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Vadose Zone Processes and Chemical Transport

Fate of Nitrate and Bromide in an Unsaturated Zone of a Sandy Soil under Citrus Production

S. Paramasivam,* A. K. Alva, A. Fares, and K. S. Sajwan

ABSTRACT

Understanding water and nutrient transport through the soil profile is important for efficient irrigation and nutrient management to minimize excess nutrient leaching below the rootzone. We applied four rates of N (28, 56, 84, and 112 kg N ha⁻¹; equivalent to one-fourth of annual N rates being evaluated in this study for bearing citrus trees), and 80 kg Br⁻ ha⁻¹ to a sandy Entisol with >25-yr-old citrus trees to (i) determine the temporal changes in NO₃-N and Br⁻ distribution down the soil profile (2.4 m), and (ii) evaluate the measured concentrations of NO₃-N and Br⁻ at various depths with those predicted by the Leaching Estimation and Chemistry Model (LEACHM). Nitrate N and Br⁻ concentrations approached the background levels by 42 and 214 d, respectively. Model-predicted volumetric water content and concentrations of NO₃-N and Br⁻ at various depths within the entire soil profile were very close to measured values. The LEACHM data showed that 21 to 36% of applied fertilizer N leached below the root zone, while tree uptake accounted for 40 to 53%. Results of this study enhance our understanding of N dynamics in these sandy soils, and provide better evaluation of N and irrigation management to improve uptake efficiency, reduce N losses, and minimize the risk of ground water nitrate contamination from soils highly vulnerable to nutrient leaching.

WATER FLOW in the unsaturated zone of agricultural soils is of great importance in determining the fate of surface-applied soluble nutrients and pesticides (Nightingale, 1972; Hallberg, 1989; Hubbard et al., 1986, 1989). Nitrate (NO₃⁻) leaching associated with routine use of nitrogen (N) fertilizers and the potential for subsequent movement below the root zone and ground water contamination is influenced by soil properties, water management, and climatic factors.

In major citrus growing regions in central Florida, soils are typically Entisols, without confining soil horizons. A combination of homogeneous sandy soils (>95% sand), shallow citrus root systems, high (approximately 1300 mm per year) and unevenly distributed rainfall (two-thirds of annual rainfall during May

through September) creates favorable conditions for leaching of surface-applied soluble nutrients and agricultural chemicals with drainage water below the rootzone. Therefore, efficient nutrient and irrigation management are critical to optimize nutrient uptake efficiency and to minimize losses of surface-applied fertilizer nutrients. Maintaining nutrients within the effective rootzone is essential for the crop to get maximum benefit from the applied fertilizer.

Previous citrus N management studies were usually conducted to evaluate the effects of rates and sources of N on the tree nutritional status, yield, and fruit quality, with very little attention to the fate of N below the rootzone and potential nonpoint-source NO₃-N contamination of ground water (Davies, 1996). Mansell et al. (1986) studied the temporal changes in distributions of NO₃-N and NH₄-N concentrations in a profile of Oldsmar fine sand (sandy siliceous, hyperthermic Alfic Arenic Haplaquod) from a citrus grove with 16-yr-old trees near Fort Pierce, Florida. This study was conducted under three different soil tillage practices (i.e., shallow-tilled [0–15 cm], deep-tilled [0–105 cm], and deep-tilled [0–105 cm]) with 56 Mg ha⁻¹ dolomitic limestone. They applied ¹⁵N-labeled (NH₄)₂SO₄ at a rate of 115 kg N ha⁻¹ and sampled the soil 12, 42, 75, and 134 d after the fertilizer application. Results of their study confirmed earlier observations (Mansell et al., 1977) that deep tillage plus lime incorporation into the profile of a Spodosol enhanced citrus root absorption of fertilizer N, minimized N leaching losses, and thus minimized ground water NO₃-N contamination. Their study also showed that to minimize leaching, N fertilizer application should not be immediately followed by excessive irrigation. The Spodosol used in this study had a slightly heavier texture compared with Entisols and an impermeable organic layer within 100 cm from the soil surface also not found in Entisols. Therefore, the results of the Mansell et al. (1986) study are not applicable to deep fine sandy Entisols. The current study was designed to provide data to increase understanding of the movement and distribution of fertilizer nitrogen in an Entisol under mature citrus production.

In recent years, solute transport models, such as the Leaching Estimation and Chemistry Model (LEACHM; Wagenet and Hutson, 1989), have been used to evaluate

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Abbreviations: ET_p, potential evapotranspiration; LEACHM, Leaching Estimation and Chemistry Model; LEACHN, one-dimensional water flow and nitrogen transport model.

the fate of contaminants in agricultural soils as basis to develop best management practices (Pennell et al., 1990; Soulsby and Reynolds, 1992; Jabro et al., 1993). Jabro et al. (1993) compared the transport of NO_3^- measured in a Hagerstown silt loam (fine, mixed, semiacative, mesic Typic Hapludalf) soil with that predicted by LEACHM (Version 3.0) (Hutson and Wagenet, 1992) and NCSWAP (Nitrogen, Carbon, Soil, Water And Plant) (Molina and Richards, 1984) models and concluded that these models did not accurately predict NO_3^- leaching to a depth of 1.2 m. They concluded that NCSWAP resulted in significant overestimation of the amount of NO_3^- leached from the soil profile due to an inability to simulate macropore flow effects. It was speculated that NO_3^- was stored in the micropore system and that percolating water bypassed this NO_3^- . However, LEACHM had the same overestimation problem as a result of its inability to estimate macropore flow effects only for the soil profile of the nontreated plot. Jabro et al. (1993) further cited the use of an inappropriate water retention function fitted by Campbell's equation (Campbell, 1974) as a reason for an overestimation of soil water content, which subsequently resulted in nonsignificant differences between LEACHM simulation and measured data of NO_3^- leaching in the profile. On the basis of overall performance of these models, Jabro et al. (1993) concluded that NO_3^- leaching was significantly better simulated by the LEACHM than by the NCSWAP model. Our parallel study (Paramasivam et al., 2000a) showed a good agreement between the measured concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ following a heavy loading of NH_4NO_3 liquid to an uncropped Entisol (Candler fine sand) through 270 cm depth and the respective concentrations simulated by LEACHM. Soulsby and Reynolds (1992) used LEACHM to model the soil water flux in an aluminum (Al) leaching study. They calibrated the model using in situ tensiometer data, then compared model predictions against measured tensiometer data for the remainder of the year and found good agreement.

