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9. ABSTRACT

I. Nitrate. Movement of applied nitrate (a concentrated solution sprayed uniformly over the soil surface) under intermittent flooding was investigated in Molokai silty clay (Typic Torrox), an important soil for sugarcane (Saccharum officinarum L.) and pineapple (Ananas comosus) production in Hawaii. Nitrate distribution in the profile was characterized under an extended irrigation scheme by in situ sampling of soil solutions with suction probes one week after each water application. The nitrate peak moved only one-third as far as would have predicted by a piston displacement model. Equilibration of applied nitrate solution with the aggregate surface soil for one week prior to flood irrigation further retarded nitrate leaching. Apparently, equilibration involved bulk flow and diffusion of nitrate into aggregate micropores in which the solute was less susceptible to transport in water being conducted mostly in the macropores during and soon after irrigation. Prediction of nitrate distribution based on dispersion (diffusion plus convection) equation approximated experimental results for successive irrigations reasonably well when equation parameters were obtained by fitting one set of experimental data. The drawback of this theoretical model is discussed. II. Picloram. Most of the applied herbicide picloram (potassium salt of 4-amino-3,5,6-trichloropicolinic acid) was retained in the top 40 cm depth of the Molokai soil with cumulative applications of 48 to 74 cm water following application of the chemical to the soil surface. Distribution of picloram in the soil profile one week after each irrigation was determined by in situ sampling of soil solution with porous ceramic cups placed at several depths. Although movement of the picloram peak was retarded more than was anticipated from equilibrium adsorption measurements, a significant fraction of the applied herbicide moved ahead of the peak deep into the profile (down to the 143 cm depth) after a single application of 24 cm water. Rapid flow through macropore sequences combined with temporary retention of

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picloram in aggregate micropores appear to be responsible for the unusual pattern of movement. Published data for nitrate movement in the same field plots of Molokai soil were compared with picloram movement data to provide a measure of the relative mobility of these solutes. A comparison of the results reported here with published field data of solute leaching in other soils indicated a greater retardation of solute peak movement in Molokai soil than in less aggregated soils.

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Field Study of Solute Movement in a Highly Aggregated Oxisol with Intermittent Flooding: I. Nitrate[1]

V. Balasubramanian, Y. Kanehiro, P. S. C. Rao, and R. E. Green[2]

ABSTRACT

Movement of applied nitrate (a concentrated solution sprayed uniformly over the soil surface) under intermittent flooding was investigated in Molokai silty clay (Typic Torrox), an important soil for sugarcane (*Saccharum officinarum* L.) and pineapple (*Ananas comosus*) production in Hawaii. Nitrate distribution in the profile was characterized under an extended irrigation scheme by *in situ* sampling of soil solutions with suction probes 1 week after each water application. The nitrate peak moved only one-third as far as would have been predicted by a piston displacement model. Equilibration of applied nitrate solution with the aggregated surface soil for 1 week prior to flood irrigation further retarded nitrate leaching. Apparently, equilibration involved bulk flow and diffusion of nitrate into aggregate micropores where the solute was less susceptible to transport in water being conducted mostly in the macropores during and soon after irrigation. Prediction of nitrate distribution based on dispersion (diffusion plus convection) equation approximated experimental results for successive irrigations reasonably well when equation parameters were obtained by fitting one set of experimental data. The drawback of this theoretical model is discussed.

Additional Index Words: water quality, pollution, fertilizers, irrigation, ground water.

Nitrogen leaching in soils reduces the efficiency of N utilization by crops and sometimes contaminates the ground waters. This is a potential problem in irrigated Oxisols planted to sugarcane (*Saccharum officinarum* L.) in Hawaii especially when the root systems are poorly developed during the first few months of crop growth. The quantities of water commonly applied with furrow irrigation during this period are frequently in excess of the evapotranspiration. Analysis of ground waters in Hawaii has indicated instances of increased nitrate levels, apparently associated with sugarcane fertilization (Mink, 1962; Visher and Mink, 1964; Tenorio, Young, and Whitehead, 1969). Studies by Takahashi (1964, 1967, 1968), Ayres and Hagihara (1960), and Ekern (1970) indicate that leaching has not caused major losses of N from these soils, especially when sugarcane was well established. Takahashi (1969) believed that any N loss through leaching occurs soon after fertilization when immobilization is minimum and nitrification is maximum. Lysimeter data reported by Dutt et al. (1970) for California soils show that even if fertilizer N fails to pass through the soil in large quantities, it may replace native N in the biological transformations of soil organic fractions causing an increase in the leaching loss of native N. Thus, it appears that nitrate either coming from applied fertilizer or mineralized from soil organic fractions does move through the soil profile.

In a chloride leaching study with packed columns of aggregated clay (Clackline Kaolinite), Aylmore and Kareem (1968) observed that leaving the chloride tracer band overnight before leaching resulted in higher chloride retention in the upper sections of the column than when a chloride slug was leached immediately after application. These authors attributed this retention to molecular diffusion of chloride into relatively stagnant intra-aggregate pores when enough time was allowed between chemical application and leaching. Since the Molokai soil (Typic Torrox) is highly aggregated with inter- and intra-aggregate pores, it was decided to characterize the nitrate movement under two different sets of initial conditions: (i) nitrate application followed by immediate leaching (nonequilibrated treatment) and (ii) nitrate application followed by a 1 week equilibration time before the first leaching (equilibrated treatment). The study was conducted concurrently with other experiments on picloram herbicide (Rao et al., 1973) and water movement in the same soil (R. E. Green, P. S. C. Rao, V. Balasubramanian, and Y. Kanehiro. Field infiltration and redistribution of water in a Hawaiian Oxisol. Manuscript in preparation for Soil Sci. Soc. Amer. Proc.).

