A Review of the Use of Dyes as Soil Water Tracers

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Abstract

Dyes have not been used extensively as water tracing agents in soils. Fluorescent dye types find greater application in soil studies due to greater detectability but may be affected by quenching transformations in field soils thus reducing their effectiveness. Compared to other tracer techniques dyes offer a simple method of tracing solute distributions while simultaneously obtaining soil physical and morphological data. This permits a characterisation of parts of the soil profile active in water transmission under various conditions. The continual supply of new types of dyestuff warrants further research into their suitability as soil water tracers.

Introduction

The movement of water through soils is important in a number of ways, not only to soil scientists but also to engineers, hydrologists, agronomists and specialists in other related disciplines. Within soil science water movement plays a prominent role in nearly every aspect of the science. Soil development is influenced to a large extent by the movement of water through the profile, while soil fertility is affected by the extent of leaching of valuable plant nutrients. Irrigation and drainage technology relies heavily on information derived from soil water movement studies, while increasing environmental concern has led to a renewed interest in the leaching of salts and nutrients from soils.

Traditional techniques of studying water movement in soils, such as the use of tensiometers and neutron or gamma probes may be unsatisfactory in certain cases because they give average values for a given volume of soil. These values do not reflect the microscale variations in flow path which tracer techniques may adequately describe (Bouma, 1981). Also solute movement in soil does not necessarily correspond directly to water movement due to interaction of ions with particle surfaces (Kurtz and Melsted, 1973). By carefully selecting a tracer with similar properties to the solute ion under study, the distribution, movement and residence time of the solute can be ascertained. For example, bromide ion can be used successfully as a tracer for nitrate ion in soils (Smith and Davies, 1974).

The ideal properties of a tracer are defined by Kaufman and Orlob (1956) as (a) the ability to correctly describe the velocity variations of the liquid being traced without modifying in any way the transmission characteristics of the porous medium; (b) detectability at low concentrations; and (c) absence of exchange or absorbance of the tracer. Additional requirements are: (d) low background levels in the environment in which the tracer is to be used; (e) high chemical and biological stability; (f) harmless at the concentrations to be used; and (g) inexpensive.

It is unlikely that any tracer could fulfil all these requirements, hence in practice one has to choose a tracer that satisfies the needs of a particular situation. Many different tracer techniques have been developed to study soil water movement with many of these being adapted from hydrological (Wright and Collings, 1964) or engineering applications (Plummer, 1945; Sturm and Johnson, 1950). The most commonly used tracers in soil studies are radio-isotopes, neutral salts, biological tracers and dyes. Radio-isotopes suffer from the disadvantage that they require specialised analytical equipment and often have short half-lives. Furthermore cationic radio-isotopes are unsuitable due to adsorption while anionic radio-isotopes may suffer similarly if used without a stable carrier (Kaufman and Orlob, 1956). Neutral salts, particularly nitrate and chloride, have been used but there are problems with high background level necessitating high concentrations in a tracer application. Nitrate will be affected by plant uptake and microbial transformations while a high salt concentration can lead to density effects, for example fingering of infiltrating water (Krupp and Elrick, 1969), and also possible modification of the transmission characteristics of the soil due to flocculation of clay particles (Quirk and Schofield, 1955; McNeal, 1974).

Biological tracers, often used as tracers in pollution studies (Rahe *et al.*, 1979), are generally unsuitable because of their size, and also because the survival of any live cell depends to some extent on its ability to move towards or stop at sites presenting favourable nurients, temperatures, surfaces, etc. (White, 1976). Dyes, however, appear to posses a number of the ideal tracer properties as defined by Kaufman and Orlob (1956), being inexpensive, non-toxic and detectable at low concentrations. However, their stability and movement in soil water has been the subject of a number of conflicting reports (Reynold, 1966; Aubertin, 1971; Omoti, 1977; Omoti and Wild, 1979b; Aulenbach and Clesceri, 1980). This review aims to discuss the suitability of dyes as soil water tracers in the light of this evidence.