Bromide has been widely used as a tracer to monitor and/or predict water and nutrient transport in soils (Smith and Davis, 1974; Bowman, 1984; Owens et al., 1985) because it is free from chemical or biological transformations in the soil (Bowman, 1984; Owens et al., 1985). Several field studies with bromide tracer were conducted in central Florida citrus groves to determine intrinsic spatial and temporal variability, travel time of bromide through the vadose zone, and lateral movement of bromide in the surficial aquifer (Hornsby et al., 1990;

Foussereau and Graham, 1997; Paramasivam et al., 1999). Comfort et al. (1993) reported a good agreement between the measured Br^- concentrations in the soil profile to a 1-m depth of an uncropped Brocko silt loam (coarse-silty, mixed, Borollic Calciorthid) soil with application of $56 \text{ kg ha}^{-1} \text{ Br}^-$ and those predicted by LEACHM.

The objectives of this study were to (i) determine temporal changes in distribution of $\text{NO}_3\text{-N}$ following a broadcast application of water-soluble dry granular fertilizer mixture containing NH_4NO_3 as the N source, (ii) evaluate the effect of water input (irrigation and rainfall) on transport and distribution of $\text{NO}_3\text{-N}$, (iii) compare the transport and distribution of $\text{NO}_3\text{-N}$ and a nonreactive tracer (Br^-) applied with the fertilizer, and (iv) evaluate LEACHM predictions of $\text{NO}_3\text{-N}$ and Br^- transport in the soil profile under standard citrus management practices and compare them with measured concentrations.

MATERIALS AND METHODS

A field study was conducted in a highly productive commercial citrus grove with 25-yr-old 'Hamlin' orange trees [*Citrus sinensis* (L.) Osbeck] on 'Cleopatra' mandarin (*Citrus reticulata* Blanco) rootstock planted ($7.62 \times 6.52 \text{ m}$) in a moderately well-drained Tavares fine sand (hyperthermic, uncoated, Typic Quartzipsamment). Physicochemical properties of the soil at various depths of the experimental site are given in Table 1. This experiment was conducted as part of an ongoing long-term experiment to evaluate the effect of various N rates and sources of N on fruit yield and quality responses in a vulnerable soil under optimal irrigation conditions. The tree response in terms of leaf mineral concentrations, fruit yield, and quality was reported earlier (Alva and Paramasivam, 1998) and a brief description is given here. Each plot covering an area of 198 m^2 consisted of four uniform trees, with the middle two trees being used for fruit yield and quality evaluation N treatments. Trees were irrigated with under-tree microsprinklers (one emitter per tree, with a delivery rate of $0.083 \text{ m}^3 \text{ h}^{-1}$ at 0.276 MPa, which wetted an area of 18.7 m^2 , approximately equivalent to the ground area under the canopy). Irrigation scheduling was based on matric potential values recorded by tensiometers at the 15- and 30-cm depths along the tree drilling. Irrigation was scheduled when the matric potential at the 15-cm depth attained -10 kPa for January through June and -15 kPa for July through December (Smajstrala et al., 1987; Parsons, 1989). Thus, irrigation water was applied to replenish soil water in the depth of maximum root activity (i.e., 90 cm) to field capacity. Total water delivery at each irrigation was recorded using a flow meter. Rainfall was recorded using an automatic rain gauge.

Experimental plots receiving 0, 112, 224, 336, and 448 kg

Table 1. Selected properties of Tavares fine sand (Typic Quartzipsamments).†

Depth cm	Horizon	Texture			Saturated hydraulic conductivity cm h ⁻¹	Bulk density g cm ⁻³	Water content at 0.33 MPa m ³ m ⁻³	pH in H ₂ O (1:1)	Organic C g kg ⁻¹	CEC‡ (sum) cmol kg ⁻¹
		Sand	Silt	Clay						
		g kg ⁻¹								
0-15	A _p	954	14	32	63.8	1.50	6.84	6.0	8.6	5.89
15-30	C ₁	948	23	29	85.5	1.48	4.10	5.9	3.4	2.74
30-60	C ₁	950	22	28	83.4	1.47	3.47	5.8	2.9	1.95
60-90	C ₂	951	18	31	80.8	1.46	2.58	5.5	1.7	1.64
90-120	C ₃	955	12	33	97.8	1.55	2.48	5.3	0.9	1.47
120-150	C ₃	962	10	28	84.2	1.58	2.40	5.3	0.6	1.47

† Paramasivam et al. (2001).

‡ Cation exchange capacity.

$\text{N ha}^{-1} \text{ yr}^{-1}$ as water-soluble dry granular fertilizer applied in four equal split doses (February, April, May, and October) were used to monitor the $\text{NO}_3\text{-N}$ and nonreactive tracer (Br^-) movement. A water-soluble granular blend containing N, P, K, Mg, and S at a ratio of 13:2.2:13.5:3.25:6.5 derived from ammonium nitrate, triple super phosphate, potassium chloride (muriate of potash), and potassium magnesium sulfate (sul-po-mag) was broadcasted using commercial broadcast equipment calibrated for single-sided application (Conibear Equipment Co., Lakeland, FL). Since this monitoring started soon after the first split fertilizer application in February, the N application rates for the purpose of this study were 0, 28, 56, 84, and 112 kg N ha^{-1} . The February application was nearly four months after the previous years' last fertilizer application. Therefore, the residual fertilizer N effects of the previous year were negligible.

Bromide was applied at a rate of 80 kg ha^{-1} (as KBr) on the treated area based on the same day as the first dose of fertilizer. The KBr was applied in solution using a herbicide boom with a band width of 2.4 m on either side of the tree trunk for four trees in each plot. The area of Br^- application per plot was $30.5 \times 4.8 \text{ m}^2$. Since this part of the study involved intensive soil sampling, bromide was applied only to three replicated plots that received water-soluble granular fertilizer out of five replicates of the original randomized complete block experiment. This experiment was conducted as a randomized complete block design, with three replications.

Field Sampling and Soil Analysis

Soil samples were taken 90 cm inside the drip line under the canopy using a 2.5-cm-diameter bucket auger at 15- and 30-cm depths, and thereafter at 30-cm increments to the soil-ground water interface. The average depth to ground water was about 300 cm. Triplicate cores of soil samples per replicate per treatment were taken from the 15 (five treatments $\times$ three repetitions) plots before fertilizer and bromide application. Soil sampling continued at weekly intervals after the fertilizer application. Most of the soil sampling was done within 24 to 48 h of irrigation or rainfall events. Soil cores were taken within the wetted zone of fertilizer and Br^- application under the tree canopy. Soil samples from each depth (cores and replicates) were stored separately in an ice chest for transportation to the laboratory and were extracted with water at 1:1 (soil to water) on a field-moist basis. At each sampling, nine samples per depth per treatment were analyzed individually for concentrations of $\text{NO}_3\text{-N}$ and Br^- and for water content.