MATERIALS AND METHODS

These experiments were conducted on Molokai silty clay (a member of the clayey, kaolinitic, isohyperthermic family of Typic Torrox of the order Oxisols). It is the most extensive soil series planted to sugarcane in Hawaii. This soil is characterized by low organic matter (3% in the surface), low cation exchange capacity (14 meq/100g), and high content of iron oxides (20% Fe_2O_3). Negative charges predominate on clay surfaces resulting in very low anion exchange capacity. The soil is slightly acid (pH = 6.4). The sustained infiltration rate was about 4 cm/hour and the water content ranged from 0.45 cm^3/cm^3 immediately after infiltration to 0.36 cm^3/cm^3 1 week after irrigation. Other physical properties of this soil are discussed elsewhere (Sharma and Uehara, 1968).

Duplicate experimental plots (2.74 by 2.74 m) were used to successively study nitrate movement for the nonequilibrated (first) and equilibrated (second) treatments. The plot area was deliniated by wooden boards wrapped in black plastic inserted about 15 cm into the soil. This arrangement facilitated ponding water on the plots when required. Individual plots were covered by a metal canopy at a height of 2.4 m.

The soil solution sampling depths (3, 15, 27, 45, 63, 81, 103, 123, and 143 cm) in each plot were duplicated by inserting the suction cups into separate holes arranged in two parallel rows 1.5 m apart. (Cups at the 103- and 123-cm depths were not duplicated.) The cups in the two rows were arranged in such a manner that the deepest cup in one replicate was opposite the shallowest cup in other. A suction system similar to that described by Reeve and Doering (1965) was established for sample collection. The cups from the different depths were connected to individual sample collection bottles which in turn were connected to a vacuum pump through a manifold. A suction of about 0.7 bar was applied simultaneously to all the cups. After 1 hour, the suction release valve was opened successively for all individual bottles and soil solution samples were collected in these bottles. Use of large porous cups (surface area $\approx$ 90 cm^2) resulted in adequate sample volumes. The volume of solution per sample ranged from 10 to 80 ml. All samples having volumes less than 10 ml were rejected. Nitrate in these samples was analyzed using a nitrate specific ion electrode.

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Before starting the experiment, all plots were leached several times to secure uniformly low nitrate levels throughout the profile. After preliminary leaching, the soil water was allowed to redistribute in the soil profile until profile water contents were relatively constant (≈ 0.36 cm^3/cm^3) prior to application of nitrate and subsequent irrigation.

The rate of fertilizer application was 100 kg N/ha; the calculated amount of the KNO_3 salt was dissolved in 5 liters of water and sprinkled uniformly over the plot with a garden sprinkler. Another 5 (0.07 cm) and 30 liters (0.40 cm) of water, respectively, for the nonequilibrated and the equilibrated experiments were added to move the nitrate into the soil surface.

In the nonequilibrated treatment, the first irrigation (8 cm water) was applied immediately after the nitrate application. In the case of the equilibrated treatment, 1 week elapsed between the N application and the first irrigation. Other procedures, described below, applied to both treatments. Soil solution samples were secured 1 week after each irrigation. All irrigations, except the first, consisted of 11 cm of water. A total of seven irrigations was given for the nonequilibrated treatment and six irrigations for the equilibrated treatment. Volumetric water contents of the soil at all depths varied from about 0.45 cm^3/cm^3 just after irrigation water had infiltrated to about 0.36 cm^3/cm^3 at the time of sample collection.

The mean movement of nitrate in centimeters was determined by the method of Bates and Tisdale (1957). The percentage nitrate for each segment of the profile was multiplied by the distance travelled in reaching the center of the segment; the sum of these products divided by 100 gives the weighted mean movement of nitrate.

Planimeter integration of areas under the curves gave an estimate of detention of applied nitrate in the soil. The theoretical area for 100% detention was calculated assuming a uniform distribution of the applied nitrate over the entire 143-cm profile with a mean water content of 0.36 cm^3/cm^3. The measured areas were compared with theoretical areas to calculate the percent detention of applied nitrate after each irrigation.

All nitrate calculations were based on *net* nitrate concentration, i.e., after deducting preirrigation (control) values.