Early uses of dyes

Dyes have been in use for almost a century as tracers of water movement. Dole (1906) quotes work done by Brard in 1887 using fluorescein as an underground water tracer and Trillat (1899) studied the use of various dyes as flow indicators and the effect of passage through the soil upon them. The application of dyes to soil water tracing, however, has developed much more recently. An early attempt at visual tracing of a dye was described by Harding and Wood (1941) for use in a laboratory flow model. Tamm and Troedsson (1957) were able to study the percolation of rainwater into wet soil. Ammonium thiocyanate was spread on the surface and allowed to infiltrate the soil with rain. Distribution of the tracer was evaluated by spraying soil faces with ferric chloride solution which gave a red ferric thiocyanate colouration on contact with the tracer. Problems were encountered however due to poor distinction from natural soil colours and also the toxic effect of the tracer on plant life.

Since these early attempts at utilising coloured tracers a number of studies have used both fluorescent and non-fluorescent tracer dyes to try and characterise the flow of water through the soil.

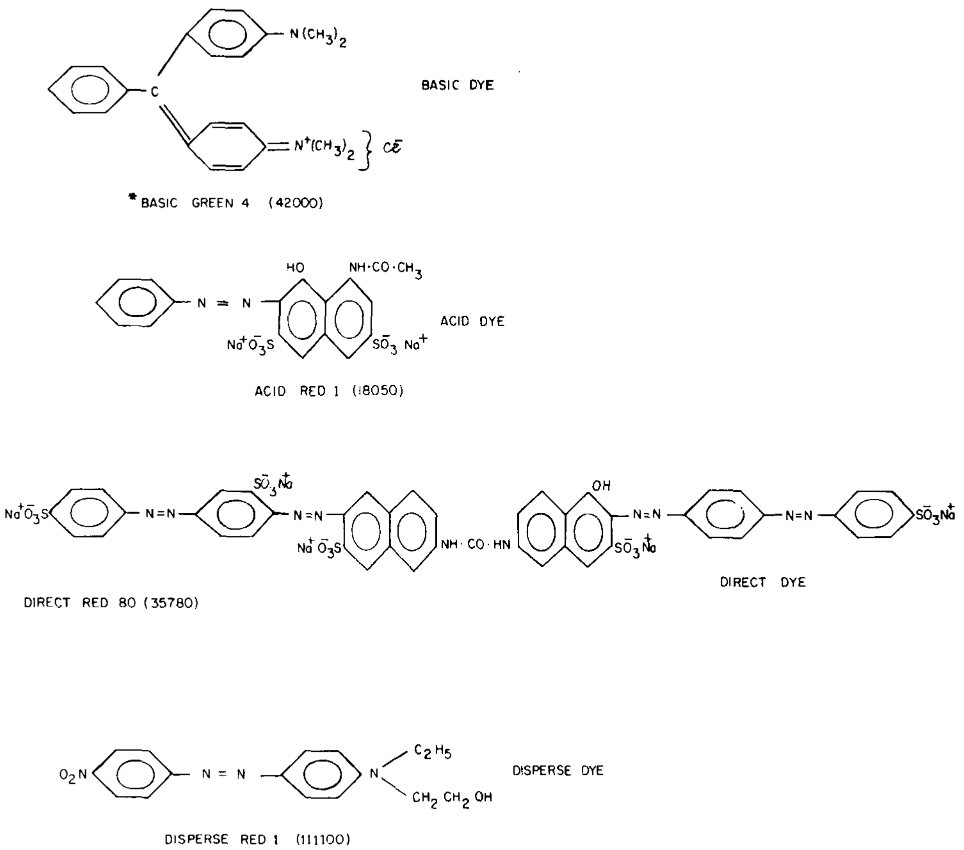

Figure 1
Structures of typical basic, acid, direct and disperse dyes (from Corey, 1968)
**Colour index name with index No. in brackets.*

Non-fluorescent dyes

Non-flourescent dyes are available in various forms. Corey (1968) evaluated a number of these types, namely direct, disperse, acid and basic, for use in acid soils. Examples of the four main types are shown in Figure 1.