Twenty grams of field moist soil were weighed into a 50-mL centrifuge tube and 20 mL deionized water were added. The solution was shaken for 30 min, centrifuged at $3270 \times g$ for 10 min, and filtered through Whatman (Maidstone, UK) 42 filter paper. The concentrations of $\text{NO}_3\text{-N}$ and Br^- were determined within 24 h of extraction using an ion chromatograph (Dionex 300 [Sunnyvale, CA]) using the procedure outlined by the USEPA (1991). Gravimetric soil moisture was determined in a subsample for each depth to calculate the soil moisture percentage on an oven-dry soil weight basis. The concentrations of $\text{NO}_3\text{-N}$ and Br^- in the soil were expressed as mg kg^{-1} dry soil basis. Soil sampling continued until the Br^- concentrations in the soil profile approached nondetectable concentrations. This simulated the time taken for the complete disappearance of Br^- from this soil profile.

Leaching Estimation and Chemistry Model Simulations

The Leaching Estimation and Chemistry Model (LEACHM) is a one-dimensional water flow, solute transport,

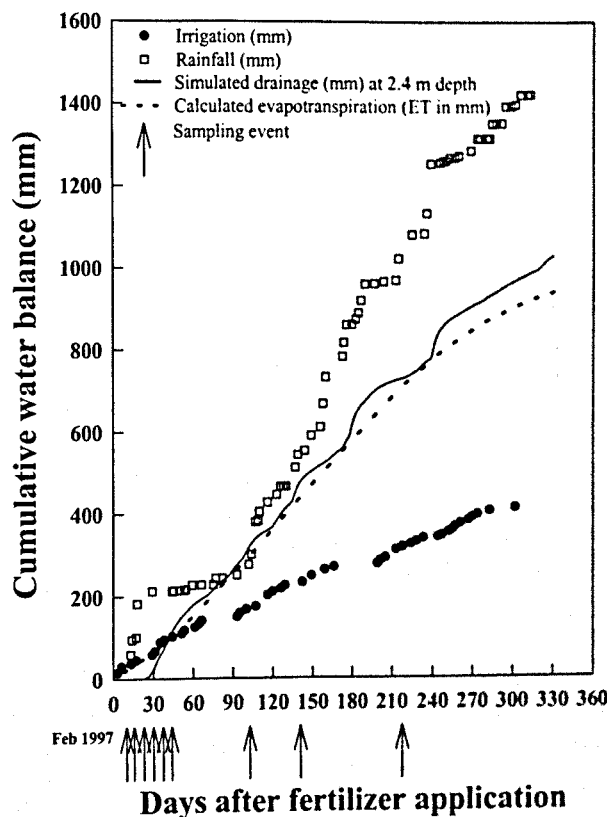


Fig. 1. Water balance components including rainfall, irrigation, simulated drainage below the rootzone, and evapotranspiration for a Tavares fine sand, with 25-yr-old 'Hamlin' orange trees on 'Cleopatra' mandarin rootstock. Arrows along the x axis show the soil sampling times during the study period.

and plant uptake model. It is composed of different submodels including LEACHN, a one-dimensional water flow and N transport model (Hutson and Wagenet, 1992). The choice of LEACHM was based on our experience (Paramasivam et al., 2000a) and that of other researchers (Pennel et al., 1990; Lamb, 1996; Graham and Wheaton, 1999; Lamb et al., 1999) under Florida sandy conditions in nearby locations. The current modeling exercise benefitted substantially from these previous works with LEACHM; thus, there was no need for an extensive calibration exercise since most of the input parameters used were taken from these simulation works specific to our current conditions.

The input parameters for LEACHN include: (i) daily water input (rainfall or irrigation) (Fig. 1), (ii) weekly potential evapotranspiration (ET_p) and minimum and maximum temperatures (Fig. 2), and (iii) soil physical properties including water retention curve parameters and hydraulic conductivity for each soil profile (Tables 1 and 2). Soil moisture content and concentrations of $\text{NO}_3\text{-N}$ and Br^- for the soil samples taken prior to fertilizer and Br^- application were the initial conditions for the model simulation. Nitrogen transformation rates and partitioning coefficients (Table 3) were the input parameters.

Soil Physical Properties

At the beginning of the study, undisturbed soil cores were taken at 0- to 0.15-, 0.15- to 0.30-, 0.30- to 0.60-, 0.60- to 0.90-, 0.90- to 1.20-, and 1.20- to 1.50-m depths, at five locations from the experimental site. These soil cores were used to determine soil water release curves (Klute, 1986) and satu-

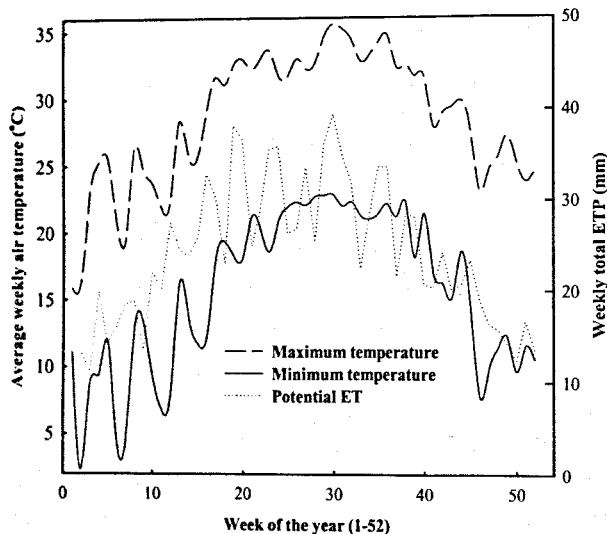


Fig. 2. Weekly minimum and maximum air temperature and total potential evapotranspiration used as input parameters for the Leaching Estimation and Chemistry Model (LEACHM) model.

rated hydraulic conductivity (Klute and Dirksen, 1986) at each of the five depths. Details of the soil water release curve were reported earlier by Paramasivam et al. (2000b). Subsamples of these cores were used to determine selected additional soil properties and reported by Paramasivam et al. (2001). These values were in agreement with those values reported by Carlisle et al. (1989) for the profile samples collected from the same site. Data from the deepest-measured soil cores were used for the remainder of the simulated soil profile. A stand-alone program, RETFIT, which accompanies the LEACHM model, was used to determine best-fit retention parameters for Campbell's (1974) water retention equation from these data (Table 2).

