DIVISION S-1—SOIL PHYSICS

Visualizing Preferential Flow Paths using Ammonium Carbonate and a pH Indicator

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ABSTRACT

Despite their negative charge, anionic dyes are less-than-ideal tracers of water flow in soil. A new method is presented here for detecting flow patterns faithfully representing the movement of water flow paths in structured and nonstructured soils. The method is based on application of ammonium carbonate during infiltration, which displays a unique color signature when sprayed with a pH indicator after excavation and exposure of the soil profile along a trench face. We compare its performance with that of the popular Brilliant Blue in a laboratory study, and show that it is a more conservative tracer of the water front. We also illustrate its use in a field experiment to detect preferential flow. In contrast to other methods, ammonium carbonate is inexpensive, nontoxic, and leaves negligible residue.

A MAJOR FACTOR LIMITING our understanding of preferential flow has been the difficulty in observing it under natural conditions (Jury and Fluhler, 1992). Soil or solution samples are likely to miss the narrow flow patterns entirely (Ghodrati and Jury, 1990), and volume-averaged collection devices such as tile lines provide no spatial resolution of the preferential flow pathways and dilute their contents with solution from other regions. For these reasons, dye tracing of pathways revealed by soil excavation has been a popular research tool in the investigation of preferential flow (see Flury and Fluhler, 1995).

Many investigators have developed methods to stain and observe preferential flow paths in soil, mostly involving the use of soluble dyes. Reynolds (1966) tested the feasibility of using fluorescent dyes in the field with ultraviolet light. Corey (1968) compared different classes of dyes and found that the anionic acid dyes were best suited for water tracing. Flury and Fluhler (1994, 1995) further recommended that Brilliant Blue FCF was the best dye for field experiments, mainly because of its low toxicity and high visibility. To date, many field investigations have been carried out using dyes to characterize water and solute transport in soils (e.g., Ghodrati and Jury, 1990; Steenhuis et al., 1990; Flury et al., 1994; Stamm et al., 1998). However, dye application in the field always requires a difficult choice between dye toxicity at high concentrations and poor visibility of stained soil at low concentrations. Several other investigators (e.g., Flury and Fluhler, 1995; Ketelsen and Mayer-Windel, 1999; German-Heins and Flury, 2000) found that

the Brilliant Blue FCF was adsorbed in soil matrix purportedly because of the molecule's large size, so that the stained part of soil lagged behind the actual wetting front.

Van Ommen et al. (1988) presented a new technique to stain and visualize preferential flow paths using an I^- solution. By adding I^- in the infiltration water, applying powdered starch on the horizontally excavated soil face, and then spraying a bleaching-liquor (Cl_2) onto the starched profile, the I^--wetted starch (the preferential flow cross-section) changes color from milky gray to dark blue-violet. The method was used by Hendrickx et al. (1993) to visualize fingered flow on vertical profiles in a water-repellent soil. Generally, this method requires uniform application of a thin layer of starch on a flat soil profile. If the starch layer is too thick or nonuniform, the I^- solution in the soil cannot wet through the starch layer, and the chemical reaction between I^- and Cl_2 is prevented. Thus, this method cannot be used to identify macropore flow in structured soils. Moreover, in relatively drier soils, e.g., after a long period of soil water redistribution, the starch layer is difficult to wet with the I^- solution in the soil. It is also difficult to apply the starch on a vertical soil profile, and I^- is quite expensive for large-volume application in the field.

To overcome the disadvantages of the dye and I^--starch applications, we present here an alternative method to stain and visualize preferential flow in both structured and nonstructured soils using a pH indicator.

MATERIALS AND METHODS

Chemicals

The chemical serving as a water tracer is ammonium carbonate, $(NH_4)_2CO_3$, at food or fertilizer grades (Chem. Lab Supplies, Placentia, CA). It is nontoxic, inexpensive, and easily soluble in water. The chemical has mobility comparable with that of water. A 2% water solution of $(NH_4)_2CO_3$ (by weight) will elevate a soil's pH to about 8.2, and a 5% solution will produce a pH of about 8.5. Once a pH indicator is applied, the colorless $(NH_4)_2CO_3$ solution becomes visible. Although several recipes of pH indicator can be found from a standard chemistry handbook (e.g., Weast et al., 1987), we propose an indicator composed of 1% weight of thymol blue (ACS Reagent, Dye content ~ 95% F. W. 466.60, m.p. 221-224[dec.], Andrich Chemical Co., Inc., Milwaukee, WI) and 1% weight of crelsol red (Indicator grade, dye content ~95% G.E. 382.43, Andrich Chemical Co., Inc., Milwaukee, WI) dissolved into methanol at 95% purity. The reason for choosing methanol is that the indicator chemicals are more soluble in methanol than in water. The methanol solution is also more volatile, thus the pH indicator will not dilute and change the pH of the wetted soil. Five to 10 min after spraying a mist of this