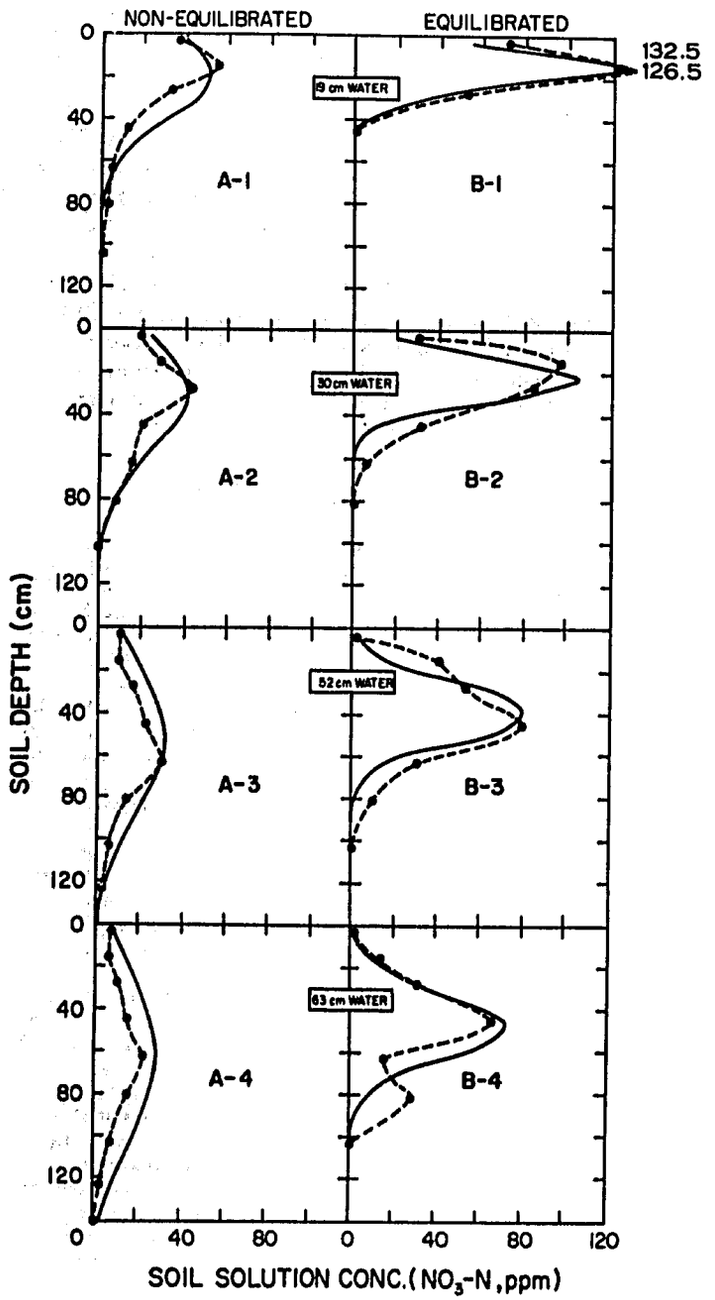

Fig. 1—Profile distribution of NO_3-N for nonequilibrated (A-1 to A-4) and equilibrated (B-1 to B-4) treatments after different amounts of water were added. Dashed line represents the actual measured distribution, whereas the solid line denotes the theoretical distribution predicted by equation [1].

RESULTS AND DISCUSSION

Experimental Results

Figure 1 shows nitrate distribution as a function of depth for different amounts of water added. A progressive downward movement with increased water added occurred both with and without equilibration. Much greater spread in the concentration profile for the nonequilibrated nitrate is evidence of the higher mobility of applied solutes when water is applied before diffusion into aggregates has occurred. The difference in mobility between equilibrated and nonequilibrated nitrate is also shown by the difference in slope for the plots of mean nitrate movement versus cumulative water added (Fig. 2). The linearity of these plots suggests uniformity of nitrate leaching

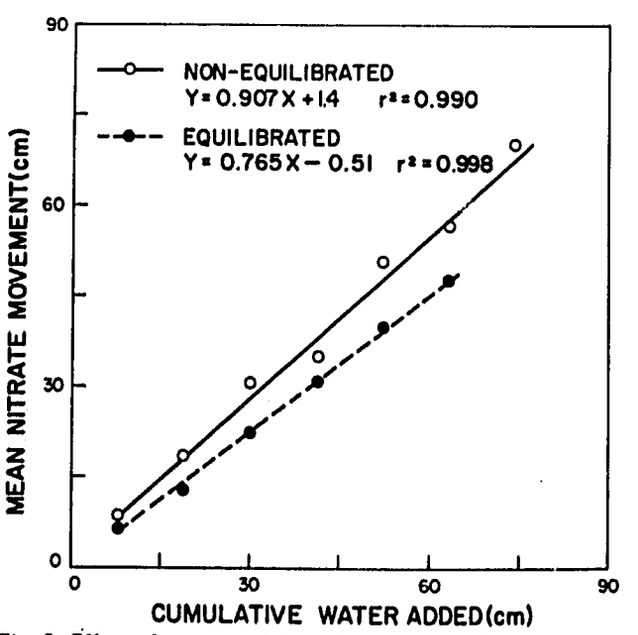

Fig. 2—Effect of amount of irrigation water on the mean movement of nitrate for equilibrated and nonequilibrated treatments.

within each treatment during the course of successive water application. The slopes for these curves show that for every centimeter of water applied, the nitrate peak moved 0.907 and 0.765 cm, respectively, for the nonequilibrated and equilibrated systems. If the average soil water content during transport was 0.36 cm^3/cm^3 and all the soil water were displaced, 1 cm cumulative irrigation would correspond to displacement of 1/0.36 = 2.78 cm in the profile. The nitrate peak moved only 0.907 and 0.765 cm, respectively, for the nonequilibrated and equilibrated treatments, suggesting retarded movement of nitrate relative to water. Representing relative nitrate movement by R (the ratio of nitrate peak movement to average pore water movement), values of 0.33 and 0.28 were obtained for the nonequilibrated and equilibrated treatments, respectively.

The striking resistance to leaching of nitrate in the Molokai profile could not be explained by nitrate adsorption. In a separate laboratory study of nitrate adsorption by the senior author, it was found that nitrate was negatively adsorbed in three horizons of this same Molokai soil (V. Balasubramanian, unpublished data). The values for negative nitrate adsorption at 0.20*N* equilibrium nitrate concentration were −1.95 meq/100 g for the 0- to 13-cm horizon and −0.40 meq/100 g for the 30- to 45-cm and 60- to 78-cm horizons. Thus the major factor responsible for the slow nitrate leaching in the well-aggregated Molokai soil is probably the solute detention in aggregate micropores. Fox et al. (1970) indicated that the role of diffusion was nonsignificant in retarding nitrate leaching under slow water infiltration due to rainfall and snow melt in the light-textured Turkish soils containing very few aggregates.

If the nitrate distribution curves (Fig. 1, A-1 to A-4) of the nonequilibrated treatment are compared with those (Fig. 1, B-1 to B-4) of the equilibrated system, it is evident that the concentration peaks in the latter were almost double those in the former. This shows that more of the applied nitrate was detained in the surface soil when the applied chemical was allowed to equilibrate than when it was immediately leached. This detention associated with equilibration is clearly illustrated in the data presented in Table 1. After equilibration almost all applied N was detained in the 143-cm profile even after the addition of 52 cm of water in five irrigations. The corresponding detention for the nonequilibrated condition was less than 60% of the applied N.

The higher detention of applied nitrate in the equilibrated than in the nonequilibrated system may be explained by the bulk flow and diffusion. When, through the addition of soluble nitrate, a sharp increase takes place in the concentration of nitrate ions in the soil solution near the soil surface, nitrate moves into the aggregate micropores both by mass flow and diffusion. Since diffusion is both concentration and time dependent, the high concentration in solution soon after chemical application and the time allowed in the equilibrated treatment were conducive to nitrate diffusion into micropore water. During subsequent irrigation, most of the applied water moves through macropores (the interaggregate pores) and carries with it only the small amounts of nitrate held in these pores. After infiltration, the nitrate concentration gradient between macropores and micropores is reversed and nitrate ions tend to diffuse back into dilute macropore water as long as there is capillary movement of water.