Crop Factor

Citrus root distribution in each soil layer was estimated from the literature. Based on Bowman (1984), as well as studies conducted by Castle (1980) and Alva and Syvertsen (1991), about 90% of the roots were found in the top 0.3 m and the remaining 10% of the roots were evenly distributed over the rest of the simulated profile. A constant mature citrus crop

Table 2. Best-fit retention parameters for Campbell's water retention equations for the different soil layers as determined by RETFIT and used by the Leaching Estimation and Chemistry Model (LEACHM).

Depth cm	Campbell's soil water retention parameters	
	A	B
0-15	-2.090	1.275
15-30	-3.510	0.580
30-90	-2.540	1.230
60-90	-1.060	3.100
90-120 and >120	-0.790	1.000

was assumed to be present throughout the simulation period, and with a crop cover fraction of 1 (fraction of land covered by the crop). Additional soil- and crop-related parameters used in the simulation are summarized in Table 3.

Weather Data

Daily potential evapotranspiration, ET_p , was calculated for the study period using daily minimum and maximum air temperatures (Fig. 2) recorded at the nearby Archbold Biological Station in central Florida as input to the potential evapotranspiration calculation model, ETM, (Fares, 1996). The ETM uses the Priestley-Taylor equation (Priestley and Taylor, 1972) to calculate ET_p . Input data for ETM include: daily minimum and maximum temperatures, altitude and latitude of the location, albedo, and sunshine ratio. More detailed information can be found about ETM in Fares (1996) and Fares and Mansell (1996). Daily ET_p data were summed to calculate a weekly total ET_p as required by LEACHM.

The model assumes no surface runoff. This is justified for the study site due to its flat terrain and its high saturated hydraulic conductivity (K_s). The LEACHM model simulated a transient or a steady state water flow. The model solves the one-dimensional Richards equation for transient water flow using a block-centered finite-difference approximation technique. The upper boundary condition of the simulated system is a flux-controlled surface boundary during the period of evaporation, nonponded infiltration, and zero flux. However, during periods of ponded infiltration, the pressure potential of the first node is set to zero. Freely draining profile boundary conditions (a unit hydraulic potential gradient = 1) were used in the lower boundary condition of the simulated system

Table 3. Nitrogen transformation rates and transport parameters as input for the Leaching Estimation and Chemistry Model (LEACHM).

Model parameters	Values	Reference
Partition coefficient, $L\ kg^{-1}$		
NH_4-N		Clothier et al. (1988)
NO_3-N	2.6	
Molecular diffusion coefficient in water, $mm^2\ d^{-1}$	0.0	Hutson and Wagenet (1992)
Bresler's equation adjustments	120	
a		Hutson and Wagenet (1992)
b	0.001	
Dispersivity, mm	10	Hutson and Wagenet (1992)
Synthesis efficiency factor	20	
Humification fraction	0.5	Johnson et al. (1987)
C to N ratio	0.2	
Minimum matrix potential for transformations	10	Stevenson (1982)
Mineralization rate constants, d^{-1}	-1500	
Litter N		Hutson and Wagenet (1992)
Manure N	0.01	
Humus N	0.02	Clark (1994)
Other rate constants, d^{-1}	0.00007	
Denitrification		Clark (1994)
Nitrification	0.001	
Ammonia volatilization	0.02	Hutson and Wagenet (1992)
Denitrification half-saturation constant, $mg\ L^{-1}$	0.6	
Limiting NO_3 to NH_4 ratio in solution for nitrification, r_{lim}	10	Hutson and Wagenet (1992)
	8	

given the absence of a water table at the simulated depth. The simulated soil profile was equally divided into 16 horizontal segments, each 0.15 m thick. The predicted concentrations of NO₃⁻ and Br⁻ and volumetric water content were reported for the center of each depth segment (0.075, 0.225, up to 2.35 m). A value of 20 mm was used for the soil dispersivity for all layers, as recommended by Hutson and Wagenet (1992). More information about model calibration and sensitivity to Florida sandy soil under similar weather conditions for citrus crop was previously given by several researchers (Pennel et al., 1990; Lamb, 1996; Graham and Wheaton, 1999; Lamb et al., 1999; Paramasivam et al., 2000a).

RESULTS AND DISCUSSION

Water Balance Components

Water balance components, including measured rainfall and irrigation, simulated drainage below the root-zone, and calculated evapotranspiration values for experimental plots, are shown in Fig. 1 and Table 2 for an entire growing season. During the first 21 d of this monitoring period, the experimental area received about 45 and 182 mm of cumulative irrigation and rainfall, respectively. For the same period, calculated evapotranspiration loss was 47 mm. The LEACHM simulation predicted no water drainage losses below the 2.4-m depth profile during this period. Drainage losses were predicted to start 28 d after fertilizer and Br⁻ application and continued through the study period (Fig. 1). During the first 42 d of intensive monitoring of nutrient movement, cumulative irrigation and rainfall accounted for 95 and 213 mm, respectively. During the same period, calculated evapotranspiration and simulated drainage loss below the depth of 2.4 m accounted for 95 and 105 mm, respectively (Fig. 1). Water mass balance for the entire crop year is presented in Table 4.

Amount of available nutrients in the soil profile, amount of available water for leaching, and soil profile characteristics are important factors to determine the nutrient leaching losses from the applied fertilizers (Staver and Brinsfield, 1990). The amount of precipitation and/or irrigation in excess of evapotranspiration along with soil profile characteristics determine the amount of drainage water below the rooting depth. These in turn control the movement of wetting front in the soil profile and thereby determine the water content and nutrient distribution at various depths in a soil profile at each sampling time. Nutrient contents measured at various depths in a soil profile at a given time represent only brief glimpses of nutrient movement in the soil profile with time and do not attempt to represent the fate of the total nutrient applied to soil in the form

of a fertilizer mixture. Campbell (1978) reported that sandy soils, along with high rainfall, create conditions conducive to rapid nutrient movement.

Measured and Predicted Soil Water Contents

Mean and standard error of measured soil water contents of samples collected at various depths in the soil profile at various sampling dates are shown with filled circle symbols in Fig. 3. Corresponding simulated water contents are shown in the same figures as continuous lines. Generally, LEACHM-predicted water content reasonably agreed with measured soil water content in the soil profile to a depth of 0.9 to 1.2 m (Fig. 3) in all treatments. Under cropped conditions the depth of root distribution was an important input for LEACHM to predict plant water uptake and subsequent volumetric water content as a function of soil depth. Since the majority of roots are in the top 90-cm depth (Alva and Syvertsen, 1991; Zhang et al., 1996), the effect of root uptake on soil water and plant nutrients would be substantial between 0 and 90 cm depth compared with the rest of the soil profile. The good agreement between predicted and measured volumetric water contents in soils indicates that the input of 90 cm as rooting depth to the LEACHM root functions accurately predicted water uptake by citrus trees.