Disperse dyes are non-water soluble but exist as discrete fine particles in suspension while basic, acid and direct dyes are generally water soluble. While direct and acid dyes hydrolyse to anionic forms, basic dyes hydrolyse to cations and therefore may be adsorbed through ion exchange (Kurtz and Melsted, 1973). Corey's (1968) results showed that the acid dyes Acid Red 1 (CI 18050*), Acid Red 14 (CI 14720) and Acid Blue 26 were most suitable for water tracing in acid soils. Direct and basic dyes were found to be adsorbed through ion exchange and Van der Waal's forces while disperse dyes, being particulate, were retained by a physical filtration effect. Despite this drawback however, disperse dyes have proved useful in some situations. For example Clarke and Vincent (1974) used "Dispersol" Orange B-2R (Imperial Chemical Industries, 1971) to trace the extent of slip circles in slope terracettes having sandy soils. Corey (1968) points out that the number of sulphonic acid groups in the dye molecule is related to its suitability as a tracer – good tracers having more than one of these functional groups. These groups probably have the effect of inhibiting adsorption through electostatic repulsion from soil particle surfaces. Strong adsorption of dye may prove desirable however in certain circumstances. Bouma *et al* (1977) and Bouma and Dekker (1978) used methylene blue (CI 52015), a strongly adsorbed dye, in infiltration experiments and found it a useful marker of soil pores actively participating in water transmission through a profile. Linden and Dixon (1976) also used methylene blue to study the effects of soil air pressure on water flow into and through soil macropores. Ehlers (1975) used Ultramarine blue (CI 77007) to mark water-conducting earthworm channels in a field soil and Omoti and Wild (1979b) found Aniline blue (CI 42755) useful in a similar experiment. Thus although the strongly adsorbed dye cannot trace the extent, or spatial distribution, of water movement it is useful in that it can act as a marker of the pathways of movement. A problem encountered with this approach, however, is that large quantities of dye may have to be applied (Bouma *et al*, 1977) in order for the dye to be detectable. Bouma and Dekker (1978) found that a strongly adsorbed dye may not be useful at low infiltration rates where water moves through smaller pores and is therefore more susceptible to adsorptive losses. At high infiltration rates, however, the dye was found to move to depths exceeding one metre.

Little information is available on the stability of non-fluorescent dyes in soils as most of the studies have been short term infiltration experiments where the dye remains in the soil only for a very short period. Clarke and Vincent (1974) report, however, that the disperse dye "Dispersol" Orange B-2R was detectable in the field 7 weeks after application.

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*Colour Index Number (Colour Index, 1971).

