Sorotion of Uranine on Forest Soils

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Abstract:
Staining substances have been widely used to visualize flow paths in soils, and recently dye concentrations in soil profiles are quantified using photographs. Fluorescent dye Uranine is one of the promising staining agents. The sorption properties of Uranine are needed to establish initial concentrations in applied solutions, determine Uranine mobility, and model solute transport. At least 65% of Uranine adsorption on subsoils from Okaya, Japan occurred after 1 h of shaking. Subsequently, equilibrium sorption was assessed for six different forest soil samples, including topsoil, subsoil, and a buried organic-rich layer of the Okaya black layer (OB); Fudoji subsoil (F) and Fudoji topsoil (FT); and Mie subsoil (M) and Mie topsoil (MT). The buried black layer at Okaya is rich in organic matter (18.6%) and possibly originated from past anthropogenic practices in this region. The residual soil at the Okaya site is derived from volcanic materials, with erosional processes possibly contributing to deposition in the upper soil profile. The Fudoji soil is poorly developed from volcanic materials, with erosional processes possibly contributing to deposition in the upper soil profile. The Fudoji soil is poorly developed from volcanic materials, with erosional processes possibly contributing to deposition in the upper soil profile.

Soil samples
Six different soil samples were collected from three forested hillslopes: (1) the headwall of a landslide near Okaya city, Nagano Prefecture; (2) Fudoji catchment in Shiga Prefecture; and (3) Konohara catchment, Mie Prefecture, Japan. At each site two soil types representing subsoil and topsoil or a buried organic-rich (black) soil were selected: Okaya subsoil (O) and Okaya black layer (OB); Fudoji subsoil (F) and Fudoji topsoil (FT); and Mie subsoil (M) and Mie topsoil (MT). The buried black layer at Okaya is rich in organic matter (18.6%) and possibly originated from past anthropogenic practices in this region. The residual soil at the Okaya site is derived from volcanic materials, with erosional processes possibly contributing to deposition in the upper soil profile. The Fudoji soil is poorly developed from volcanic materials, with erosional processes possibly contributing to deposition in the upper soil profile.

Adsorption isotherms
Initially, the calibration curve for Uranine fluorescence in pH = 10 solution was measured to relate fluorescence intensities measured by a spectrofluorometer with concentrations of Uranine in solution. This curve was linear for a wide range of concentrations (1 μg L⁻¹ to

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2 mg L⁻¹). Assuming that concentrations of Uranine applied in field experiments are much higher and detection limits in soils are likely higher than 1 µg, concentrations < 1 µg L⁻¹ were set to zero. Batch kinetic and equilibrium studies were conducted by mixing different solution concentrations with soil. Samples were shaken in a reciprocal shaker at 20°C for up to 48 h. All of the solutions contained 0.01 M CaCl₂ background electrolytic solution. At least 0.5 g of each sieved soil was placed in a plastic bag and carefully mixed prior to adding solution to ensure homogeneous samples. A series of experiments with the same mixing ratio yielded negligible differences in sorption indicating that the sample preparation procedure was satisfactory. Preliminary experiments with mixed 1:1 and 1:2 solution-soil weight ratios showed no differences in results. For kinetic studies, 30 samples were prepared by mixing 10 g of dry soil from Okaya with 20 mL of solution with the same Uranine concentration (0.01 g L⁻¹). Ten samples were prepared for each of the following initial pH values: 1, 6.65, and adjusted by either HCl or NaOH. Each series of the same pH was shaken for wide range of times (1, 3, 5, 15, and 30 min, and 1, 5, 15, 24, and 48 h). After shaking, samples were immediately centrifuged at 860×g for 20 s, which was sufficient to separate liquid and solid phases as verified in preliminary experiments where further centrifuging or higher rpm values did not change measured concentrations except in the high pH solution. In the pH = 13 solution, the suspended colloids in some soils remained in suspension even after longer centrifugation at high rpm. Once the solution pH was measured, it was diluted and buffered to pH 10 with NaOH and then measured on a Toshiba fluorescent spectrophotometer using the calibration curve. Dilutions (from 1:1 up to 1:2000) were performed because some concentrations in this study were higher than the linear range of the calibration curve; also their pH had to be adjusted to 10. Dilution was also important to suppress the influence of colloids on fluorescence. Suspended colloids can affect fluorescence in two different ways: (1) dense colloidal suspensions can lower the fluorescence by restricting the passage of excitation light in the cuvette; and (2) moderate to low concentrations of colloids may amplify fluorescence by scattering incident light or contributing their own fluorescence intensity. A 1:10 dilution was found to be sufficient in tests with known concentrations of Uranine containing fixed amounts of colloids in different ratios.

For equilibrium sorption, 120 samples were evaluated. Each soil type was mixed with 10 different concentrations of Uranine (4, 2, 0.2, 0.1, 0.02, 0.01, 0.002, 0.001, 0.0002 and 0.0001 g L⁻¹) in solutions of two different initial pH levels (6.5, 13) and shaken for 48 h. Acidic pH solutions were not investigated as it would be unpractical to add initial acidic solution to field soils because it does not decrease the sorption rates and increases the sorption kinetics. To obtain concentrations after shaking, samples were treated in the same manner as in kinetic sorption experiments.