Temporal Changes in Bromide Distribution in the Soil Profile

Variability in Br⁻ concentration in samples collected from different N treatments and replicates was nonsignificant ($P \leq 0.05$). Data were pooled and the mean Br⁻ concentration was calculated across all N rates and replicates (Fig. 4). Soil samples taken 7 d after Br⁻ application showed 20 mg kg⁻¹ Br⁻ in the top 15-cm depth, which decreased to 10 mg kg⁻¹ by 14 d following a 15.3-mm irrigation water application (Fig. 4). The Br⁻ concentration in the 0- to 15-cm layer of soil further decreased to about 2 mg kg⁻¹ 28 d after surface application of Br⁻. For the same period, the cumulative water input was 57.6 mm cumulative (Fig. 1). A trace amount (0.04 mg kg⁻¹) of Br⁻ appeared at the bottom of this soil profile for the same period. However, continuous monitoring of Br⁻ indicated that the Br⁻ concentration increased up to 1 mg kg⁻¹ at the bottom of the sampling depth (2.4 m) 98 d after Br⁻ application. This is an indication of downward movement of Br⁻ beyond the rooting depth with drainage water. During the period in between 28 and 98 d, the cumulative water input (rainfall + irrigation) was 410 mm, of which 293 mm of water drained below the 2.4-m depth (Fig. 1).

Simulation of water movement through the soil profile using LEACHM indicated that drainage water beyond the soil profile depth of 2.4 m began 28 d after Br⁻ and N application (Fig. 1). Presence of Br⁻ was continuously observed at each sampling event at the bottom of the soil profile (2.4 m) up to 98 d after surface application. However, Br⁻ became nondetectable through the entire depth of sampling by 214 d, indicating that all of the surface-applied Br⁻ was taken up by the trees

Table 4. Water and bromide mass balance as simulated by the Leaching Estimation and Chemistry Model (LEACHM).

	Input yr ⁻¹		Output yr ⁻¹		Soil storage variation: initial - final
	Rain	Irrigation	Plant uptake	Drainage	
	mm				
Water	1612	335	920	985	-39
	kg				
Bromide	80.0		32	48	0

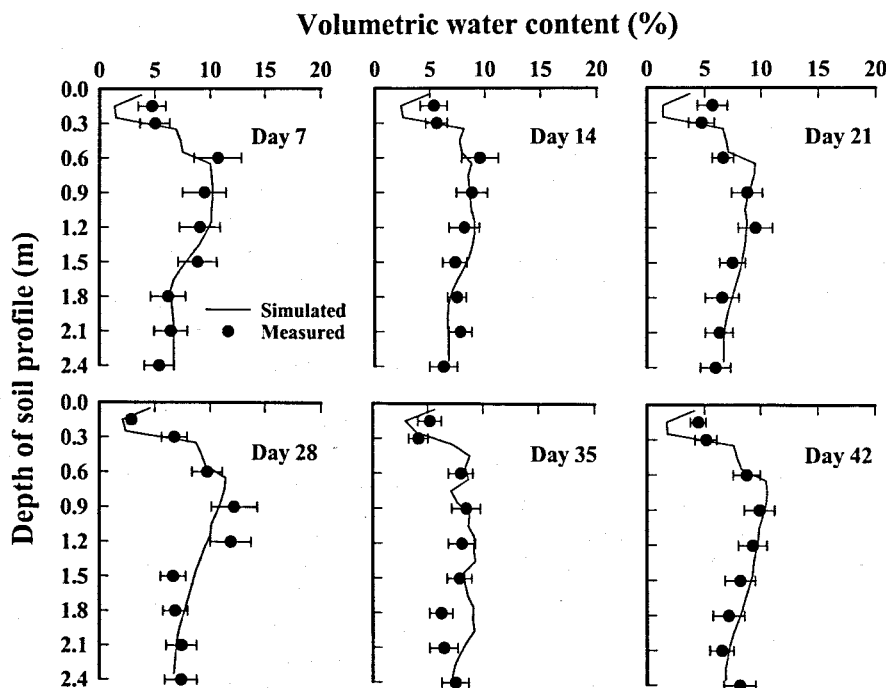


Fig. 3. Distribution of measured and Leaching Estimation and Chemistry Model (LEACHM)-simulated volumetric water content in the soil profile of a Tavares fine sand at various sampling times following an irrigation and rainfall events. Measured values are the mean and standard error of 45 samples per depth profile (five treatments $\times$ three repetitions $\times$ three cores).

and leached through the 2.4-m-deep soil profile. Cumulative water input from 98 to 214 d was 872 mm, of which about 434 mm water drained below 2.4 m. (Fig. 1). The cumulative water input during the 98- to 214-d period represented 37 and 50% of the annual irrigation and

rainfall, respectively, coinciding with the rainy months (May–September) in the study area. The quantity of water leached during this period was 42% of the average total annual drainage. Water and bromide mass balance for the entire period of this study is given Table 4.

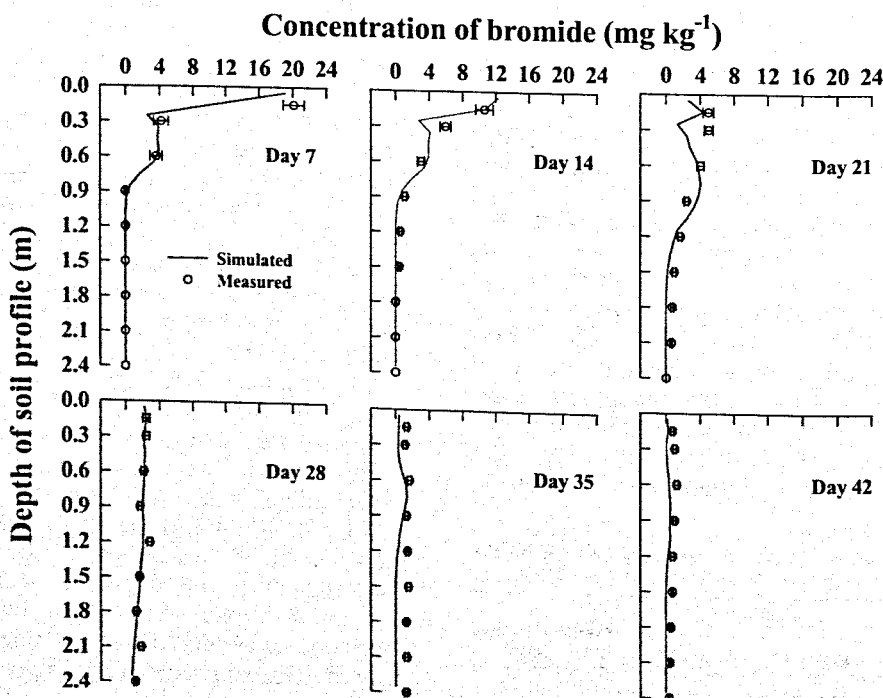


Fig. 4. Distribution of measured and Leaching Estimation and Chemistry Model (LEACHM)-simulated Br^- concentrations in the soil profile of a Tavares fine sand at various sampling times following the application of $80 \text{ kg Br}^- \text{ ha}^{-1}$ as KBr under the citrus tree canopy. Measured values are the mean and standard error of 45 samples per depth profile (five treatments $\times$ three repetitions $\times$ three cores).

