na salt BB dye solution movement in soil pedon after irrigation experiment within the spatial-temporal framework,

- (II.) To analyse and to quantify the spatial-temporal chemical changes in concentration of Na^+ in soil exchangeable complex and corresponding changes at pH (H_2O) induced by application of Na salt BB dye solution,

- (III.) To evaluate the consequences of finding obtained regarding the concept of spatial-temporal controlled movement of dye solution in soils proposed.

2. Material and methods

2.1. Description of the experimental site

The research was performed at Panský diel (N 48°48'25,76", E 19°09'20,47") in Slovakia at altitude of 910 m above sea level, covered by a 90-year old mixed forest of Norway spruce (*Picea abies* [L.] Karst.), as a dominant species, silver fir (*Abies alba* Mill.), and European beech (*Fagus sylvatica* L.), Weymouth pine (*Pinus strobus* L.) and European larch (*Larix decidua* Mill), where the climate vary from moderately warm, humid to moderately cold with mean annual temperature of 4.1 °C, and where the mean annual precipitation is 1,023 mm.

The experimental site was located on a flat area with negligible inclination, and its geology contained complexes of sediments formed from schist, acidic granites, arkoses, greenish and reddish mica-slates and quartzite (Andrusov et al. 1985). These rocks were also the forming substrate of the local soil. The soil in the experimental site is *Dystric Cambisol* (IUSS Working Group WRB, 2015), with three mineral horizons (Au, 0 – 5.0 cm, Bv horizon 5 – 110 cm with gradual transition to C horizon).

2.2. Field and laboratory work

2.2.1 Dye tracer application

In April 30, 2012, BB solution with 10 g l⁻¹ concentration was applied by a sprinkler with 100 mm h⁻¹ intensity over a 1 × 1 m plot. Prior to the BB application, the litter horizon was removed because of its high interception capacity. After the dye application a series of four vertical profile cuts were excavated at different times after 2 (CUT 2), 24 (CUT 24), 27 (CUT 27), and 504 hours (CUT 504) after the application of the BB solution. The air temperature, precipitation, and potential evapotranspiration at the experimental site monitored by automatic station of the EMS Brno Company, are presented in Fig. 1. As can be seen from the Fig. 1, no rainfall was fell during the period between the BB application and the excavation of the CUT 2, CUT 24, and CUT 27 profiles, but some rains fell between the CUT 27 and CUT 504 exposition times (Fig. 1).

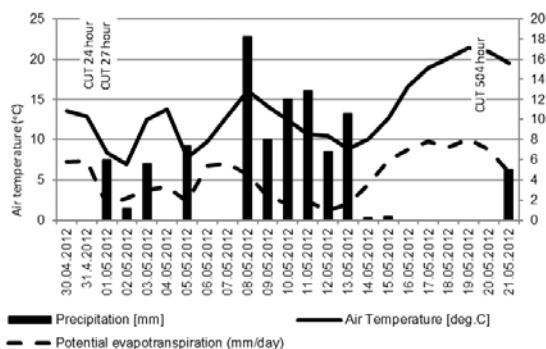


Fig. 1. Temperature, potential evapotranspiration and precipitation at the experimental site.

2.2.2 Dye coverage determination

After exposition of particular CUTs, the 1×1 m grey frame was installed around each soil profile and digital photographs were obtained. After taking digital photographs several procedures were performed to evaluate the spatial concentration of the BB dye (i) Geometric correction; (ii) white-balance and exposure correction; (iii) calibration and (iv) evaluation of the dye concentration. To evaluate dye coverage (D_c) the processing framework in GNU R (R Development Core Team) and C with help of ImageMagick image processing library and with a resolution of $500 \times 1,000$ pixels (i.e., one pixel represents a 1×2 mm), were used.

Dye coverage (D_c) calculation is described in Eq. [1] (Flury et al. 1994):

$$D_c = \left(\frac{D_a}{D_a + ND_a} \right) \times 100 \quad [1]$$

where, D_a is the surface area in the cut that stained by dye, and ND_a is the surface area in the cut that is not stained.

2.2.3 Sampling procedure

Three samples from each 10 cm layer of each CUTs by Kopecky-cylinder with volume of 100 cm^3 were taken with consideration of colouring intensity: samples labelled as NC (from sites not affected by BB dye), MC (taken from zones with middle colouring) and IC (samples intensively coloured by BB dye solution). Totalling, 120 soil samples were taken for physical and chemical analysis during 20 days from CUT 2 to CUT 504 soil profiles, but only NC and IC samples (80 samples in total) were taken into the account regarding proposed article. Finishing the sampling at experimental site, the soil samples were taken from the both the right and the left sides of CUTs located approx. 35 cm apart from 1×1 m experimental plot, where no BB tracer had been applied on soil surface (referred as REFs). Two samples were taken from each 10 cm layer, i.e. 20 samples in total from REF zone.

2.2.4 Soil texture and skeleton content determination

In order to specify soil skeleton volume in soil samples from both the CUTs and the REF profiles, separation of the skeleton from the fine earth was achieved by dry and wet sieving, additional washing of the rock fragments gave clast with clean surfaces following the procedure proposed by Corti et al. (1998) and Certini et al. (2004). The soil skeleton volume was obtained by water displacement after the clast were completely water saturated (Corti et al. 1998). Soil texture, or size distribution of mineral particles was determined by standardized sedimentation pipette method in water column in sense of Fiala et al. (1999).