Table 1—Comparison of nitrate detentions in the top 143-cm profile for both the nonequilibrated and the equilibrated treatments following successive irrigations

Irrigation no.	Amount of water added, cm	Percentage detention of applied NO_3^- in the top 143-cm profile	
		Nonequilibrated	Equilibrated
1	8	43	62
2	19	58	90
3	30	60	100
4	41	55	100
5	52	56	100
6	63	39	82
7	74	44	--

The slow movement of nitrate peaks for both the equilibrated and nonequilibrated treatments relative to average pore water movement suggested by Fig. 2 (mean R = 0.30) provides evidence that much of the percolating water bypasses the nitrate in the micropores; it is likely that nitrate movement in smaller pores occurs during the downward redistribution of profile water due to capillarity in the 7-day period following infiltration. The comparatively high loss of nitrate due to initial leaching in the nonequilibrated treatment (Fig. 1, A-1 to A-4 and Table 1) appears to be the result of displacement by macropore water of relatively concentrated nitrate solution held in the macropores soon after fertilizer application. The apparent low nitrate detention following first irrigation in both treatments (Table 1) may be the result of concentration peak being between the suction probes at 3 and 15 cm, and thus not detectable. Thus, rapid water movement through macropores soon after infiltration is probably important only when solute application is immediately followed by irrigation or when fertilizers are applied in irrigation waters.

Computed Results

Gardner (1965) successfully employed the dispersion equation of Day (1956) to describe the nitrate distribution in field soil observed by Wetselaar (1962). Use of such a predictive model allows calculation and comparison of constants characterizing solute transport in different soils. The usefulness of this theoretical model was further evaluated with the present set of field data.

The concentration, C, of the nitrate at any point in the profile is given by the equation

$$C = C_O x_O (4\pi kt)^{-1/2} \exp -(x-vt)^2/4kt \qquad [1]$$

where C_O is the initial concentration of nitrate to a small depth x_O below which there is no nitrate; v is the velocity of water, t is the time, and k is the dispersion coefficient, characteristic of the soil pore space and flow process. Equation [1] can be obtained by integrating the dispersion equation (diffusion plus convection)

$$\partial C/\partial t = k(\partial^2 C/\partial X^2)$$

where $X = (x - vt)$. Another coefficient characterizing dispersion in porous media is β which is related to k by

the equation, $\beta = 2k/v$. The maximum concentration, C_{max}, is given as a function of depth by

$$C_{max} = C_o x_o (2\pi\beta x_m)^{-1/2} \quad [2]$$

where x_m is the depth at which maximum concentration occurs.

The values of β were estimated for both equilibrated and nonequilibrated treatments by fitting equation [2] to the data obtained after applying 19 cm of water. These values were then used to predict nitrate distribution after the addition of 30, 52, and 63 cm of water. The agreement between theory and experiment is good (Fig. 1); such a desirable predictive capability is suggested by the linear relationship between the position of nitrate peak (mean nitrate movement) and the amount of water applied (Fig. 2).

The main drawback of this theoretical model is that one set of experimental data must be obtained to derive the coefficients of β and k which are then used to predict the solute movement with further additions of water. In addition, the β value obtained is not necessarily unique for a given soil-solute combination, and hence cannot be used for the prediction of solute transport under different sets of conditions. For instance, two widely different values of β were obtained in this study for the equilibrated (β = 5 cm) and nonequilibrated (β = 24 cm) treatments conducted on the same plots. Similar observations were reported by Nielson and Biggar (1963) for chloride dispersion in glass beads. Because of the complicated nature of the pore-size distribution, the consequent variability in pore-water velocity, and the susceptibility of nitrate to biological transformations, it is not yet possible to come up with characteristic constants or coefficients to exactly describe the movement of nitrate in soils.

CONCLUSION

The mobility of applied fertilizer N in the aggregated Molokai soil was low relative to that of water. Nitrate detention was further enhanced when applied fertilizer was equilibrated with the soil before irrigation. Equilibration prior to irrigation apparently allows bulk flow and diffusion of nitrate into aggregate micropores where the solute is less susceptible to transport in macropore water. This temporary detention of fertilizer nitrate in aggregate micropores may significantly reduce the possibilities of ground water contamination by nitrate. With subsequent irrigations, the detained nitrate may become available to plants by capillary movement of concentrated nitrate solution towards root surfaces.

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Field Study of Solute Movement in a Highly Aggregated Oxisol with Intermittent Flooding: II. Picloram

P. S. C. Rao, R. E. Green, V. Balasubramanian, and Y. Kanehiro

Field Study of Solute Movement in a Highly Aggregated Oxisol with Intermittent Flooding: II. Picloram[1]

P. S. C. Rao, R. E. Green, V. Balasubramanian, and Y. Kanehiro[2]

ABSTRACT

Most of the applied herbicide picloram (potassium salt of 4-amino-3,5,6-trichloropicolinic acid) was retained in the top 40-cm depth of the Molokai soil with cumulative applications of 48 to 74 cm water following application of the chemical to the soil surface. Distribution of picloram in the soil profile one week after each irrigation was determined by *in situ* sampling of soil solution with porous ceramic cups placed at several depths. Although movement of the picloram peak was retarded more than was anticipated from equilibrium adsorption measurements, a significant fraction of the applied herbicide moved ahead of the peak deep into the profile (down to the 143-cm depth) after a single application of 24-cm water. Rapid flow through macropore sequences combined with temporary retention of picloram in aggregate micropores appear to be responsible for the unusual pattern of movement. Published data for nitrate movement in the same field plots of Molokai soil were compared with picloram movement data to provide a measure of the relative mobility of these solutes. A comparison of the results reported here with published field data of solute leaching in other soils indicated a greater retardation of solute peak movement in Molokai soil than in less aggregated soils.

Additional Index Words: water quality, ground water, pesticides, herbicides, irrigation, tropical soils.