Measured Temporal Changes in Nitrate Distribution in the Soil Profile

Nitrification occurs quite rapidly under these prevailing conditions (<7 d) as demonstrated by Khakural and Alva (1995). Therefore, although N was applied as NH_4NO_3 , transport of $\text{NO}_3\text{-N}$ in the soil profile was evaluated in this study. Soil samples were taken to quantify the background levels of $\text{NO}_3\text{-N}$ and Br^- prior to application of the respective sources 120 d after the last fertilizer application of the previous cropping year (1996). Variability in background concentrations of soil profile $\text{NO}_3\text{-N}$ in samples collected at different depths across different N treatments and replicates was nonsignificant ($P \leq 0.05$). Therefore, the data were pooled and the mean $\text{NO}_3\text{-N}$ concentration was calculated across all N rates and replicates and reported here. The background concentrations of soil profile $\text{NO}_3\text{-N}$ were varied within a range of 0.3 to 0.8 mg kg^{-1} in the soil profile (data not presented). The concentrations of $\text{NO}_3\text{-N}$ in the soil samples within the top 0.3 m were reasonably related to the rate of N application during the first 28 d of fertilizer application. Thereafter, the differences were not significant ($P \leq 0.05$) and approached the background concentrations (0.2 to 0.9 mg kg^{-1}) by 42 d (Fig. 5). These plots received about 213 mm rainfall and about 58 mm irrigation during 28 d after fertilizer application, which could have resulted in significant downward transport of nitrate. However, the water balance calculations (net water input; i.e., cumulative water input minus losses) and the soil water content measurements from various depth samples (with the exception of the soil samples taken on 28 d and thereafter) showed no water leaching during the first 28 d after the fertilizer application (Fig. 1 and 3). The nutrient requirement of a citrus tree is maximum from early spring through early summer (Tucker et al., 1995). Since the majority of active fibrous roots are in the top 15- to 30-cm depth (Alva and Syvertsen, 1991; Zhang et al., 1996), the effect of root uptake on soil moisture and other plant nutrients would be greatest at this depth. Nutrient uptake is rapid and substantial during the initial 30 d after the fertilizer application. This explains the rapid and significant decrease in $\text{NO}_3\text{-N}$ concentrations in the top 15- to 30-cm depth during the 28 d after N application. The results also show some redistribution of N from the surface into the deeper soil with the downward-percolating water front.

Nitrate N concentrations through the 2.4-m-deep soil profile decreased to almost background concentrations regardless of N rates by 42 d after fertilizer application. For the same period, the cumulative water input (irrigation and rainfall) was 308 mm. During 28 to 42 d after the fertilizer application, LEACHM simulation indicated a loss of about 122 mm water through drainage beyond the 2.4-m depth in this soil profile (Fig. 1). Disappearance of most N from the soil profile during the 28- to 42-d period could be due to $\text{NO}_3\text{-N}$ leaching below the rootzone. Leaching loss of N during this period could be from residual $\text{NO}_3\text{-N}$ in the soil profile, decomposition and transformation of plant residue, or residual fertilizer N.

Plant residue mineralization, including root turnover, has been reported to contribute up to 156 $\text{kg N ha}^{-1} \text{yr}^{-1}$ for bearing citrus trees under field conditions (Dou et al., 1997). Mineralization parameters used for the current work were based on the work of Clark (1994) and Dou et al. (1997) conducted under Florida sandy soils and used for LEACHM. Further, mineralization rate used in this LEACHM simulation was verified with similar simulation studies conducted in nearby citrus-growing sandy Entisols of central Florida (Pennel et al., 1990; Lamb, 1996; Graham and Wheaton, 1999; Lamb et al., 1999; Paramasivam et al., 2000a). More details about mineralization can be obtained from Clark (1994) and Dou et al. (1997). Mineralized N would affect the distribution pattern of $\text{NO}_3\text{-N}$ in the soil profile and leaching, although the contribution may vary with time since the mineralization process is affected by various factors in the soil environment (i.e., soil temperature and water content).

Comparison of Measured and Predicted Nitrate and Bromide Values

Under mature citrus tree growth conditions, concentrations of $\text{NO}_3\text{-N}$ at various depths within the entire profile were predicted reasonably by the LEACHM and compared favorably with the measured values at various sampling events across all N rates (Fig. 5). Variations between the measured and predicted $\text{NO}_3\text{-N}$ values were within 1 to 2 mg kg^{-1} over most of the sampling period. Similarly, predicted Br^- concentrations were very close to measured Br^- values for all the sampling events at various sampling points. Weekly profile soil sampling indicated that the concentrations of $\text{NO}_3\text{-N}$ and Br^- in the top 15 cm were almost reduced by half of their respective concentrations at the previous sampling at least for the first 28 d of their application. Since the sampling was carried out following every irrigation or rainfall event, this could be considered as a similar transport response of $\text{NO}_3\text{-N}$ and Br^- to downward movement of water. The LEACHM model predicted that about 40% of the applied Br^- was taken up by the trees and the remaining 60% leached below 2.4 m of the simulated profile (Table 5). Similar high Br^- uptake by different crops has been reported in the literature. Owens et al. (1985) found that plant uptake of Br^- accounted for about 32% of that applied, which was about the same amount that was recovered in drainage water. Even high Br^- uptake by plants was reported by Kung (1990) and Schnabel et al. (1995), who found that as much as 55 and 38% of the applied Br^- was taken up by potato (*Solanum tuberosum* L.) and ryegrass (*Lolium perenne* L.), respectively. This high Br^- plant uptake simulated by LEACHM could be due to citrus tree uptake, since the application time coincided with a period of very high plant nutrient uptake demand (i.e., N; Tucker et al., 1995). However, we do not have analytical information to ascertain the Br^- plant uptake component other than Br^- plant uptake simulated by LEACHM. Therefore, based on the available information, leaching and plant uptake would have been the major processes