2.2.5 Determination of Na^+ in soil exchangeable complex

The concentration of Na^+ in soil exchangeable complex was determined by its replacing with $0.15 \text{ M NH}_4\text{Cl}$ and by AAS analysis of leachate via Avanta AAS, with nitroacetylene burner with automatic rotation.

2.2.6 Determination of pH (H_2O)

The pH (H_2O) as an indication of the acidity or alkalinity of soil was measured according to Fiala et al. (1999), by pH meter Hamma HI 221 of soils suspended in a distilled water (from which CO_2 was abstracted via 30 min. boiling), under 1 : 2.5 soil : water ratio and mechanical stirring. Laboratory balance Mettler PL 1200 were used for weighing of fine earth (20.00 g).

2.2.7 Determination of total content of Al, Si and Fe

Total chemical analyses of soil (called as silicate analysis) of REF soil profiles were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) by EL spol. s r. o. accredited laboratory. However, before the ICP-AES analyses, the soil samples were crushed and pulverized in agate mill. After that, the specific dissolution was made.

The dissolution of Na_2O , K_2O , LiO_2 , P_2O_5

The HF and HClO_4 were added into the samples in the Teflon dishes and the samples were evaporated. After cooling, HF and a the saturated H_3BO_3 solution were added. After drying, the samples were dissolved in nitric acid (1 : 1) and transferred into the graduated flasks. After evaporation to dryness and next cooling, the samples were dissolved in HNO_3 1 : 1 and, after cooling, the samples were transferred into the polypropylene graduated flasks.

The dissolution of SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , MnO , CaO , MgO

Na_2O_2 and samples were weighed into the Pt crucibles, where they were thoroughly mixed with plastic rod. The crucibles with the lids were put into the muffle furnace. After removing the crucibles from the furnace, the samples were cooled, transferred into beakers and sprinkled with hot distilled water. After 20 minutes, concentrated HCl was added into the samples and the samples were leached in the baths. Subsequently, the crucibles, as well as the lids, were rinsed with distilled water and the resulting aliquots were poured into the graduated flasks, to which the internal standard solution, as well as the distilled water were added to the marks, and after that, the samples were mixed.

S – Total

The samples were weighed into the beakers, where a 1 : 3 mixtures of HCl and HNO_3 were added. The beakers were covered with a glass slides where they cooled to next day. After that, the solutions were heated for 1 hour in sand bath. Subsequently, the glass slides were rinsed with distilled water and the solutions were evaporated to dryness. Concentrated HCl was added, causing the dissolution of samples under a clock glasses in a sand bath for 30 minutes. After that, the glass slides were rinsed with distilled water, the solutions were cooled, and transferred with distilled water into the graduated flasks. The graduated flask was filled with distilled water to the marks and thoroughly mixed.

S – SO_3

The samples were weighed into the breakers. HCl 1 : 1 was added, the beakers were covered with a glass slide and, upon completion of the reaction, they boiled on a cooker. After cooling, the slides were rinsed and the samples were poured into graduated flasks filled with distilled water and thoroughly mixed.

S sulphidic: S total – SO_3

The XRF spectrometry for analysis of Al, Si, Fe concentration in fine earth soil samples was applied, as validation characteristics of this analytical method provided by Vojteková et al. (2010) to show its compatibility with the methods used in reference laboratories. We used Thermo Scientific Niton XL3t Series XRF analyzer with GOLDD technology, with low detection limits of light elements (e.g., Mg, Al, Si, P). The sensitivity, or limits of detection (LOD) in ppm (mg kg^{-1}) of the Niton XL3t GOLDD technology analyzer, for SiO_2 matrix, SiO_2 matrix with 10% iron, and a typical Standard Reference Material (SRM) can be find on thermofisher.com website. During the measurement, the Mining Calibration Mode was used and the MAIN, HIGH, LOW, LIGHT filters with time measurement of 30.0 s. per filter were applied.

The fine earth soil samples were before XRF analyses pulverized and homogenized using the RETSCH Mixer

Mills (MM 301). After that, by SPECAC hydraulic press with a maximum pressure limit of 15.000 kg, the pellets with diameter (32 mm) were prepared. In total, 80 pellet samples from IC and NC zones of CUT2 – CUT 504 were measured, 20 pellet samples from REF profile, and each sample were measured twice, to ensure representativeness of acquired chemical analyses.

2.2.8 The stocks of elements

Because we knew the bulk density and volume of the soil (as the soil samples were taken by Kopecky cylinder of 100 cm^3), i.e., fine earth + soil pores, without coarse fragments with diameter $>2 \text{ mm}$, the concentration of chemical elements, or Na^+ concentration in soil exchangeable complex (CC) stock (CCS) was computed by assuming the CCS in all ten 0.1 m layers of all four soil profiles (CUTs) derived from both the IC and the NC zones surrounding the PF pathways as well as separately for the REF CUTs not affected by BB dye, at each sampling point according to:

$$CCS = BD \times CC \times d \times (1 - cf) \quad [2]$$

where CCS , BD , CC , d and cf are, element stock (kg m^{-2}), bulk density (kg m^{-3}), element stock (kg kg^{-1}), soil layer thickness (0.1 m) and volumetric fraction of soil skeleton ($\text{m}^3 \text{ m}^{-3}$), respectively.

3. Results

3.1. Verification of working hypothesis

The study of soil texture differences among the particular CUTs and the REF zone according to USDA soil taxonomy detected minimal differences regarding soil texture (Fig. 2) and volumetric skeleton contents (Fig. 3). The homogeneity of soil pedon under investigation was confirmed by both the electric resistivity and the GPR measurements (Bebej et al. 2013) to suggest, the minimal spatial variances in soil pedon exist. From mineralogical point of view, the soil skeleton is monotonous and consist of clasts of extremely acid quartzite, sandstones and mica slates.