Most of the previous work on persistence and movement of picloram herbicide (4-amino-3,5,6-trichloropicolinic acid) has been limited to laboratory and greenhouse studies. Field studies have involved application of the herbicide to field plots and evaluation of its persistence and movement under natural climatic conditions over long periods of time. Hamaker et al. (1967) showed that rates of decomposition of picloram in soils fit Michaelis-Menten or half-order kinetics. Picloram applied at normal application rates disappears in about 4.5 months to 4.6 years depending on the given set of environmental factors (Goring and Hamaker, 1971).

The influence of soil texture and amount of precipitation (Herr et al., 1966; Merkle et al., 1967; and Bovey et al., 1969), tillage (Keyes and Friesen, 1968), and rate of application (Scifres et al., 1969) on movement of picloram have been investigated. More recently Davidson and Chang (1972) and Green et al. (1972) have characterized picloram transport in saturated soil columns under controlled conditions.

Since field conditions differ greatly from those imposed on soil columns in the laboratory, actual movement of picloram in field plots may be very different from that in soil columns. Water and solute transport in field soils is expected to be sensitive to soil structure and horizination which are difficult to duplicate in the laboratory, hence the need for well-characterized field studies.

Although picloram is not used in irrigated agriculture in the United States at the present time, there has been an interest in its use in Hawaii for spot weed control in sugarcane and also for brush clearance in pasture development. The study described here was designed to provide measurements of picloram movement in a field soil in which water application and movement were carefully monitored. Concurrent application of nitrate with picloram prior to irrigation allowed a comparison of the movement of these two solutes; the nitrate movement was reported by Balasubramanian et al. (1973). Detailed results of water movement will be reported elsewhere.

A principal objective of the study was to measure the nature of picloram movement in a highly structured Hawaiian Oxisol to determine if laboratory measurements of adsorption could be used to estimate the penetration of the picloram peak for a given amount of applied water.

MATERIALS AND METHODS

Field Studies

These studies were conducted on Molokai silty clay, a member of the clayey, kaolinitic, isohyperthermic family of Typic Torrox of the order Oxisols. Soils belonging to the order Oxisols are extensively planted to sugarcane (*Saccharum officinarum* L.) and pineapple (*Ananas comosus*) in Hawaii. Molokai surface soil is characterized by low organic matter content (2%), low cation ex-

[1]Journal Series Paper No. 1581 of University of Hawaii, College of Tropical Agriculture, Honolulu. This research was conducted under Western Regional Research Project W-82. Received 19 January 1973.

[2]Graduate Assistant, Professor, Graduate Assistant, and Professor, respectively. Department of Agronomy and Soil Science, University of Hawaii, Honolulu 96822.

change capacity (15 meq/100 g) and a high content of iron oxides (20% Fe_2O_3). The soil is slightly acid (pH = 6.4).

At the location of the field study, the tilled Ap horizon is about 40 cm deep and is underlain by a relatively dense B horizon which is massive in place but breaks into highly stable aggregates upon disturbance. The bulk densities of the Ap and B horizons are 1.1 and 1.4 g/cm^3, respectively. In some places there appeared to be a distinct plow-pan formed below the Ap horizon, but this was not continuous over the entire area. The physical characteristics of the Molokai soil and the nature of water retention and movement in disturbed samples of this soil are discussed by Sharma and Uehara, 1968a, b.

Duplicate experimental plots (2.74 by 2.74 m) were surrounded by plastic-covered wooden boards which were inserted 15 cm into the soil to facilitate ponding of water and minimize lateral water movement near the soil surface. Individual plots were covered by a metal canopy at a height of 2.4 m to prevent rainfall from reaching the plot surface and to reduce temperature fluctuations at the soil surface. Air temperatures over the soil surface were approximately 30C during the day and 20C in the night.

Soil solution samples were obtained at six depths between 3 and 81 cm and also at 143 cm below the soil surface with porous ceramic cups having a diameter of 5.7 cm and length of 6.0 cm (surface area approximately 90 cm^2). Preliminary laboratory studies indicated that the porous ceramic cups did not adsorb picloram. The cups with their access tubes were arranged in a line parallel to the plot border and 80 cm from the border toward the center of the plot. A duplicate set was located on the other side of the plot and arranged so that the deepest cup on one side corresponded to the shallowest cup on the other side. A suction system similar to that described by Reeve and Doering (1965) permitted simultaneous sampling to soil solution from all depths. A suction of 0.7 bar for about 1 hour usually resulted in sample volumes of 10 to 80 ml. Samples having volumes less than 10 ml were rejected.

After installation of suction cups and other instrumentation (tensiometers and neutron access tube) the soil surface was tilled lightly with a hoe and pre-irrigated with sufficient water to wet the soil profile beyond 1 m. One week was allowed to elapse with the plots covered by plastic sheets to preclude evaporation prior to commencement of solute movement studies.

Picloram was applied at 20 kg acid equivalent per hectare in the form of Tordon 22K[3]. The herbicide and KNO_3 (100 kg N/ha) were dissolved in 5 liters of water and sprinkled uniformly over the entire plot area with a garden sprinkler. Another 5 liters of water were applied to move the solutes into the soil prior to subsequent irrigation.

Two separate applications of picloram, each followed by a series of water applications 1 week apart, were carried out. Water was ponded on the soil surface at depths varying between 2 and 8 cm while water infiltration proceeded, and the soil surface was covered with a plastic sheet between irrigations to preclude evaporation. The sequence of irrigations following the first application of picloram consisted of 24 cm (surface depth) of water immediately following the herbicide application, and two subsequent irrigations of 12 cm each, 1 and 2 weeks later, resulting in a total of 48 cm of water applied.

Prior to the second application of picloram, the plot was leached with about 60 cm of water to remove picloram retained in the soil profile from the first application. However, the leaching was not as complete as was anticipated. Soil solution samples obtained prior to the second picloram application showed an initial picloram concentration of about 6 μmoles/liter throughout the profile. This background was substracted from the analysis of the data from the second picloram application-irrigation sequence.