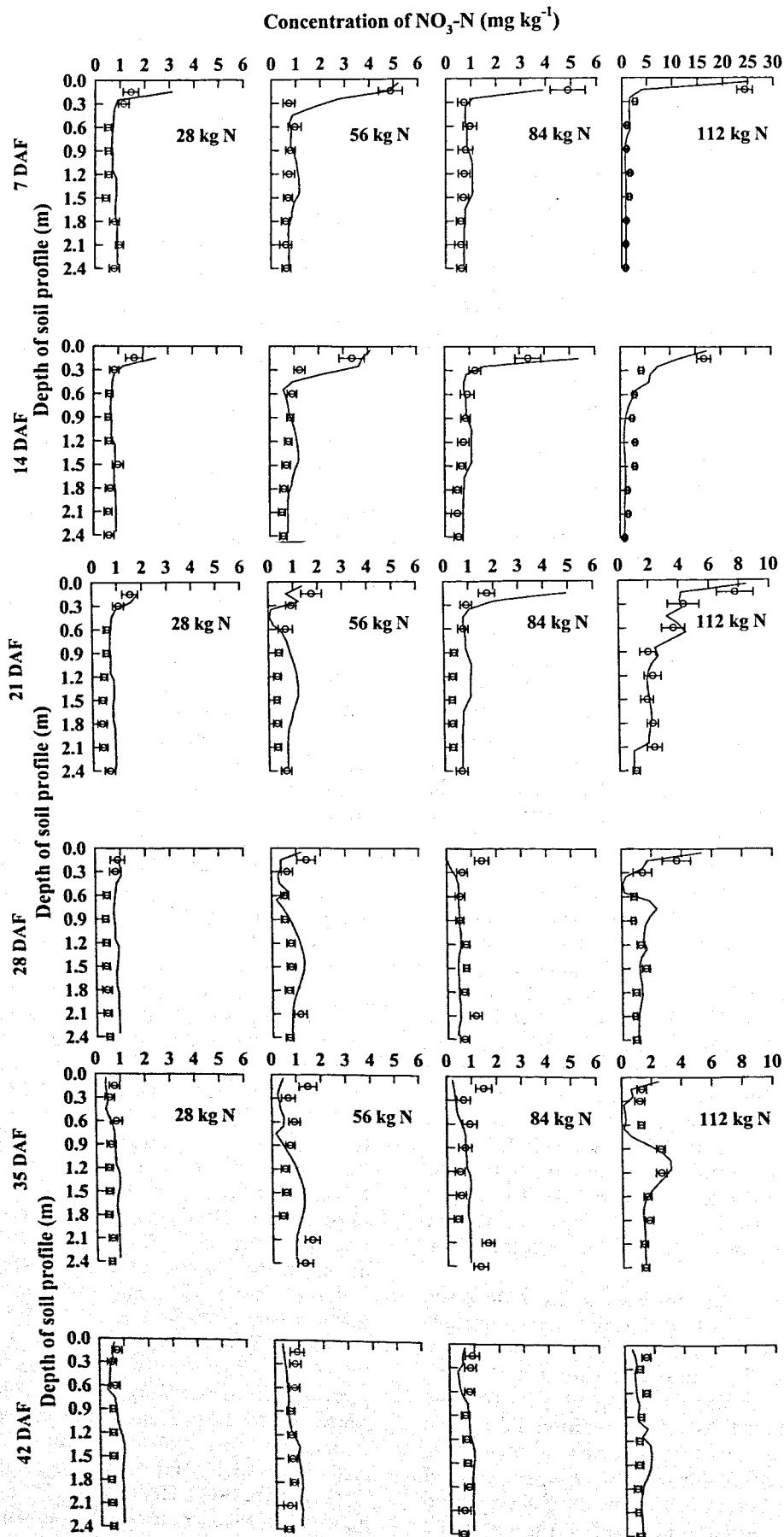


Fig. 5. Distribution of measured and Leaching Estimation and Chemistry Model (LEACHM)-simulated $\text{NO}_3\text{-N}$ in the soil profile of a Tavares fine sand at various sampling times following the broadcast application of water-soluble dry granular fertilizer containing NH_4NO_3 . Measured values are the mean and standard error of nine samples per depth profile per treatment (three repetitions $\times$ three cores).

Table 5. Nitrogen mass balance for different fertilization rates as simulated by the Leaching Estimation and Chemistry Model (LEACHM).

N rates	Input application ⁻¹		Output application ⁻¹				Soil storage variation: initial - final
	Mineral	Organic	Plant uptake	Leaching	Volatilization	Microbial	
$\text{kg ha}^{-1} \text{ yr}^{-1}$	kg ha^{-1}						
112	28	14	20	15	10	2	-5
224	56	14	32	15	14	2	7
336	84	14	39	28	19	2	10
448	112	14	51	30	29	2	14

responsible for the nondetectable amount of Br^- in the soil profile at the end of the experiment.

Predicted Cumulative Losses from Applied Fertilizer Nitrogen and Nitrogen Mass Balance

Nitrogen mass balance simulated by LEACHM is presented in Table 5. A one-fourth split of the annual application of various N rates (28, 56, 84 and 112 kg N ha^{-1}) resulted in loss of 15, 15, 28, and 30 kg N ha^{-1} , respectively, with 122 mm cumulative water leached during the 42-d period. Various factors could have contributed to N loss from the soil profile, probably a significant contribution from applied fertilizer N and mineralized N under the tree canopy. Even though it is difficult to separate the contribution of mineralized N for leaching, we can estimate the leaching losses of N from applied fertilizer N on a proportional basis. For the calculation of amount of N leached from applied fertilizer, it was assumed that the contribution of mineralized N for leaching had been consistent across all N treatments. Based on these calculations, about 10 (i.e., $[(15/(28 + 14)) \times 28]$), 12 (i.e., $[(15/(56 + 14)) \times 56]$), 24 (i.e., $[(28/(84 + 14)) \times 84]$), and 27 (i.e., $[(30/(112 + 14)) \times 112]$) kg N ha^{-1} loss came from applied fertilizer N during this 42-d period. Thus, 36, 21, 29, and 24% of the applied fertilizer N from low to high N fertilizer rates, respectively, would have been lost in the leachate. As per LEACHM prediction, other components of N mass balance such as plant uptake, volatilization losses, and variation in soil N storage increased with increasing rate of mineral N fertilizer input.