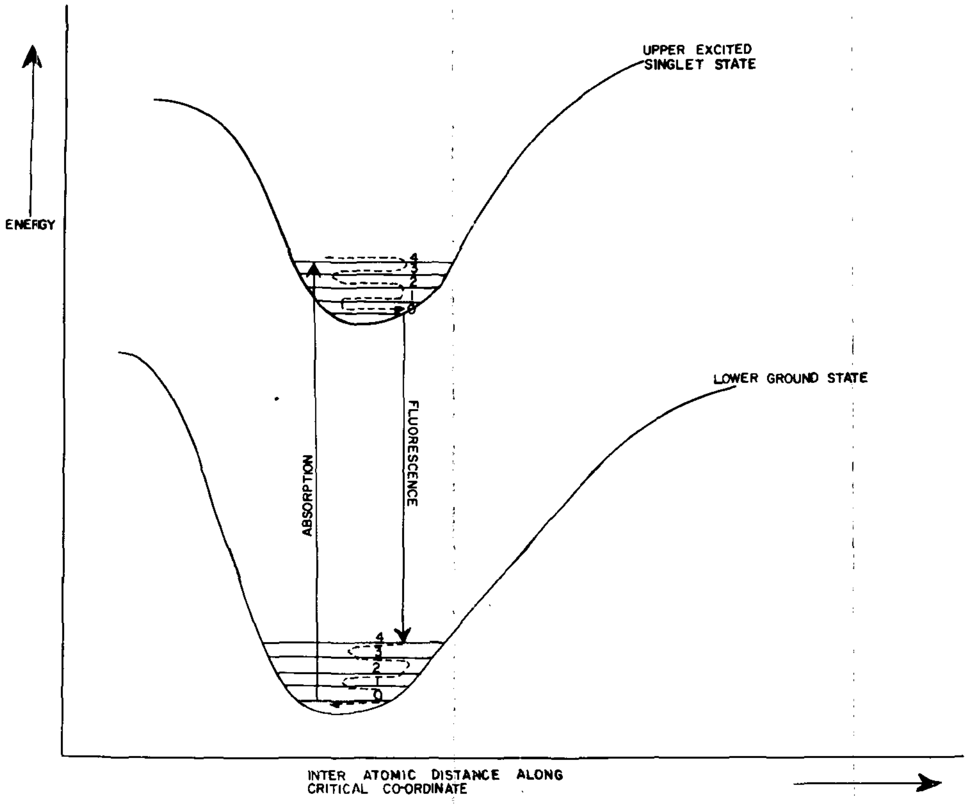

Figure 2

Schematic energy level diagram for a simple fluorescent molecule. The numerals represent vibrational energy levels while the broken line (———►) represents the loss of vibrational energy by collision processes.

Fluorescent Dyes

Fluorescent dyes have the advantage over non-fluorescent varieties in that the fluorescence of compounds can be used to measure concentrations as low as 10^{-5} to 10^{-7} g/ℓ, whereas few substances can be estimated colorimetrically below 10^{-4} g/ℓ (Williams and Bridges, 1964). In simplified terms the process of fluorescence can be envisaged as a sequence of events –

- Absorption of energy by the molecule from an outside source such as the sun or an ultraviolet lamp (a quantum of light is absorbed by a molecule in about 10^{-15} s), and a transition to a higher electronic state takes place (see Figure 2). This state is known as the excited singlet state.
- The molecule then relaxes from the highest to the lowest vibrational level of that state. Energy is lost in this process.
- If all the excess energy is not further dissipated by collisions with other molecules the electron returns to the ground electronic state with the emission of energy. This phenomenon is called fluorescence.

As some energy is lost before emission can occur the emitted energy is of longer wavelength than that absorbed i.e. Stokes fluorescence (Figure 2). It is this property of dual spectra – a different specific combination of excitation and emission spectra for each fluorescent substance – which is utilised to make fluorimetry an accurate and sensitive analytical tool.

A more detailed description of the theory of fluorescence can be found in Guibault (1973), Barrow (1979) or Hercules (1966).

Fluorescent dyes have gained greater acceptance as water tracers primarily because of this greater detectability, compared to non-fluorescent types. Examples of some of the more commonly used dyes are shown in Figure 3.

The green fluorescent dyes, particularly fluorescein, have usually been preferred to other types because they fluoresce in the green band of the visible spectrum – a band to which the human eye is particularly sensitive. In water tracing for hydrological purposes fluorescent dyes have been in use since the turn of the century (Dole, 1906) and are now a generally accepted technique in hydrology (White, 1976). They have also found applications in engineering (Sturm and Johnson, 1950; Plummer, 1949), in pollution studies (Rahe *et al*, 1979; Aulenbach and Clesceri, 1980) while Robinson and Donaldson (1967) studied water uptake in plants using these tracers. Feurstein and Selleck (1963) and Smart and Laidlaw (1977) have assessed a number of dyes for suitability as water tracing agents in hydrology, and some of their findings can be applied to the use of dye tracers in soil.

While fluorescence offers analytical sensitivity, it is necessary however to know the limitations of the technique as fluorescence of a dye is sensitive to a number of factors:

- Firstly dye fluorescence is found to display a negative temperature coefficient. The effect can be marked with a reduction in fluorescence of up to several per cent per degree Celcius for the rhodamine dyes for example (White, 1976). Smart and Laidlaw (1977) have produced temperature correction data for a number of commonly used dyes.
- Intensity of fluorescence is also dependent on concentration. At high dye concentrations fluorescence is no longer proportional to concentration due to quenching (Williams and Bridges, 1964), some of the emitted fluorescent light being reabsorbed by other molecules (see Figure 4).