Irrigations following the second application of picloram consisted of 8 cm water immediately after the herbicide application, and 6 subsequent irrigations of 11 cm each at weekly intervals, resulting in a total of 74 cm of water applied. The second sequence also involved simultaneous application of nitrate (at 100 kg N/ha, as KNO_3) and these results were separately reported by Balasubramanian et al. (1973). The second sequence is referred to as nonequilibrated in their discussion of nitrate movement. Picloram and nitrate movement could be compared only in the second solute application-irrigation sequence, discussed in this paper, due to high background of nitrate in the first sequence.

Solution samples were taken 5 to 7 days after each irrigation to allow water redistribution in the soil profile and equilibration of solutes between inter-aggregate and intra-aggregate pores. Preliminary samplings showed that samples taken only one day after irrigation contained much lower solute concentrations than those obtained after longer periods. The soil water suction at 20 cm depth changed from 60 mbars 1 day after irrigation to 155 mbars at 1 week, while at the 80 cm depth the suction changed from 27 mbars to 112 mbars. The suctions at one week corresponded to volumetric water contents of about 0.36 and 0.43 cm^3/cm^3 obtained from neutron probe readings at the 20 and 80 cm depths, respectively.

Solution samples were stored in the refrigerator at 4C soon after collection. Picloram was determined in 2 ml aliquots of the samples by the colorimetric procedure of Cheng (1969). The lower limit of detection was approximately 2 μmoles/liter.

Laboratory Adsorption Measurements

Adsorption of picloram on Molokai soil from three depths of the soil profile (0-30, 30-45, and 60-78 cm) was determined in the laboratory by measuring the change in solution concentration after equilibrating 2 g soil samples with 10 ml of 10, 100, and 1,000 μmoles/liter ^{14}C-labeled picloram solution for 24 hours. Adsorption data were used to predict retardation of picloram movement in the profile due to adsorption, as compared to actual retardation as indicated by the measured picloram concentration profile.

RESULTS

Picloram Movement-Irrigation Sequence No. 1

Picloram concentration profiles in Fig. 1 show the concentration of picloram in soil solution samples obtained 1 week after successive irrigations of 24, 12, and 12 cm water, corresponding to cumulative water applications of 24, 36, and 48 cm water. The data shown are mean values for samples obtained from duplicate sampling cups in one plot and are similar to results obtained on the other plot. Samples sucked prior to picloram application contained no picloram, hence the data in Fig. 1 show that picloram moved beyond the 80-cm depth after application of 24 cm water. A single sampling cup at 143 cm contained solution having 9.6 μmoles/liter picloram, indicating movement of picloram with the advancing water deep into the profile. If we assume that a soil water content of 0.36 cm^3/cm^3 corresponds to water which actively participates in solute transport, then a non-adsorbed solute undergoing piston displacement is calculated to move about 67 cm (=24/0.36). Adsorption would be expected to retard peak movement, and other dispersion processes

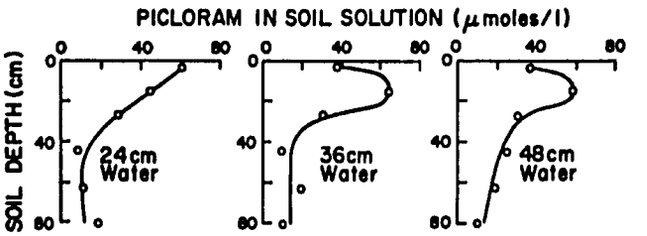

Fig. 1—Picloram concentration in soil solution sampled *in situ* from Molokai soil profile under irrigation sequence no. 1. Mean deviation in data = ± 5 μmoles/liter.

[3]Potassium salt of picloram, 21.5% acid equivalent, registered trade mark of Dow Chemical Company.

would spread the peak or cause asymmetry in peak shape. The left-hand curve in Fig. 1 shows that surface-applied picloram moved past the 80-cm depth with an irrigation of 24 cm of water, but the peak concentration remained near the soil surface. Subsequent irrigations moved the peak to about 15 cm with little change in picloram concentration at greater depths.

It is of interest to know what percentage of the applied picloram is retained in the upper portion of the soil profile after a designated amount of irrigation. Calculations of profile retention of picloram based on the data in Fig. 1 can only be approximate in that the following assumptions are required: (i) The concentration measured in the sucked samples is representative of all (or a designated portion) of soil solution at that depth (i.e. equilibrium has been attained between the herbicide and soil water at that depth); (ii) Picloram was applied uniformly over the entire plot surface and moved uniformly downward (in the horizontal plane) with leaching. An estimate of retention was obtained by graphically integrating the right-hand curve in Fig. 1 and assuming that nearly all soil water (0.36 cm^3/cm^3) was in equilibrium with the sucked sample. The calculation indicated that about 97% of the applied picloram was retained in the soil water above the 81-cm depth 1 week after the last irrigation (total of 48 cm water). This retention appears to be much too high in that it does not include the adsorbed fraction of the picloram nor that which was leached beyond the 81 cm depth. Perhaps the first assumption above was invalid. Equilibrium may have been incomplete due to inaccessibility of intra-aggregate water in extremely small pores, which would also reduce the surface available for adsorption. Even so the results suggest that while most of the applied picloram remained in the upper 40 cm, a significant fraction was leached beyond 81 cm with the first irrigation.

Picloram and Nitrate Movement Compared—Irrigation Sequence No. 2

Picloram and nitrate results for this sequence of seven samplings are shown for three soil depths as plots of relative concentration versus cumulative water infiltration (Fig. 2). Each was followed by an irrigation after a single initial application of picloram and nitrate. The use of relative concentration, C_i/C_o, where C_o is the initial concentration of solute in the applied picloram or nitrate solution and C_i is the concentration of picloram or nitrate measured in the sucked sample after each irrigation, provides a comparison of the movement of the two solutes in equivalent concentration units, i.e. measured concentration relative to the initial concentration in the applied solution. The initial concentrations, C_o, calculated on the basis of 10 liters applied were 3,122 μmoles/liter for picloram and 7,500 μg/ml for nitrate. Although these concentrations are not exact due to further dilution of the applied solution by soil water prior to irrigation, the error would be similar for picloram and nitrate so that the comparison of the two solutes is valid. Nitrate data plotted in Fig. 2B are given as concentration profiles in Fig. 1A of Balasubramanian et al., 1973; for the three depths in our Fig. 2B, we present concentration data for seven irrigations, while Balasubramanian et al. (1973) presented data for only four of the seven irrigations in their graphs. The data points plotted at a given value of cumulative infiltration are for data obtained after the corresponding irrigation.