Analyses of soil cores from plots receiving various amounts of N as dry granular fertilizer revealed that there was very little variation in movement and distribution of $\text{NO}_3\text{-N}$ in the soil profile across all N rates. This observation clearly suggests a negligible preferential flow effect under field conditions of this study and further justifies the use of LEACHM. Preferential flow would be an important phenomenon under which soil has layering, cracks, and fissures as a result of the presence of shrinking and swelling clay, natural soil pipes, and dead plant roots and residues (Hillel, 1998). These preferential flow factors are unlikely to be present under a structureless homogeneous sandy soil (>96% sand). Thus, it is not expected that preferential flow could play a dominant role in water and solute movement in extremely sandy soils.

SUMMARY AND CONCLUSION

Transport and distribution of water, $\text{NO}_3\text{-N}$, and Br^- in a sandy soil profile were studied under mature citrus

tree production conditions. Nitrate N concentrations through the 2.4-m-deep soil profile decreased to levels very close to the background concentrations by about 42 d, irrespective of N rates. Rapid decrease of $\text{NO}_3\text{-N}$ concentrations in the top 15- to 30-cm depth occurred during the 28 d after N application, possibly attributable to high plant uptake demand during the early spring season. The results also showed some downward movement of N with wetting front following water application from the surface layer deeper into the soil profile, which could have contributed to a decrease in the $\text{NO}_3\text{-N}$ concentration in the topsoil. Bromide, used in this study as a tracer, indicated a somewhat similar trend of distribution and disappearance pattern as fertilizer $\text{NO}_3\text{-N}$. However, about 214 d was taken for the surface-applied Br^- to become nondetectable within the 2.4-m soil profile. The LEACHM simulations and mass balance of simulations indicated an increasing trend of leaching losses of applied N (15 to 30 kg ha^{-1}) with increasing N rate of application used in this study. This study also indicated the usefulness of a numerical modeling approach to estimate the N leaching losses and predict other mass balance components of N and water simultaneously and accurately for the entire crop year. Results of this study further suggest that, under extremely sandy nature of soils, leaching losses and ground water contamination of $\text{NO}_3\text{-N}$ are driven by excess water leaching and thus could be minimized by maintaining irrigation practices to supply water only to replenish the water deficit within the rooting depth of citrus and applying N fertilizers in small quantities but with more frequent applications. Results also suggest that repeated intensive monitoring of nutrient movement in the soil profile following each split fertilizer application coupled with a numerical modeling exercise might help us to enhance our understanding of N dynamics more thoroughly and to fine tune N and irrigation management practices in similar types of sandy soils. However, the authors are not advocating repeated intensive sampling following each split fertilizer application by every farmer because it is very laborious and not feasible.

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Waste Management

Phosphorus Leaching from Biosolids-Amended Sandy Soils

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ABSTRACT

Increasing emphasis on phosphorus (P)-based nutrient management underscores the need to understand P behavior in soils amended with biosolids and manures. Laboratory and greenhouse column studies characterized P forms and leachability of eight biosolids products, chicken manure (CM), and commercial fertilizer (triple superphosphate, TSP). Bahiagrass (*Paspalum notatum* Flugge) was grown for 4 mo on two acid, P-deficient Florida sands, representing both moderate (Candler series: hyperthermic, uncoated Typic Quartzipsamments) and very low (Immokalee series: sandy, siliceous, hyperthermic Arenic Alaquods) P-sorbing capacities. Amendments were applied at 56 and 224 kg P_T ha⁻¹, simulating P-based and N-based nutrient loadings, respectively. Column leachate P was dominantly inorganic and lower for biosolids P sources than TSP. For Candler soil, only TSP at the high P rate exhibited P leaching statistically greater ($\alpha = 0.05$) than control (soil-only) columns. For the high P rate and low P-sorbing Immokalee soil, TSP and CM leached 21 and 3.0% of applied P, respectively. Leachate P for six biosolids was <1.0% of applied P and not statistically different from controls. Largo biosolids, generated from a biological P removal process, exhibited significantly greater leachate P in both cake and pelletized forms (11 and 2.5% of applied P, respectively) than other biosolids. Biosolids P leaching was correlated to the phosphorus saturation index ($PSI = [P_{ox}]/[Al_{ox} + Fe_{ox}]$) based on oxalate extraction of the pre-applied biosolids. For biosolids with $PSI \leq$ approximately 1.1, no appreciable leaching occurred. Only Largo cake ($PSI = 1.4$) and pellets ($PSI = 1.3$) exhibited P leaching losses statistically greater than controls. The biosolids PSI appears useful for identifying biosolids with potential to enrich drainage P when applied to low P-sorbing soils.

BENEFICIAL REUSE OF BIOSOLIDS and manures based on crop nitrogen (N) requirements usually supplies phosphorus (P) in excess of crop needs. Excess soil P is not harmful to plants when biosolids are used for N fertility (Peterson et al., 1994). Off-site migration to aquatic systems is, however, a major concern because P is the limiting nutrient in most freshwaters (Sharpley

and Beegle, 1999). Phosphorus moves from agricultural fields in a dissolved form or attached to soil particles. When soil P levels are not excessive, up to 90% of the P transported from cropland is bound to soil particles (Sharpley and Beegle, 1999). Thus, erosion control measures prevent significant off-site P movement. Yet, some agricultural fields have soil test P levels in the high and very high categories, and off-site transport of soluble P can be important. Soluble P is directly available to algae (Sonzogni et al., 1982) and thus particularly relevant to water quality degradation.

The growing concern over excess P in soils has led to regulatory changes that could dramatically affect land-based recycling of biosolids. For example, the Water Quality Improvement Act in Maryland mandates P-based nutrient management for manures and biosolids by 2005 (Simpson, 1998). Recent Florida legislation requires P-based biosolids application rates in watersheds associated with P-sensitive water bodies (Sec. 373.4595 FL Statutes). Compared with N-based nutrient management, a P-based approach dictates substantially lower waste application rates. This means larger land area requirements and higher costs to transport wastes outside sensitive watersheds. Increasingly stringent effluent discharge limits exacerbate the problem because more efficient P removal from wastewaters elevates biosolids P. Municipalities are concerned that mandated P-based nutrient management may force them to abandon biosolids recycling programs in favor of landfill disposal.

Sound management of land-based biosolids recycling demands a full understanding of P transformations in the soil-plant environment, but leaching of biosolids P has received limited investigation (Kyle and McClintock, 1995; Sui et al., 1999). Unlike nitrogen, leaching of P has not traditionally been viewed as a major ground water problem. In many soils, abundant P-sorbing oxide components in surface horizons and subsoils keep leachate P levels well below eutrophication thresholds. Pe-

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Abbreviations: BPR, biological phosphorus removal; CM, chicken manure; PSI, phosphorus saturation index; TSP, triple superphosphate.