The mica slates are represented by grey-green one's, and red coloured varieties, but its chemical composition, as compared with the fine earth soil samples (Table 1), is relatively similar. Generally, the silicate analyses of fine earth soil samples to show no differences in chemical and mineralogical composition of soil in upside of REF profile (0 – 60 cm), therefore regarding the skeleton composition, its volumetric content and soil textures in the CUTs soil profiles we can propose the chemical composition is similar that determined in REF profile, and working hypothesis proposed about spatial homogeneity of soil pedon is true.

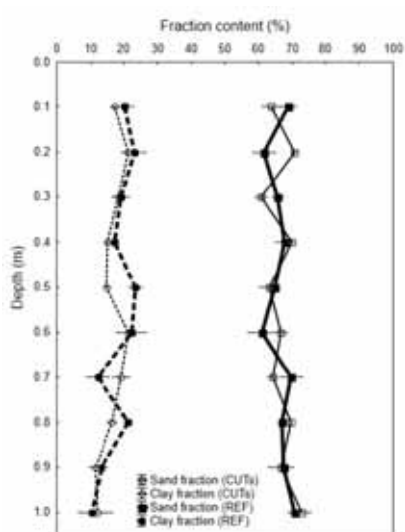


Fig. 2. Particle size distribution of sand and clay fractions within the CUTs and REF zone profiles.

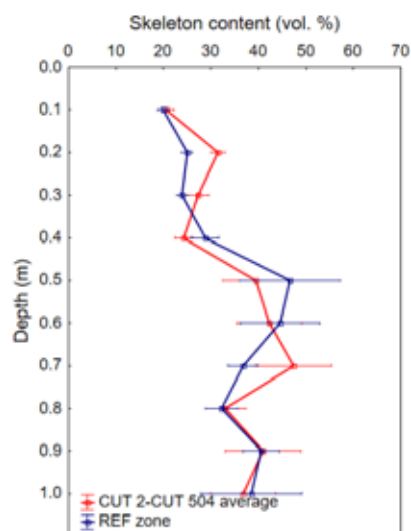


Fig. 3. Volumetric skeleton contents in soil samples with-drawal from both the experimental plots (CUT 2 – CUT 504) and the REF zone.

3.2. Characterisation of dye pattern profiles

Typical infiltration patterns observed in particular CUTs, as well as their dye coverages (Dc) are documented in Fig. 3. In all soil profiles macropore dye pathway structures are well visible, but some differences among them also manifested. Within the CUT 2, macropore pathways are narrow and the top of CUT 2 profile is only slightly covered by BB dye. On the contrary, within the CUT 24 the top layer of soil profile is heavily covered by BB dye and in both the CUT 24 and CUT 27 profiles the macropore pathways are broad what indicate the growth in macropore-soil matrix interaction. The macropore pathways in CUT 504 is different the rest CUTs and finger-like structures are evident.

3.3. pH (H₂O) values

The distribution of pH (H₂O) values in both the experimental plot (CUT 2–CUT 504) and the REF soil profile are presented in Fig. 4. It can be seen from Fig. 4, that irrigation with BB dye solution (pH = 7) abruptly increased the pH (H₂O) values recorded in soil profiles of experimental plot, and that these changes are visible in all soil samples from both the IC and the NC zones. The second important feature is zonal character of pH (H₂O) curves regarding the REF zone, while this trend abruptly changes about 60 cm depth (Fig. 4): in the top part of the soil profiles the drop in pH (H₂O) is observed from CUT 2 and CUT 24 to CUT 505 profiles, while below 60 cm this trend is opposite.

Surprisingly, the pH (H₂O) changes observed in both the IC and the NC zones manifest, in general, in similar intensity, hence colouring intensity of soil samples is not the indication of pH changes.

Table 1. The silicate analyses of fine earth soil samples from soil profile of REF zone as compared with chemical composition of grey-green slates (GGS), and red-coloured slates (RS) of soil skeleton.

| | REF 10 cm | REF 20 cm | REF 30 cm | REF 40 cm | REF 50 cm | REF 60 cm | REF40 cm (GGS) | REF40 cm (RS) |
|--------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|----------------|---------------|
| SiO ₂ | 68.96 | 68.05 | 68.76 | 68.94 | 70.04 | 68.81 | 74.81 | 70.04 |
| Al ₂ O ₃ | 14.75 | 14.91 | 14.68 | 14.83 | 14.13 | 14.86 | 14.02 | 14.13 |
| Fe ₂ O ₃ | 4.28 | 4.41 | 4.33 | 4.41 | 4.21 | 4.36 | 1.93 | 4.21 |
| FeO | 0.6 | 0.74 | 0.4 | 0.3 | 0.41 | 0.14 | 0.2 | 0.41 |
| TiO ₂ | 0.612 | 0.636 | 0.613 | 0.631 | 0.613 | 0.629 | 0.188 | 0.613 |
| MnO | 0.033 | 0.027 | 0.042 | 0.026 | 0.025 | 0.024 | 0.039 | 0.025 |
| CaO | 0.03 | 0.04 | 0.12 | 0.06 | 0.05 | 0.06 | <0.01 | 0.05 |
| MgO | 1.38 | 1.4 | 1.4 | 1.4 | 1.36 | 1.48 | 1.27 | 1.36 |
| Na ₂ O | 0.49 | 0.46 | 0.48 | 0.46 | 0.46 | 0.44 | 0.69 | 0.46 |
| K ₂ O | 4.07 | 4.04 | 4.13 | 4.08 | 3.85 | 4.17 | 4.23 | 3.85 |
| Li ₂ O | 0.009 | 0.01 | 0.009 | 0.01 | 0.009 | 0.009 | 0.005 | 0.009 |
| P ₂ O ₅ | 0.08 | 0.12 | 0.08 | 0.08 | 0.08 | 0.09 | 0.07 | 0.08 |
| S ²⁻ total | 0.01 | 0.01 | 0.02 | 0.02 | 0.01 | 0.01 | <0.01 | 0.01 |
| S sulfidic | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.01 |
| Loss of ignition | 4.94 | 5.01 | 4.78 | 4.56 | 4.66 | 4.46 | 2.83 | 4.66 |
| Loss of drying | 0.66 | 0.68 | 0.62 | 0.64 | 0.55 | 0.84 | 0.27 | 0.55 |
| Total | 100.9 | 100.5 | 100.5 | 100.4 | 100.5 | 100.4 | 100.6 | 100.5 |