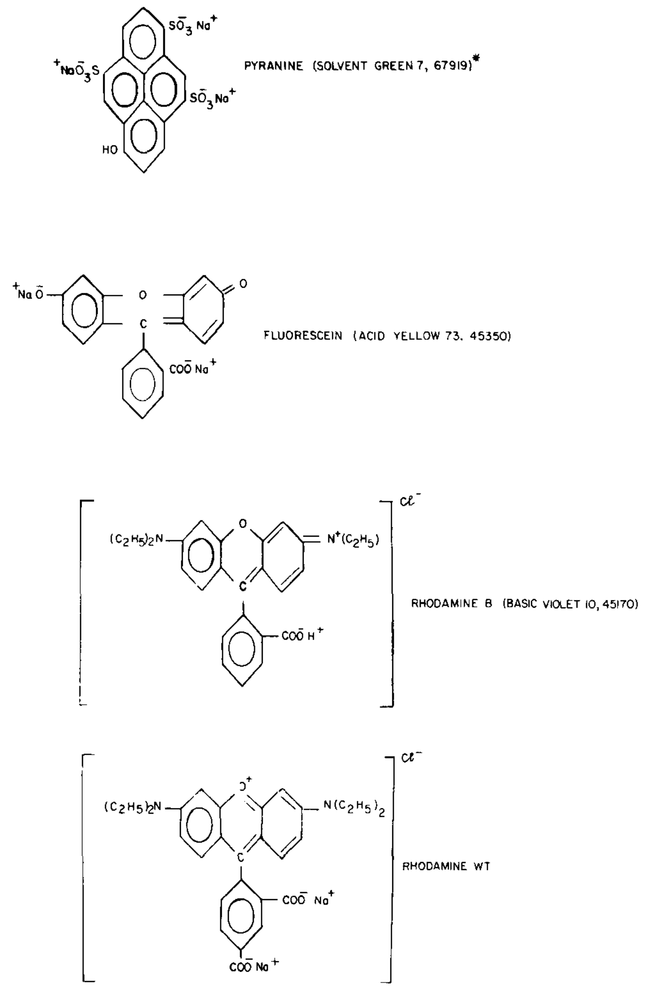

Figure 3
Structures of typical fluorescent dyes commonly used for tracing purposes
**Common name followed by colour index name and number*

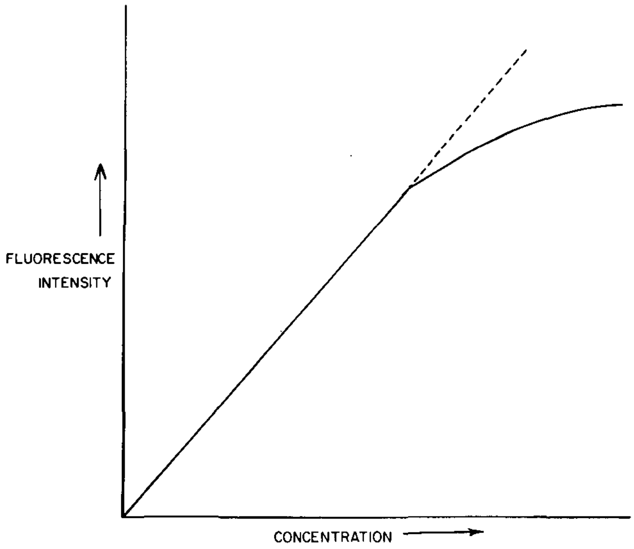

Figure 4
Fluorescence vs. concentration. At high concentrations quenching occurs due to fluorescence being reabsorbed. Samples in the upper range must be diluted to fall on the linear portion (from Wilson, 1968).

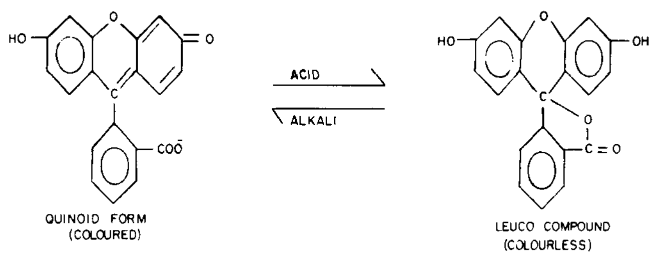

Figure 5
Structure of fluorescein under acid and alkali conditions (from Smart and Laidlaw, 1977)

Thus dye fluorescence in soil is sensitive to soil moisture content (Omoti and Wild, 1979a).