Both picloram and nitrate decreased rapidly at the 3-cm depth with successive irrigations. As the solutes moved downward through the profile the concentrations at 15 and 63 cm increased, reached a peak, and then decreased. Relative concentrations for picloram at a given value of cumulative infiltration are lower than nitrate

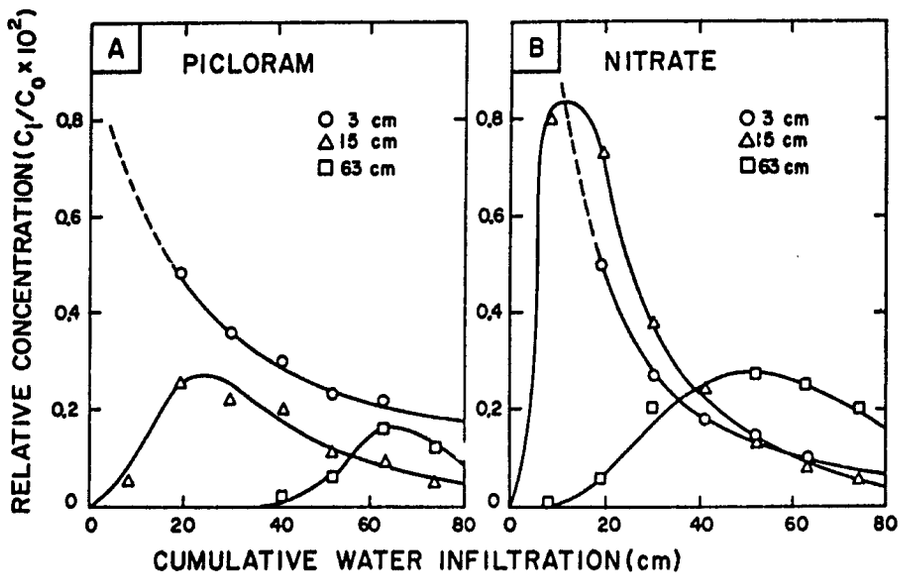

Fig. 2—Relative concentrations of picloram and nitrate at selected depths in Molokai soil profile in relation to cumulative water infiltration under irrigation sequence no. 2. Each datum corresponds to a separate irrigation. The dashed portion of the curve for 3-cm depth is estimated since sample size was too small for measurement.

concentrations, the difference being about the expected magnitude if adsorption of picloram is principally responsible. Picloram peaks for the 15- and 63-cm depths are also displaced to the right relative to nitrate; this result is also consistent with the retarding effect of adsorption on solute movement. Picloram concentration at 3 cm, while decreasing steadily with cumulative infiltration, continued to exceed the concentrations at lower depths even after 60 cm of water were applied. This tendency for picloram to be retained near the soil surface is evident in Fig. 1 also.

Picloram Retardation Calculation Based on Adsorption Measurement

Picloram adsorption on soil from three depths of the Molokai profile is described by a single linear isotherm $x/m = kC$, in which the quantity adsorbed, x/m (μmoles/kg) is plotted against equilibrium solution concentration, C (μmoles/liter). The constant distribution coefficient, k, has a value of 0.2. The distribution coefficient was used to calculate a "retardation factor" (Davidson and Chang, 1972) for picloram movement to obtain a quantitative expression of the extent to which the picloram peak would be retarded by adsorption relative to water movement. The retardation factor is given by $R = 1 + \rho k/\theta$, where ρ is the bulk density of the soil, θ is the volumetric water content corresponding to that soil water which is presumed to be actively participating in solute transport, and $\rho k/\theta$, represents the apparent increase in pore volume resulting from the adsorption process. The calculated value of the retardation factor (based on laboratory adsorption measurements) can be compared with the field-measured ratio of distance water moved/distance solute peak moved to determine if adsorption alone is responsible for retarded peak movement.[4]

Using $k = 0.2$ cm^3/g, $\rho = 1.1$ g/cm^3, and $\theta = 0.36$ cm^3/cm^3 for the conditions of our field study, we calculate $R = 1.6$ which indicates that the water front should penetrate about 1.6 times the depth of picloram penetration. In the first irrigation sequence of the actual field experiment, the applied 48 cm of water probably moved at least 133 cm (= 48/0.36) while the picloram peak moved only 15 cm (Fig. 1). Thus, the field data give $d_w/d_s = 8.9$ compared to 1.6 obtained from a retardation factor based on adsorption measurement. Despite the approximations involved in these calculations, it is apparent that adsorption alone cannot account for the retardation of picloram observed in the field.

A limited number of other field studies have yielded data on solute peak position and water movement. Values of d_w/d_s calculated from these data are given in Table 1 for comparison with data from our study. Considering the likelihood of negative adsorption of chloride and nitrate on all of these soils and especially on Panoche and Svea, one might expect the value of the ratio d_w/d_s for these solutes to be less than or equal to 1.0, indicating that the solute peak is very near the water front. The measured values for chloride and nitrate, however, are 1.3 to 1.4 on Panoche and Svea soils and 2.8 on Molokai soil. The higher ratio for Molokai is undoubtedly the result of the higher water flow rate (infiltration rate of 4.0 cm/hour) and a wider range in pore sizes. The additional effect of adsorption retarded picloram movement even more, giving $d_w/d_s = 8.9$ for picloram. Although movement of the picloram peak in the Molokai soil was much more retarded than was anticipated from laboratory adsorption measurements, a significant fraction of the applied picloram moved ahead of the peak deep into the soil profile (Fig. 1).