3.4. Na⁺ concentration in soil exchangeable complex

The sodium represents 5,8% of BB FCF dye molecule weight component; therefore, the sodium represents important part of dye solution to be applied into the soil during irrigation experiment.

The analyses of Na⁺ in dye pattern profiles compared to REF revealed, that in CUT 2 there are biggest differences in Na⁺ concentration between IC zones and REF (Fig. 5), and that in the top part of the soil profile (0 – 60 cm) the gradual drop in Na⁺ concentration i from CUT 2 to CUT 505 profiles s observed in such a way as in case of pH (H₂O) (Fig. 4).

In case of soil samples extracting from NC zones of macropore PF pathflows the differences in Na⁺ concentration between particular CUTs and REF are marginal, especially in bottom part of soil profiles (Fig. 4 b). The discrepancies between pH (H₂O) values and Na⁺ concentration in both the IC and NC soil samples can be accounted by increasing of exchangeable sodium in soil exchangeable complex as compared of different soil-water ratio existing in IC and NC zones of macropore pathflow (Abrol et al. 1988). In sodic soil, the different Na⁺ concentration in soil exchangeable complex existing at different soil : water ratios in IC and NC zones can produce identical pH (H₂O) values.

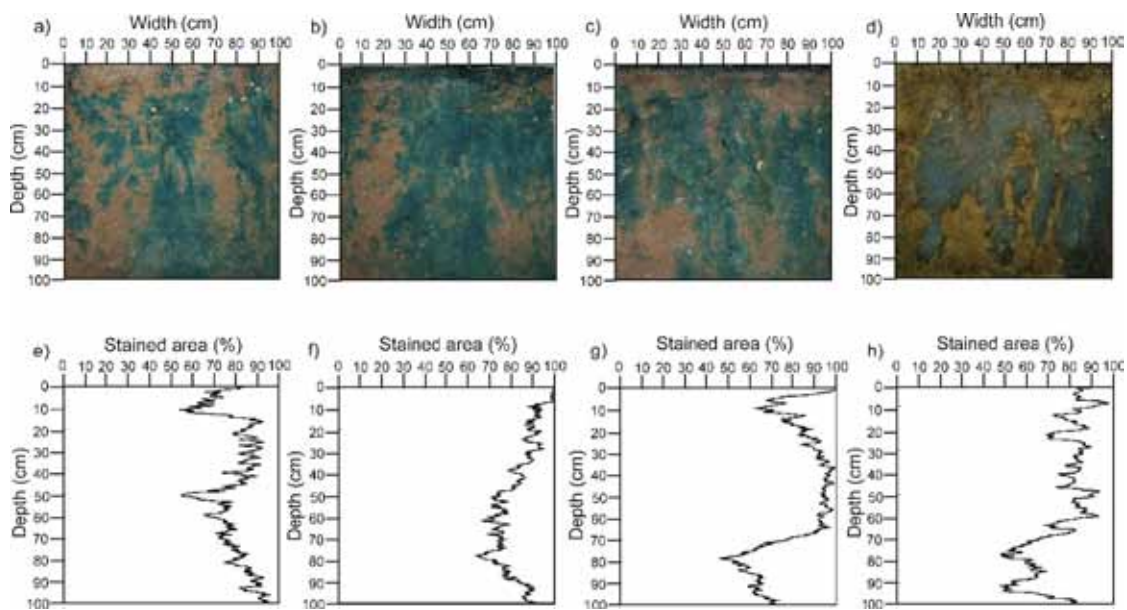


Fig. 4. Infiltration patterns and dye pattern coverages (bottom) within the CUT 2 (a), CUT 24 (b), CUT 27 (c) and CUT 504 (d).