For high Uranine concentrations in solution (> 1 g L⁻¹), crystallization sometimes occurred on the walls of the flasks. If this occurred, the samples were first treated as usual, but after carefully removing the soil from the flask, a known amount of hot distilled water was added and solution concentration was measured after decrystallization. These data were used to correct the concentration values obtained by the typical procedure.

### Data analysis

Equilibrium sorption data were fit to both Langmuir and Freundlich isotherm models with non-linear least squares. The Langmuir isotherm is given by:

\[
q_e = \frac{QbC_e}{1 + bC_e}
\]

where \(q_e\) is the amount of Uranine adsorbed per unit weight of soil (g kg⁻¹), \(Q\) (g kg⁻¹) is the solid phase concentration corresponding to complete coverage of available sites or the limiting adsorption capacity, \(b\) (L g⁻¹) is a constant, \(C_e\) (g L⁻¹) is the residual liquid phase concentration at equilibrium. The Freundlich isotherm is given by:

\[
q_e = KC_e^n
\]

where \(K\) (L kg⁻¹) and \(n\) (dimensionless) are characteristic constants, that can be interpreted as a relative indicator of adsorption capacity and energy or intensity of the reaction, respectively.

### RESULTS AND DISCUSSION

#### Kinetic sorption

All of the kinetic experiments indicate that more than a half of the adsorption occurs during the first hour for all pH values (Figure 1). After 5 h the solution concentrations gradually stabilized, suggesting that the upper limit of adsorption for particular solution concentrations was achieved. Kinetics of sorption may be an important factor in preparing calibration samples for quantifying dye concentrations in natural soil profiles; according to our observations, adsorbed Uranine on soil does not or only partly contributes to fluorescence. Because the difference in sorption between samples shaken for 24 and 48 h was up to 8.5%, equilibrium sorption was investigated after 48 h of shaking.

The amount of Uranine adsorbed by the Okaya subsoil (O) was much lower in alkaline solution; the initial pH of 13 gradually declined to 8 after 48 h of shaking. Similar amounts of Uranine were adsorbed in both neutral and acidic solutions, but in low pH solution adsorption occurred more rapidly during the first 15 min of the experiment (Figure 1d). After pH in acidic solution increased to pH 3 (Figure 1c), the adsorption kinetics became equal to that of the neutral solution (Figure 1b). This phenomenon can be explained by the form of the Uranine molecule in different pH solutions. At high solution pH (> 9) Uranine is exclusively in the dianionic \(R^–\) form, at pH 5 it is mostly in the monoanionic \(HR^–\) form, at pH 3 it is mostly in the neutral \(H_2R\) form, and at pH 1 it is in the monocationic \(H^+R\) form (Mota et al. 1991). After pH rises above 1, the concentration of the \(H_2R^–\) form of the molecule increased until it reached the value close to that in the neutral solution. Although the pH of the initial solution can be easily adjusted, it is difficult to control the pH of the
resulting solution because of the strong buffering capacity of the soil. Thus, it is important to measure not only the pH of the initial solution, but also the pH after shaking, as it can change drastically during sorption experiments. For example, when an initial solution of pH 10 was used, because of the strong buffering capacity of the Okaya soil (O), the final solution pH after shaking became almost the same as in the final solution with initial pH 6.65.

Equilibrium sorption

Adsorption curves of all samples fit both Freundlich and Langmuir isotherms well ($R^2 > 0.99$ and $R^2 > 0.81$, respectively); however, because experimental data showed typical Freundlich behavior (Figure 2), Langmuir parameters are not presented. The limiting adsorption capacities ($Q$ values) in the Langmuir isotherm are somewhat questionable in terms of the adsorption behavior of our soils. Uranine adsorption in alkaline solution (pH = 13) was definitely much lower than in neutral solution. The Mie topsoil (MT) exhibited the highest sorption among all of the samples, while Mie subsoil (M) soil had the highest sorption among all subsoils. Adsorption did not show any correlation with either organic matter or clay content; however, clay content was low and quite similar for all soils. This finding agrees with other research which found that Uranine sorption appears to mostly depend on mineralogy (Sabatini 2000) and aquifer media charge (Kasnavia et al. 1999). Since most soils are negatively charged, the influence of charge may not be so important in using Uranine for soil staining. However, different mineralogies, including different clay contents or aluminum and iron oxides, may be serious factors to consider; such interactions need more investigation. Depending on the form of the molecule, it will be more easily attracted to grains or surfaces with opposite charge. Given the negative charge on soils, Uranine in high pH solution (in $R^2$ form) was adsorbed less than in neutral solution where it existed in the $HR^-$ and $H_2R^+$ forms.