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pH indicator onto a soil profile, the $(NH_4)_2CO_3$-affected soil will change color to purple-red, while the unaffected soil becomes light yellow. The yellow-red contrast is highly visible for video and photographic recording.

Field Preparation and Application

Ammonium carbonate is a strong smelling and volatile chemical. It must be stored and transported in sealed containers, and the solid $(NH_4)_2CO_3$ should be mixed with water only a few hours before application. The solution must be fully stirred to create a uniform concentration in the water tank. The chemicals for making the pH indicator (i.e., thymol blue and crelsol red powders) are not readily soluble in methanol. They should be mixed and shaken for ~1 h or until fully dissolved. The pH-indicator solution should be applied using a pressurized hand sprayer that will release a continuous and fine mist of spray. Upon soil excavation, the sprayer needs to be pumped to its maximum air pressure so as to provide a continuous and uniform spray to the entire soil profile.

Continuous rather than pulse application of the tracer solution is advised for field experiments investigating preferential flow to prevent undue dilution of preferential flow paths by the *converging flow* (Ritsema et al., 1993) of water that is applied following the pulse. It is also suggested that higher concentrations of the $(NH_4)_2CO_3$ (e.g., 5%) may be applied when the initial soil water content is high to ensure good visibility of the preferential flow patterns.

Experiment

Two field sites were used for characterizing preferential flow under various soil and fluid conditions. The first site was inside the University of California Kearney Research Station located in Parlier, CA, and the second site nearby on private land located on the old Kings River bed. Soil at the first site was Hanford sandy loam (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents) and at the second site was Delhi sand (mixed, thermic Typic Xeropsamments). Soil moisture at both sites varied from near 0 (mostly in the top 20 cm) to a maximum of 8% (below 50 cm). The relevant textural and chemical properties of the two soils are listed in Table 1. Preliminary laboratory experiments were conducted to compare the method of dye tracing with the present method.

Laboratory Setup

Bulk soil samples were collected from the two field sites, and were oven dried and ground to size (2 mm for infiltration tests). We used a water solution that contained a 2% weight of Brilliant Blue Dye (Acid Blue 9, Keystone Aniline Corp., Chicago, IL) and 2% of $(NH_4)_2CO_3$. The soil was gravitation-ally packed into a slab chamber constructed using two pieces of 1 by 1 m^2 plexiglas plates, bolted together at a 1-cm spacing. After filling the soil from bottom up to an ~95-cm height, the chamber was gently tapped using a rubber hammer until the soil was consolidated to a 90-cm height. Then the soil surface was carefully leveled. A pump-pressurized spray line with six nozzles was set at the top of the chamber for applying the infiltration solution. We applied 10 cm of the solution into the Hanford sandy loam, and 15 cm into the Delhi sand. In both cases, the soil surface was ponded during infiltration.

Field Setup

In the field sites, the experimental setup consisted of a 2 by 1.2 m^2 plot, which was irrigated continuously using a moving spray line system designed by Ghodrati et al. (1990). The $(NH_4)_2CO_3$ solution was at 2.6% concentration for Hanford sandy loam and 2% for Delhi sand. The infiltration solution also contained 0.5% weight of KBr, so that the Br^- concentration could be used to check the utility of the pH-indicator method. Bromide concentrations were intensively sampled across the trench face (120 by 100 cm^2) from the center of each 10 by 10 cm^2 grid using a soil corer (5.4 cm i.d., 6 cm long). The total application was 12 cm and the application rate was about 2.3 cm h^{-1}, which resulted in ponded infiltration on the Hanford sandy loamy and unsaturated infiltration on the Delhi sand. After infiltration, vertical soil profiles were excavated across the plot at different times to visualize preferential flow patterns. Upon excavation, each profile was smoothly shaved using a flat shovel, then sprayed with the pH indicator. After 5 to 10 min, colored patterns of preferential flow paths emerged. The images were photographed using a digital camera (1600 by 1200 pixels). The photographs were selectively edited for contrast analysis using a commercial photo editor.