Table 1—Comparison of field-measured retardation factors for solute movement with flooding in three soils

Source	Soil	Solute	Sustained infiltration rate*	Distance water moved d_w	Distance solute peak moved d_s	d_w/d_s
			cm/hour	cm	cm	
Miller et al. (1965)	Panoche	Cl^-	0.5	200	150	1.3
Warrick et al. (1971)	Panoche	Cl^-	1.6	180	85	2.1
Cassel (1971)	Svea	NO_3^- Cl^-	0.2	144	105	1.4
Balasubramanian et al. (1973)	Molokai	NO_3^-	4.0	175	63	2.8
This paper	Molokai	Picloram	6.0	133	15	8.9

* Infiltration rates were either given in the source publication or were calculated from pertinent data reported by the authors.

DISCUSSION

The results of the field studies reported here indicate significant retardation in leaching of picloram herbicide in Molokai soil. This resistance to leaching could not be explained by adsorption alone. Some additional factors are responsible for retarded movement of picloram in this soil. The most probable explanation appears to be the retention of herbicide in soil micropores. Green et al. (1972) have demonstrated the significance of micropore retention in picloram displacement through saturated columns of sieved aggregated soil. Aylmore and Karim (1968) have also demonstrated micropore retention to be important in retarding movement of fertilizers and salts in columns of sieved soil. In contrast to our field results, some soil column studies with picloram (Davidson and Chang, 1972; Evans and Duseja, 1973) have indicated less retardation in the transient system than predicted from equilibrium measurements. It is likely that by-passing of solutes in micropores is most important in highly structured field soils having a much wider range of pore sizes than sieved samples of the same soils (Balasubramanian et al., 1973).

The following mechanism is suggested on the basis of our field observations. With the application of a concentrated solution of herbicide to the soil surface a sharp increase takes place in the concentration gradient between micropore and macropore water. Also, at the water content of 0.36 cm^3/cm^3 (equivalent to about 250 mbars suction) pores larger than 10 μm in radius are emptied of water. The concentrated solution enters drained pores by means of bulk flow (pores > 10 μm), while solutes must move by diffusion into water-filled pores < 10 μm radius.

[4] The equivalence of the field measured ratio and the calculated retardation factor is shown in the following brief derivation: Let d_w and d_s represent respectively the depth of water penetration and depth of solute peak penetration with an application of V cm water to the soil, and $\theta/(\theta + \rho k)$ represents the fraction of solute in solution, where θ, ρ, k are as defined previously. Then $d_w = V/\theta$ and $d_s = d_w \cdot [\theta/(\theta + \rho k)]$. Rearranging and substituting in these two equations yields $d_w/d_s = 1 + \rho k/\theta$.

The entry of picloram into micropores appears to be a rapid process, probably due to the extremely high concentration gradient existing soon after herbicide application.

In this study, herbicide application to the soil surface was immediately followed by irrigation. During water infiltration, most of the water was apparently conducted through macropore sequences, as evidenced by a drop in suction from > 110 mbars to < 30 mbars at the 80 cm depth about 1 hour after initiation of infiltration. This resulted in rapid transport of picloram contained in the larger pores to lower depths in the profile, as shown by the presence of picloram at all depths of sampling after only one irrigation. Micropores near the soil surface, which contained solution with a higher picloram concentration, possess very low flow velocities, and thus do not participate significantly in the flow process. Release of herbicide from these micropores is a slow diffusion-controlled process resulting in retarded leaching. The wide range of pore-velocities occurring in the aggregated Molokai soil during infiltration tends to result in extremely high dispersion, as evidenced by double peaks and large apparent diffusion coefficients measured on packed Molokai soil columns (Green, Rao, & Corey, 1972). Such effects are expected to be even more extreme in the highly structured field soil.

Cassel (1971) reported that the movement of both nitrate and chloride in Svea loam with intermittent flooding was retarded considerably due to variations in pore-velocities between micro and macropore sequences. Similar results were obtained also by Miller et al. (1965) for chloride transport through Panoche clay loam. Krupp et al. (1972) have proposed a new model based on Gouy double layer theory and the dispersion equation to describe the effects of mobile and nonmobile zones of soil water on solute dispersion. The Molokai soil is highly structured with a much wider range of pore-velocities than either Svea or Panoche. The micropore water in Molokai soil might be expected to be relatively immobile. This probably explains why nitrate movement was more retarded in Molokai soil than in Svea and Panoche soils (Table 1).

The measured difference between nitrate and picloram mobility suggests that picloram retention is complicated by the interaction of adsorption and diffusion into and out of micropores. The rate of equilibrium of adsorbed herbicide in aggregate micropores with water external to the aggregates has been shown to be dependent on the level of adsorption; a higher distribution coefficient resulted in slower equilibration (Green and Obien, 1969). Nitrate ion, on the other hand was shown to be negatively adsorbed by the Molokai soil (Balasubramanian et al., 1973). Repulsion of nitrate ion from the negatively charged micropore walls probably reduced the effects of micropore retention, resulting in greater mobility of nitrate as compared to picloram.

There are some practical implications of these results. Preemergence herbicides are usually applied in concentrated form in solution volumes as small as 250 liters/ha. At the time of spraying, the surface soil is often nearly air-dry, thus the applied herbicide solution is presumably absorbed into aggregates by means of bulk flow, resulting in a relatively high concentration of herbicide within intra-aggregate pores. Transport of the herbicide downward in the soil with subsequent irrigations should be retarded by this micropore retention, especially in highly aggregated soils such as the Molokai used in this study. Application of chemicals to moist aggregated soils, on the other hand, may result in rapid leaching of chemicals when irrigation occurs soon after chemical application. This excessive displacement of solutes can be reduced by allowing time for solute equilibration with surface soil prior to irrigation (Balasubramanian et al., 1973). Such chemical application and irrigation management practices can be used to minimize contamination of ground waters and also increase the efficiency of agricultural chemicals.

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