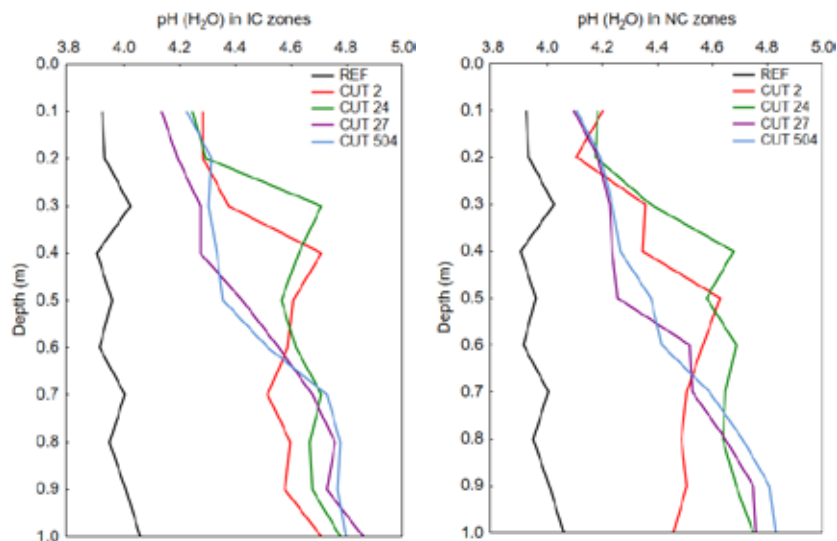


Fig. 5. The pH (H₂O) changes in IC and NC zones of macropore PF pathflows of CUT 2 to CUT 504 soil profiles regarding the pH (H₂O) in soil profile of REF zone.

According to Abrol et al. (1988) difference about 1 pH unit indicates that the soil contains more than 15 percent exchangeable sodium. The principal cause of alkaline reaction of sodic soils is the hydrolysis of the exchangeable sodium by H_2O which results in an increase in the OH^- ion concentration and increased soil pH. Ions such as Na^+ are unable to compete as strongly as the more tightly held ions such as Ca^{2+} and Mg^{2+} , so exchangeable Na^+ is hydrolysed to a much greater extent and produce a higher pH than do exchangeable Ca^{2+} or Mg^{2+} (Abrol et al. 1988).

3.5. Al, Si and Fe concentration in fine earth soil samples

The XRF analyses of Al, Si and Fe of fine earth soil samples extracted from IC zones of macropore PF path flows of CUT 2 – CUT 405 soil profiles (Fig. 7) in general to show great concentration changes regarding REF soil profiles and this changes reaches its maximum within the CUT 2 profile. In this case for all analysed elements marked depletion in concentration – regarding to REF – is observed. On the other hand, in the case of CUT 27 and CUT504 soil profiles, the concentration of Al, Si and Fe is close to concentration measured in REF soil profile.

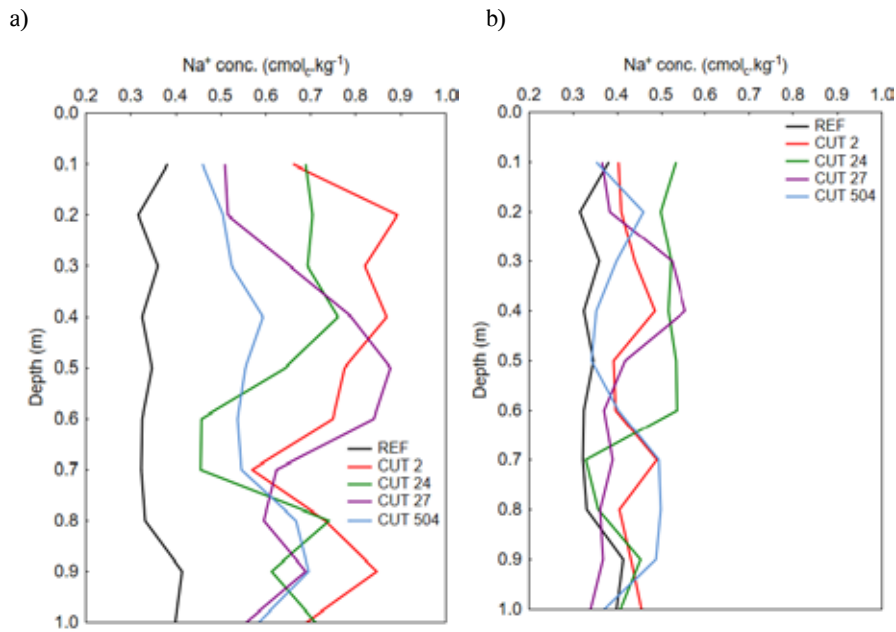


Fig. 6. The concentration changes of Na^+ ($cmol_c\ kg^{-1}$) in soil exchangeable complex extracting from IC (a) and NC (b) zones of macropore PF pathflows of CUT 2 – CUT 504 dye pattern profiles regarding the REF soil profile.