RESULTS

Laboratory Results

Figure 1 shows the pictures taken at 0, 2, and 24 h after infiltration began in the slab chamber. Due to matrix adsorption, the dye-stained areas in both the Hanford sandy loam sand and Delhi sand were considerably smaller than the total wetted areas. The separation of dye and water started ~2 h (Fig. 1a,d) after infiltration began. Five to 10 min after application of the pH indicator on the final infiltration profiles (Fig. 1b,e), the wetted areas near the bottom of the front which had not been stained by dye (Fig. 1c,f) became red, showing that the $(NH_4)_2CO_3$ was a more conservative water tracer.

Table 1. Textural and chemical properties of the two soils used in this study.

Soil	D_b	Sand	Clay	Silt	S.P.	OM	OC	EC‡	ph‡	CEC
	g cm⁻³			%				MS cm⁻¹		cmol kg⁻¹
Hanford sandy loam	1.56	85	11	4	22	0.58	0.26	0.591	7.45	6.72
Delhi sand	1.53	93	4	3	20	0.73	0.33	0.433	6.76	3.04

Soil	Ca^{++}	Mg^{++}	Na^+	K^+	NO_3^-	SO_4^{2-}	$H_2PO_4^-$	Cl^-
		Major exchangeable cations and anions						
					cmol kg⁻¹			
Hanford sandy loam	2.331	0.985	0.069	0.019	5.226	0.3	0.3958	1.014
Delhi sand	1.313	0.097	0.013	0.208	3.29	0.125	0.0928	0.1183

† D_b, bulk density; S.P., water saturation percentage; OM, organic matter content; OC, the organic C content as measured in saturated pastes of soil; CEC, the cation-exchange capacity.
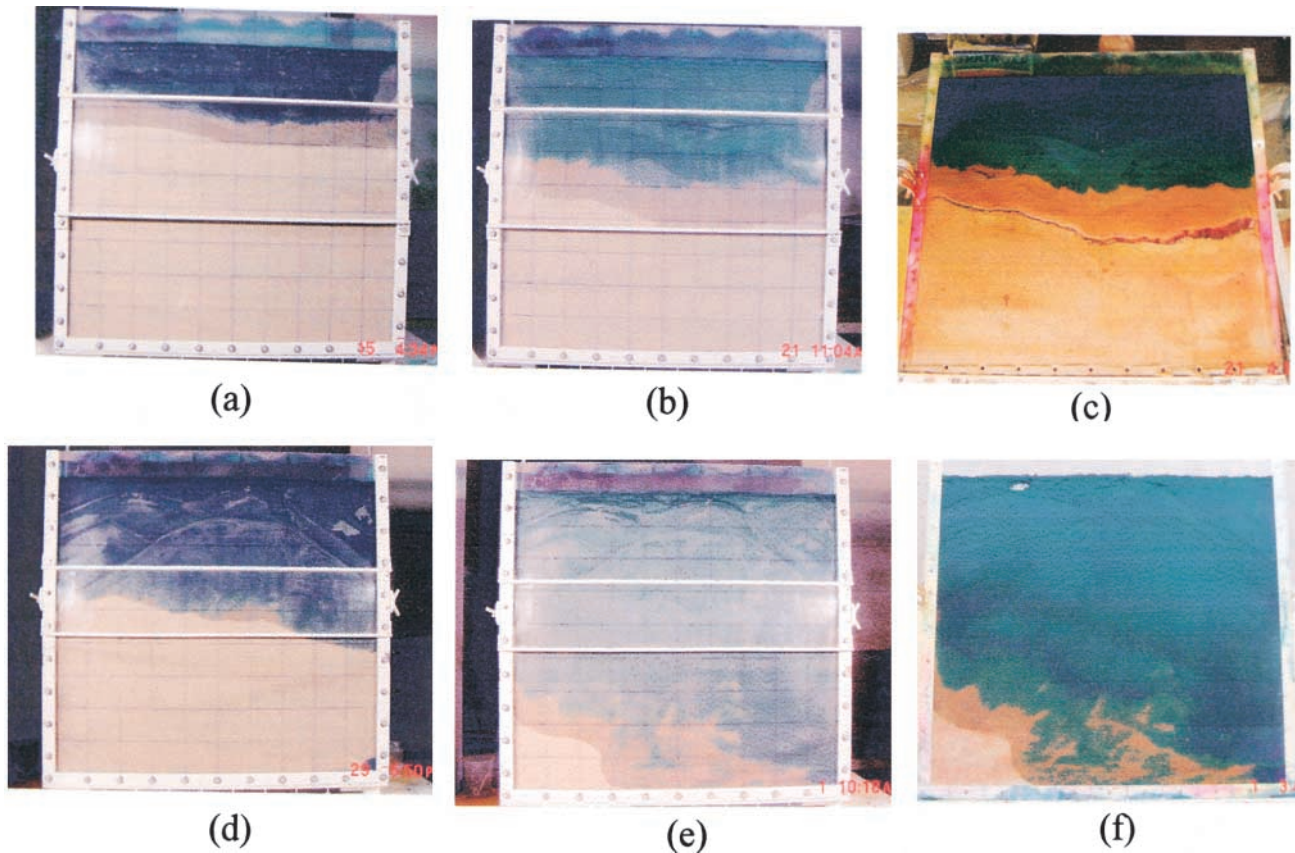‡ EC and pH were measured in extracts of soil pastes.