- Intensity and wavelength of fluorescence can also be affected by the solvent used but the effect is unpredictable. Other chemicals in the dye solution can cause quenching through (a) absorbance of exciting light; (b) absorbance of light emitted by the dye (as in concentration quenching); and (c) degradation of the excited state (Wilson, 1968). A further possibility is that the quenching agent may chemically change the fluorescent compound. Chlorine, for example, is a known quencher of tracer dyes (Wilson, 1968) and therefore tap water should not be used to prepare dye solutions. pH is another factor which can markedly affect fluorescence of dyes in solution. For example fluorescein changes from a quinoid structure to a colourless leucocompound under acid conditions (see Figure 5), while the fluorescence of pyranine varies markedly with pH due to ionization of the phenolic OH group (Smart and Laidlow, 1977).

For soil tracer studies therefore, it is necessary to choose a dye which is fairly insensitive to changes in pH, temperature and quenching effects, and is not adsorbed by the soil. Reynolds (1966) screened twelve fluorescent dyes for use in soils and concluded that pyranine (CI 57917) was most suitable for field experiments due to minimum adsorption and high stability, while Aubertin (1971) found fluorescein (CI 45350) useful in tracing pathways of flow in forest soils. A more comprehensive screening of dye suitability by Omoti (1977) found the rhodamine dyes to be unsuitable due to their temperature sensitivity and high adsorption losses. Aulenbach and Clesceri (1980), however, found Rhodamine WT very useful for tracing water movement in wastewater application to land, with the dye being detected as far as 321 m from the point of application. In this experiment, however, the sandy medium tested would not be expected to sorb the dye to any large extent. Omoti and Wild (1979a) concluded pyranine and fluorescein were the most suitable dyes for use in soil studies. Fluorescein suffers from photo-decomposition but this can be overcome by adapting the experimental technique while pyranine has been found to be unstable in some field experiments (Omoti and Wild, 1979a) lasting over 24 h. This contrasts with the results of Reynolds (1966) who was able to detect pyranine in the field 97 days after application. Instability of pyranine appears to be due to its ability to solubilise organic matter in the soil thus causing colour quenching (McLaughlin, 1979).

The variable field results reported may therefore be due to differences in soil organic matter content and composition. Low recoveries of both pyranine and fluorescein in the field (Rahe *et al*, 1979) can also be attributed partially to adsorption as both dyes are large molecules and therefore subject to Van der Waals forces (Grim *et al*, 1947). Fluorescein can also form a basic cation susceptible to ion exchange (Omoti and Wild, 1979a). Further losses of dye may be due to quenching by electron transfer (McLaughlin, 1979) whereby the dye molecule acts as an electron donor or acceptor (Weiss, 1943) in soil oxidation/reduction transformations. Most fluorescent dyes are large molecules having conjugated double bonds and because fluorescence requires the molecule to have "Π" or "delocalised" electrons (Williams and Bridges, 1964) it is likely therefore that any fluorescent tracer may be affected by such redox reactions. In short term laboratory column leaching experiments (Omoti, 1977), pyranine was found to be the dye which most closely followed water movement in the profile (providing no degradation occurred). This, as pointed out by Corey (1968) for non-fluorescent dyes, may be related to the dyes molecular structure – pyranine having a large number of sulphonic acid groups. Further research is required however to determine the exact relationship between molecular structure and dye performance in soil.

Fluorescent dyes presently available therefore appear to be unsuitable for the quantitative determination of soil water movement and distribution especially when assessed photographically (Omoti and Wild, 1979b). However, the dyes are useful in that they give a visual non-destructive indication of the pathways of movement in the profile. The continual discovery of new types of dye warrants further research to assess their use as water tracing agents. Optical brightening agents from the detergent industry are a case in point. Glover (1972) found these compounds useful in hydrological studies but as yet they have found little application as soil water tracers.

Analytical Methods

Non-fluorescent dyes generally require no special equipment for use. Dye solutions or suspensions are applied to the soil and distributions assessed visually or the concentration of the dye measured colorimetrically in a soil extract. An unusual method suggested by Clarke and Vincent (1974) for a disperse dye is to select a dye which sublimes on heating. If soil samples containing such dyes are pressed against "Melinex" polyester film and heated, the dye sublimes onto the film, dyeing it to give a permanently coloured picture of the flow lines through the soil. If required the dye can then be extracted from the "Melinex" film using monochlorobenzene in a Soxhlet apparatus and the dye concentration determined colorimetrically.