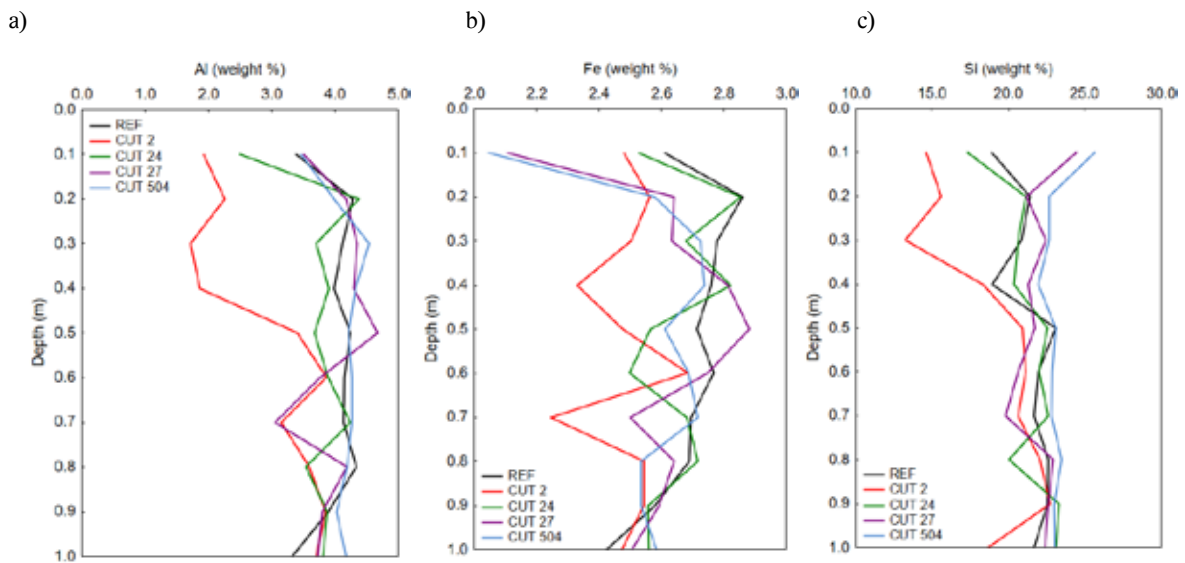


Fig. 7. The concentration changes (weight %) of Al (a), Fe (b) and Si (c) in fine earth soil samples extracted from IC zones of macropore PF path flows of CUT 2 – CUT 405 soil profiles determined by XRF analyses regarding the REF zone soil profile.

4. Discussion

The mobility and transport of Al, Fe, Si and organic matter in soils at present is especially related with the podzolization process issue. According to Bloomfield (1954) dissolved organic matter play an important role in the translocation of Al and Fe in podzols. By fulvate theory (e.g. Petersen 1976) the fulvate acids dissolves primary and secondary minerals as well as the amorphous materials in the E horizon to form dissolved organic Al/Fe complexes. By “anorganic” podzolization theory (Anderson et al. 1982; Farmer & Lumsdon 2001) inorganic Al, Si and Fe are translocated via (proto)imogolite sols from the eluvial to the illuvial horizons, where its precipitation in the form of imogolite, causes the development of Bh and Bs horizons. Gustafsson et al. (2001) propose immobilization of Al in B horizons in the form of inorganic precipitates at the higher pH values (> 4.2), however, they suggest that precipitation is induced by the equilibrium of dissolved Al with $\text{Al}(\text{OH})_3(\text{s})$. Lundström et al. (2000), in contrast with the classical fulvate theory propose that complexation of Al and Fe to low-molecular weight (LMW) organic acids plays a main role in the mobilization of Al, Fe and organic matter from podzol E horizons and microbial degradation of the LMW organic in the soil causes precipitation of inorganic Al and Fe complexes. Mossin et al. (2002), Van Breemen & Burman (2002) supposed that different mechanisms of podzolization taken place in different locations, regarding the composition of parent materials and climate conditions.

Total aluminum is measured in soils because it provides useful information on the characterization of soils with respect to the origin of parent materials and weathering (Mulder et al. 1989), however, much higher attention is addressed to exchangeable and extractable aluminium study, due to formulation of lime requirements for acid soils (Kamprath 1970, 1980; Juo & Kamprath 1979; Oates & Kamprath 1983) and because of its importance as a predominant cation in acid soils, where the exchangeable aluminum is a critical variable in establishing effective cation exchange capacity (ECEC) values. (Mulder et al. 1987; Rasmussen et al. 1991).

Once soil pH is lowered much below 5.5, aluminosilicate clays and aluminum hydroxide minerals begin to dissolve, releasing aluminum-hydroxy cations and $\text{Al}(\text{H}_2\text{O})_6^{3+}$ that then exchange with other cations of soil colloids. The fraction of exchange sites occupied by $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and its hydrolysis products can become large once the soil pH falls below 5.0. Furthermore, as the pH is lowered, the concentration of soluble aluminum, which is toxic, increases.

Generally, the mobilization of aluminium may be due to: dissolution of Al-compounds via acidification process, ion-exchange of Al-ions with cations as H^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , and finally, by complexation with organic substances, like humic and fulvic acids (Kotowski et al. 1994). Kotowski et al. (1994) studied the mobilization of aluminium in laboratory experiments using podzol

soils and mineral acids (H_2SO_4 , HNO_3) and fertilizer salts i.e. $(\text{NH}_4)_2\text{SO}_4$ and HN_4NO_3 . They found, that mobilization of aluminium by HNO_3 was in most cases higher than by H_2SO_4 for the same concentrations, while for fertilizer salt solutions the mobilization of aluminium was between that observed for H_2SO_4 and HNO_3 . These results demonstrate the sodium as essential constituent of BB dye (sodium salt) may mobilize the aluminium from soil exchangeable soil complex of acidic soils, via soil-exchangeable processes.

In acid soils, Al^{3+} and the associated hydrolysis products AlOH^{2+} , and $\text{Al}(\text{OH})_2^+$ dominate exchange phase charge followed by Ca, Mg^{2+} , Na^+ and K^+ (Essington 2015). However, high concentration of one cation will displace an adsorbed cation from the exchanger even if adsorbed cation is higher on the lyotropic series by Mass Action Law. High concentration of sodium in the initial BB solution may indicate situation the mass action law can come in force and Na^+ will displace an adsorbed cation from the exchanger even if the adsorbed cation is higher on the lyotropic series – e.g., Al^{3+} (Plaster 2014).