Fig. 1. Dye and ammonium carbonate infiltration into two initially dry soils. Pictures (a), (b), (c) show wetting front propagation in the Hanford sandy loam; (d), (e), (f) show the process in the Delhi sand. Pictures (c) and (f) show that the wetted but unstained areas by the blue dye became red after application of the proposed pH indicator.
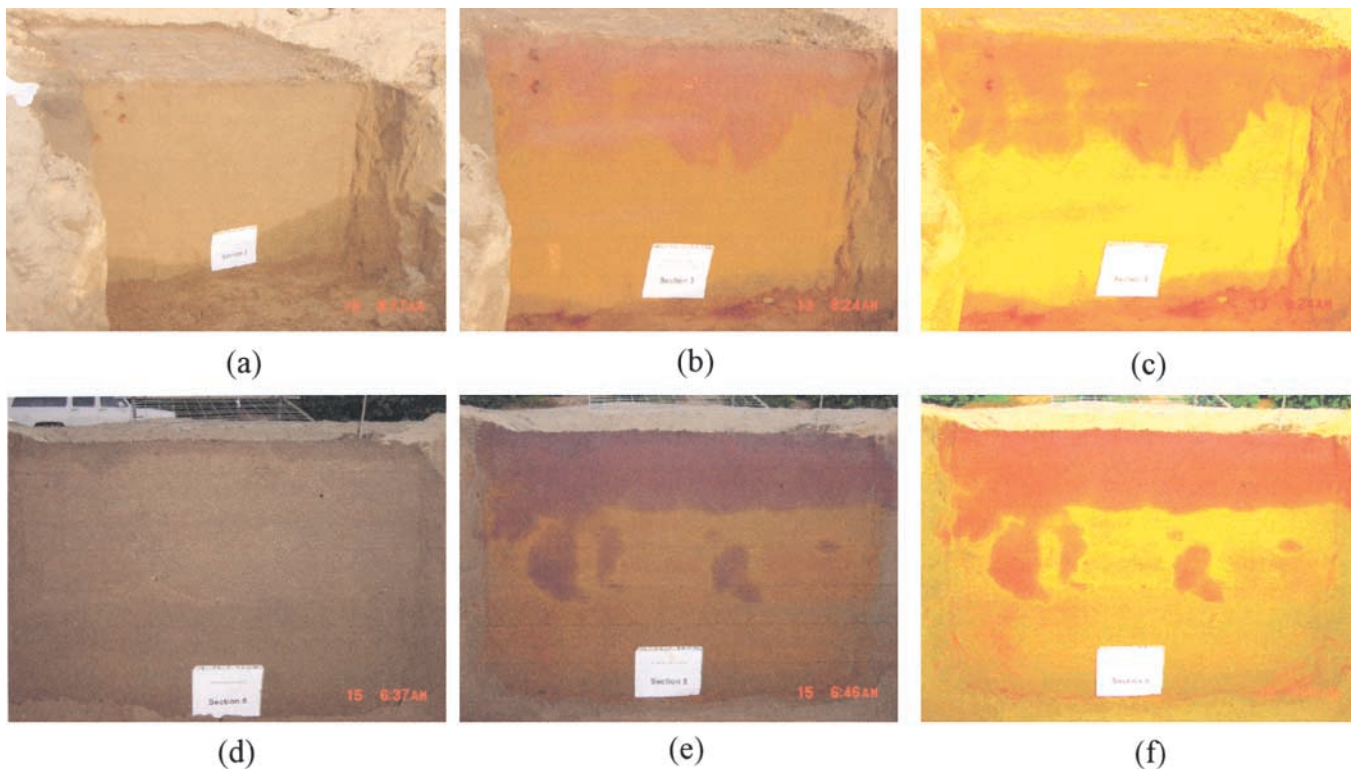