While sorption parameters for different staining dyes that have been fit to different adsorption isotherm models cannot be directly compared with our results, one can easily plot these graphs within the solute concentration ranges of interest and compare adsorption rates. In Table II, adsorption isotherm parameters from our Uranine experiments are compared with sorption parameters for other dyes and soils in order of decreasing sorption rate within the range of the residual concentrations from 0 to 4 g L$^{-1}$. The Fudoji subsoil (F) equilibrated with alkaline (pH = 13) initial solution experienced the least sorption for all soils in our study, while Mie topsoil (MT) equilibrated in neutral solution (pH = 6.65) had the highest adsorption rate for all soils reported in Table II. All of our soils buffered to pH 13 as well as the Okaya and Fudoji subsoils in neutral solution showed sorption rates comparable to Brilliant Blue FCF and Pyranine dyes, but the Okaya black layer, Mie subsoil, and Fudoji and Mie topsoils experienced very high sorption rates compared to other dye studies. These differences clearly show the importance of buffering the applied field solution to high pH levels to...
This study presents the first results for adsorption of Uranine on forest soils. Experimental data for sorption of Uranine on all forest soils best fit the Freundlich isotherm. Adsorption rates varied widely and were considerably higher for topsoils than for subsoils. Adsorption of Uranine on subsoils is comparable with the popular Brilliant Blue staining dye. Sorption rates can be minimized by adjusting initial pH of solution to high values, which does not adversely impact the environment because the alkaline solution rapidly neutralizes in acidic forest soils.

Suppression of topsoil that was apparent in our study sites. However, the influence of topsoil may not be that strong because Uranine will pass this relatively thin layer quite rapidly.

CONCLUSIONS

This study presents the first results for adsorption of Uranine on forest soils. Experimental data for sorption of Uranine on all forest soils best fit the Freundlich isotherm. Adsorption rates varied widely and were considerably higher for topsoils than for subsoils. Adsorption of Uranine on subsoils is comparable with the popular Brilliant Blue staining dye. Sorption rates can be minimized by adjusting initial pH of solution to high values, which does not adversely impact the environment because the alkaline solution rapidly neutralizes in acidic forest soils. Adsorption isotherm parameters can be used to estimate the mobility of Uranine in forest soils, determine initial concentrations for application in field staining experiments, and for solute transport modeling by adding a retardation factor into advection-dispersion, which can also be corrected with kinetics of sorption.

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SUPPLEMENTS

S1. Soil profile stained with Uranine (raw digital image).
S2. Scheme of this study (including photos of used equipment).
S3. How to compare different adsorption isotherms (example using some isotherms represented in Table II).

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Table II. Comparison of adsorption in different studies (K, n, Q and b are parameters of Freundlich and Langmuir adsorption isotherms respectively).

| Soil          | pH  | Texture   | Dye  | K (L kg⁻¹) | n  | Q (g kg⁻¹) | b  |
|---------------|-----|-----------|------|------------|----|------------|----|
| MT (pH 7)†    | 3.32| sand      | U    | 260.8      | 1.14| na         | na |
| F (pH 7)†     | 3.75| sand      | U    | 154.1      | 1.02| na         | na |
| FT (pH 7)*    | 3.88| sand      | U    | 123.4      | 1.31| na         | na |
| OB (pH 7)*    | 4.94| loamy     | U    | 98.65      | 1.05| na         | na |
| MT (pH 13)*   | 3.32| sand      | U    | 11.53      | 2.05| na         | na |
| F (pH 7)†     | 4.37| sand      | U    | 7.17       | 2.26| na         | na |
| O (pH 7)†     | 4.46| sand      | U    | 6.49       | 1.72| na         | na |
| F§*           | 7.6 | solid     | BB   | na         | 5.87| 4.71       |
| ASS†          | 6.3 | silt loam | P    | na         | 5.66| 7.11       |
| M (pH 13)     | 3.75| sand      | U    | 1.75       | 1.22| na         | na |
| FT (pH 13)    | 3.88| sand      | U    | 2.03       | 1.6 | na         | na |
| OB (pH 13)    | 4.94| loamy     | U    | 1.92       | 1.43| na         | na |
| O (pH 13)     | 4.46| sand      | U    | 0.46       | 1.08| na         | na |
| Elk River     | 4.5 | silty loam| BB   | na         | 3.27| 0.12       |
| C1**          | 4.85| loamy     | BB   | na         | 1.32| 0.15       |
| F (pH 13)     | 4.37| sand      | U    | 0.09       | 1.0 | na         | na |
| D2**          | 5.6 | sand      | BB   | na         | 0.22| 1.42       |
| Vantage**     | 7.1 | sand      | BB   | na         | 0.44| 0.0065     |

* This study
** Data from Ketelsen and Meyer-Windel (1999)
† Recalculated from German-Heins and Flury (2000)
† Data from Duwig et al. (2008)
pH in 0.01 M CaCl₂
§ U–Uranine, BB–Brilliant Blue FCF, P–Pyranine
* Data is not available