The irrigation experiment with BB dye solution on experimental plot caused dramatic changes in pH (H_2O) characteristics of soil samples from CUT 2 – to CUT 504 (Fig. 1). The abrupt increase of pH observed in CUT 2 and CUT 24 profiles to show, the dissolved Na^+ ions of dye solution caused increase of exchangeable sodium in acid soil exchangeable complex and Al^{3+} and its hydrolysis products were partly displaced and mobilised. The Fig. 4a and Fig. 5b to illustrate the antagonistic behaviour of Na^+ as constituent of soil exchangeable complex and the aluminium in fine earth soil samples of IC zones within the CUT 2 profile what indicate the ion-exchange reaction can partially explain the chemical changes observable in Al concentration in CUT 2 profile. However, the overall Al, Si and Fe chemical changes recorded within the CUT 2 profile regarding the REF soil profile to suggest the another processes governs the observable mass depletion of fine earth soil samples within this profile and that is way the observed Al (%) vs. Na^+ ($\text{cmol}_c \text{kg}^{-1}$) negative correlation is statistically non-significant ($p = 0.082$) for IC zones.

Existing breaking point in concentration of Al, Si and Fe observed between the CUT 2 and the rest CUTs was changed by slow gradation changes in the case of rest CUTs, and generally, the mass depletion of Al, Si and Fe in top part of CUT 2 soil profile suddenly turned into the enrichment at the same part of the CUT 27 – CUT 505 profiles (Fig. 6). All this means the time factor play key role and that the reasons of dye solution transport inversion should be understood and explained.

The basic characteristics of two factorial ANOVA for concentration of Al, Fe and Si in fine earth soil, as well as for concentration of Na^+ in soil exchangeable complex in soil samples from CUT 2 to CUT 504 soil profiles are presented in Table 2. As can be seen, depth, time as well as their concurrence is statistically very significant for Al, Fe and Si, besides the Na^+ , where statistical dependence

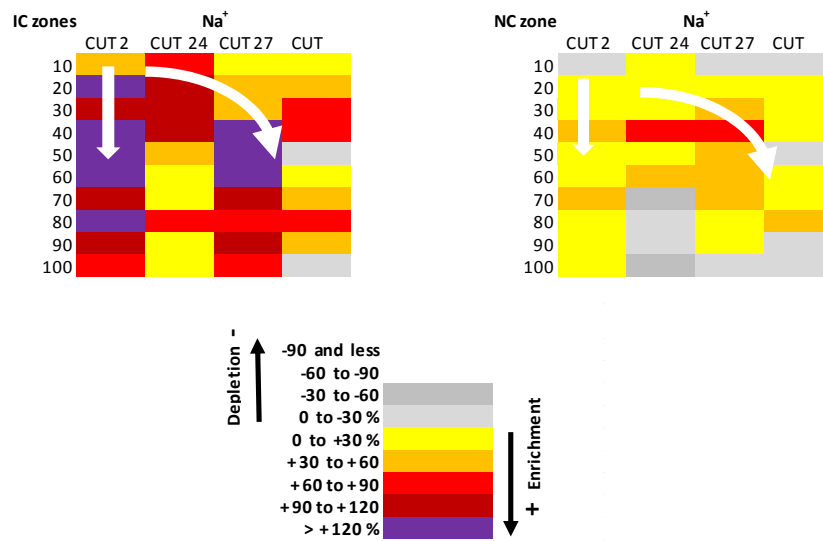
was supported only by one factorial ANOVA. It follows from these data, that the Na⁺ concentration is very significantly influenced by colouring intensity ($p = 0.000$) and time ($p = 0.001$), while for Al, Fe and Si the colouring intensity (IC and NC zones) is non-significant factor from statistical point of view.

Different behaviour of Na⁺ on one hand, and Al, Fe and Si regarding to IC and NC zones on other hand, is key in order to understand the specific behaviour of sodium:

- 1). sodium is essential part of BB dye solution and regarding to other elements present in soils, his concentration is non-stoichiometric, and is controlled by

- 2). sodium as part of dye solution is transported in soil according the processes of adsorption isotherm, where the partitioning of a solute between the aqueous solution and the sorbed phase take place (Kasteel et al. 2002).
- 3). on the interfaces between the dye solution and surrounding soil also the ion exchange processes take place, principally different of sorption processes which take place on free surface sites, while the ion exchange is controlled by the ionic composition of

Na⁺ concentration changes in soil exchangeable complex



Corresponded Al, Si and Fe concentration changes detected by XRF analyses in IC and NC zones