Fig. 2. Visualized preferential flow in the field using $(NH_4)_2CO_3$ and a pH indicator. Pictures (a), (b), (c) show a section of the three-dimensional preferential flow plumes in the Hanford sandy loam 48 h after the end of infiltration. Pictures (d), (e), and (f) show a plume section in the Delhi sand 64 h after the end of infiltration. Preferential flow was not visible in (a) and (d). However, after application of the pH indicator, fingered flow patterns emerged as shown in pictures (b) vind (e). Pictures (c) and (f) are computer enhanced pictures of (b) and (e), respectively.
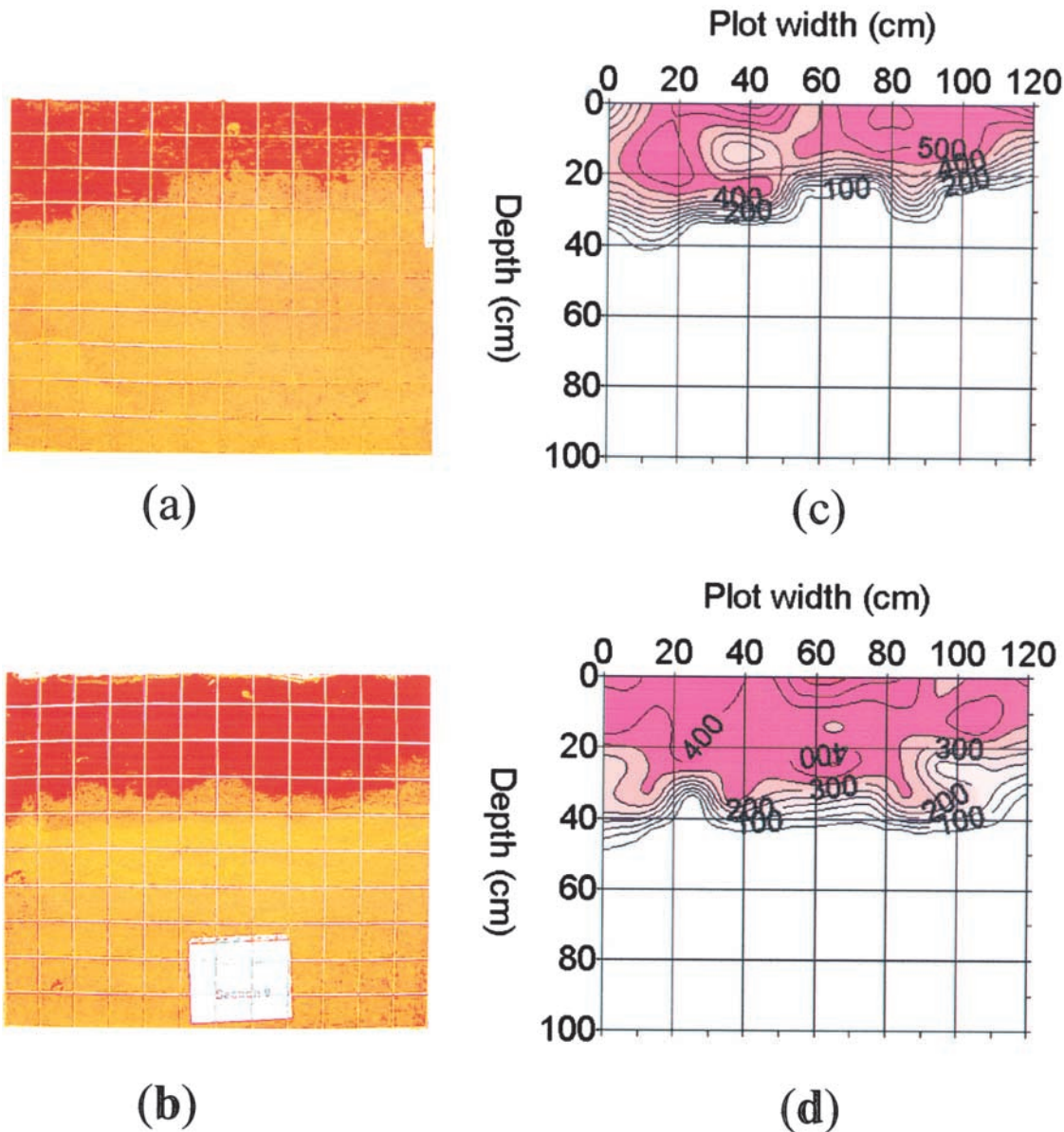
Fig. 3. Flow patterns captured by the camera 30 min after the end of infiltration in (a) the Hanford sandy loam and (b) the Delhi sand. The corresponding Br concentration contour maps in mg L^{-1} are shown in (c) and (d), respectively.