Fluorescent dye distributions can be measured fluorimetrically in soil extracts, (Omoti and Wild, 1979a; 1979b; McLaughlin, 1979), visually (Reynolds, 1966; Aubertin, 1971) or photographically *in situ* after excitation with an ultraviolet light source (Reynolds, 1966; Ritchie *et al*, 1972; Omoti and Wild, 1979a; McLaughlin, 1979). Fluorimetric analysis can be done with either a spectrofluorimeter or a filter fluorimeter, the latter being less sophisticated and less expensive. These instruments excite the sample using a replaceable light source, usually a low pressure mercury lamp with or without a phosphor coating. Excitation light passes through a primary filter before being absorbed by the dye, and emitted fluorescence is measured at 90° to the excitation light path after passing through a secondary filter. Careful selection of primary and secondary filters depending on dye characteristics increases analytical sensitivity (Smart and Laidlaw, 1977). Further details of fluorimetric procedures can be found in Wilson (1968) and Smart and Laidlaw (1977).

Photographic recording of dye distribution favours the use of fluorescent dyes which give a sharper distinction from natural soil colours compared to non-fluorescent types. Soil samples are usually photographed in darkness with only an ultra violet lamp for illumination thus eliminating background interference. Careful selection of film, lamp and filter combinations increases the sensitivity of the technique (Omoti, 1977; McLaughlin, 1979) but the results cannot be assessed quantitatively (Omoti and Wild, 1979a).

Summary and Conclusions

Relatively little work has been done using dyes as water tracers in soil studies. Non-fluorescent dyes are suitable for some applications because they are relatively stable in soil and are inexpensive to use. Fluorescent dyes have the advantage that they are detectable at lower concentrations, but different dyes vary in their susceptibility to environmental conditions, especially under long term field experiments. No one dye is suitable for all applications and the user must carefully select a dye which will satisfy the needs of the particular situation. Also because most of the dyes studied (both fluorescent and non-fluorescent) are large molecules they will be adsorbed to a certain extent by *all soils*, even if electrostatically uncharged. Adsorption may be desirable in certain cases in order to identify the pathways of flow through soils. (Bouma *et al*, 1977; 1979; Bouma and Dekker, 1978). Bouma (1981) stresses the importance of dyes in the functional characterisation of soil pores and emphasises that dyes are essential in establishing pore continuity patterns which influence the dynamic physical characteristics of soil. Data obtained through staining techniques can be used quantitatively in the calculation of hydraulic parameters in soil (Bouma *et al*, 1979). Although these adsorbed dyes can indicate pathways of flow they provide little information of the distribution and residence time of water in soil. As yet no dyes have been developed which follow exactly the movement of water in soil. It appears that tracer dyes which perform well as water tracers possess more than one sulphonic acid group, an observation which holds for both fluorescent and non-fluorescent dye types. The continual supply of new dye molecules having different structures warrants that further research be carried out to assess their suitability as soil water tracers and also to ascertain the relationship between molecular structure and dye performance within the soil environment.

Compared to other types of tracer (salts, radioisotopes and biological tracers) dyes appear to offer great potential for similtaneously relating solute distribution in soils to soil physical and morphological characteristics, (autoradiography being rather complex in comparison).

Parts of the profile active in water movement can be identified without destroying soil structure, thereby enabling valuable soil physical information to be obtained simultaneously with tracer distribution data.

Much valuable information could be gained using dyes to characterise water movement under various conditions. The different transmission characteristics of structured soils could be assessed using dyes as could the effect of soil cultivations on water movement through the profile.

Acknowledgements

Much of the original information was gathered for research carried out under the supervision of Prof A. Wild (Reading University, England) and financially supported by the Ministry of Agriculture, Fisheries and Food for Northern Ireland, whose support is gratefully acknowledged. Thanks are also due to the Director and Staff of the Soil and Irrigation Research Institute (Pretoria) for encouragement and advice during the preparation of the paper.

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