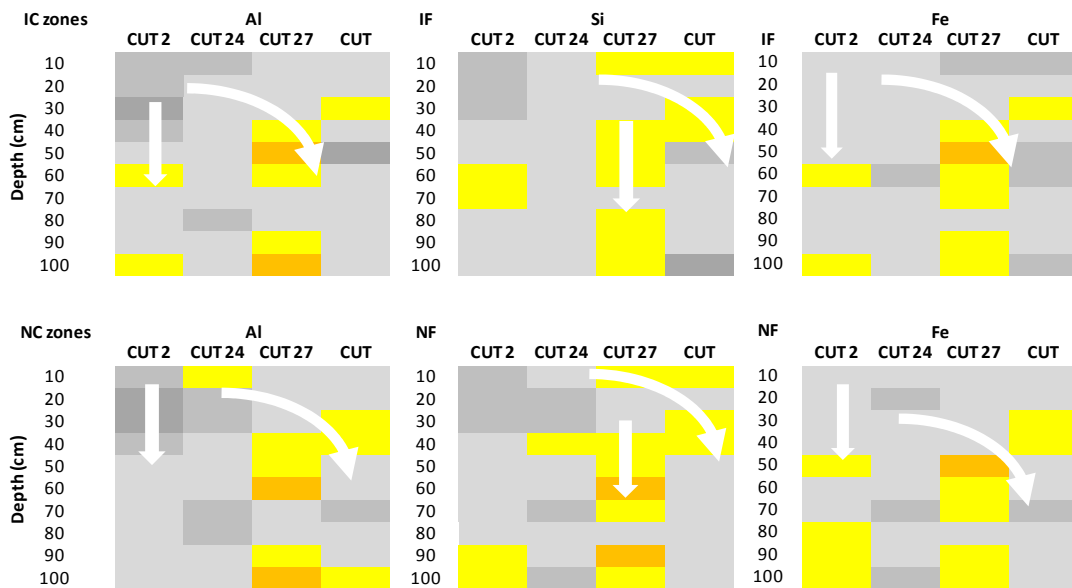


Fig. 8. The concentration changes (%) of Na⁺ in soil exchangeable complex (a), and corresponded Al, Si and Fe concentration changes in coexisted fine earth soil samples extracted from both the IC and NC zones of macropore PF pathflows of CUT 2 – CUT 405 soil profiles (b).

the liquid phase (Nagy & Kónya 2009). In the case of common action of sorption and ion exchange processes, the spatial separation of sodium and the cations displaced of soil exchangeable complex to be the consequence, and coloured, sodium rich IC zones will not spatially coincide with zones, where the displaced cations to be accumulated,

- 4). the chemical changes observed in the CUT dye pattern profiles to show the younger processes to be superimposed to older ones', or depletion in concentration of chemical elements suddenly change to enrichment. The effect of such a processes, in consequences, destroy former NC and IC zones, and the statistical dependencies between the sodium (coloured IC zones) and other chemical components activated by dye solution: soil interaction will reduce.

Table 2. Two factorial analyses of variance of Al, S, Fe and Na concentration according to depth and time and its interactions.

| Parameter | Tested factor | | | | | |
|-----------------------|---------------|-------|----------|-------|-----------------------|-------|
| | Depth [cm] | | Time [h] | | Depth [cm] * Time [h] | |
| | F-ratio | p | F-ratio | p | F-ratio | p |
| Al conc. | 19.58 | 0.000 | 220.26 | 0.000 | 12.62 | 0.000 |
| Fe conc. | 13.10 | 0.000 | 12.90 | 0.000 | 7.05 | 0.000 |
| Si conc. | 17.20 | 0.000 | 86.68 | 0.000 | 7.40 | 0.000 |
| Na ⁺ conc. | 0.63 | 0.771 | 2.58 | 0.059 | 0.71 | 0.845 |

The interesting fact to imply from documented analytical data regarding the statement of Allaire et al. (2009) suggested, the standardization of tracer application methods is needed in order the results between different studies to be comparable. For an example, the time of vertical soil profile exposition usually vary from 12 hours (Kasteel et al. 2002) to 1 day (24-hour) after finishing the infiltration experiment (Flurry & Flühler 1994; Flurry et al. 1994; Hagedorn & Bundt 2002; Bogner et al. 2012; Bundt et al. 2001; Garrido et al. 2014), or the samples from several vertical profiles exposed on one experimental plot are interpreted without consideration of time factor role (Bundt et al. 2001; Alaoui & Goetz 2008). The same statement concerns the concentration of applied BB dye tracers, from 3 g l⁻¹ (Bundt et al. 2001), 4 g l⁻¹ (Flurry et al. 1994; Alanoui & Goetz 2008) to 10 g l⁻¹ (Kasteel et al. (2002)). Different concentration of BB dye tracers means that different concentration of Na⁺ in dye solution, and different interaction effects of dye solution with surrounding soil will lead to different chemical footprints observed in exposed soil profiles.

The cause of the time-controlled breaking point in observed chemical changes seems to be the spatial-temporal controlled mechanism of dye solution transfer in soil. While classical theory supposes the PF zone to be temporal and spatially stable within the soil (Ritsema & Dekker 2000; Hagedorn & Bundt 2002; Bogner et al. 2012), we suppose dye solution movement via PF to be limited to brief period (CUT 2 profile), as long as are fulfilled the physical preconditions of non-equilibrium flow (Jarvis & Dubus 2006). After that, at moment when

all pores at the soil surface are filled with water, and lateral movement of dye solution from macropore to surrounding soil matrix prevailed, the macropore flow will terminate (Jarvis & Dubus 2006) and homogenous flows of dye solution became dominant (CUT 24 – CUT 504 profiles).

5. Conclusion

The results of small-scale irrigation field experiments to show heavy chemical changes be caused in soil via interaction of BB dye solution with surrounding soils. Observed spatial-temporal changes in pH (H₂O), chemical composition of fine earth soil, as well as in concentration of Na⁺ in soil exchangeable complex suggested, the BB dye solution didn't represent an inert tracer, but its compounds are involved in mass reaction with surrounding soils. Recorded chemical trends seems to be also the result of competitive processes between the Na⁺ of BB dye solution (representing Na-salt) and composition of surrounding soil exchangeable complex, and observed distribution of chemical components around the zones of preferred flows stained by BB dye may cause the risk of fatal misinterpretations in line with the statement of both the Flurry & Flühler (1994) and Flurry & Wai (2003).

The observed breaking point in concentration of Al, Si and Fe we preliminary links with breaking point of dye solution movement, when macropore preferred flow changed to equilibrium one. In order to support proposed scenario, detail analyse of dye pattern profiles and its morphometric parameters is needed.

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