Field Results

Figure 2 shows the visualized preferential flow patches detected in the field experiments. Because both the field soils contained background water contents, the preferential flow paths were invisible as shown in Fig. 2a and 2d. However, 5 min after application of the pH indicator, fingered flow patterns became visible (Fig. 2b,e). Notice that the Hanford sandy loam was exposed to direct sunlight (Fig. 2a,b,c) and experienced high losses of ammonia by evaporation. A 2-min delay in applying the pH

Table 2. Materials and procedures for preparing the infiltration solution and pH indicator.

Application solution	Material composition	Quantity	Preparation procedure
Infiltration solution	Water	Infiltration requirement	Mix ammonium carbonate with water and stir until there is no residue in the solution.
	Ammonium carbonate	2% weight of water for soil with low initial water content and up to 5% for soil with high initial water content.	
pH indicator solution	Methanol (95% purity)	About 0.2 L m^{-2} of soil profile.	Dissolve thymol blue and cresol red in methanol and shake until there is no residue in the solution.
	Thymol blue (ACS reagent, 95%)	1% weight of methanol	
	Cresol red (indicator grade 95%)	1% weight of methanol	

indicator resulted in less resolution of the colored flow pattern. The computer enhanced pictures as shown in Fig. 2c and 2f manifested clearer images of the preferential flow pattern. Those reddish areas at the bottom of the soil profile are artifacts from shading and leaked indicator solution.

Figure 3 shows the comparison of the colored picture of flow pattern with the Br concentration map about 30 min after the end of water application. The Br-concentration map was plotted using Surfer 7.0—a commercial software package (Golden Software Inc., Golden, CO). We used the minimum curvature method of interpolation to construct the contour map. It is clear from Fig. 3 that the flow pattern captured by the camera is similar to the water front revealed by the tracer.

CONCLUSION

Based on an elevation of soil pH value using a strong buffering $(NH_4)_2CO_2$ solution at concentrations of 2 to 5%, we found the pH-indicator method to be a useful tool for field investigation of preferential flow. Compared with the existing dye and I^--starch application, the new method is more capable of producing flow patterns faithfully representing the movement of water flow paths in soils while leaving negligible residue. It is simpler and considerably cheaper for field applications than previously reported methods. Although the ammonium ion (NH_4^+) introduced in the process may be adsorbed to or evaporated from soil, the critical ion OH^- (derived from the hydrolysis of NH_4^+) that determines the pH value of the soil is neither volatile nor adsorbed, and moves along with water. The color signature can last for 1 to 2 h depending on soil and weather conditions, then will disappear because of gradual decomposition of thymol blue and cresol red. Evaporation of NH_3 will reduce the concentration of OH^- and the value of pH. Therefore, exposure of the wetted soil profile to windy and hot air conditions or delay in applying the pH indicator after excavation should be minimized.

A list of the materials needed for preparing the infiltration solution and pH indicator is summarized in Table 2. This method is applicable to most natural soils with pH ≤ 8. For soils with pH >8, the current method is not applicable and other appropriate chemicals and corresponding pH-indicators must be found separately. We therefore suggest that soil pH value be tested before application of this method.

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