CHARACTERIZING SOLUTE MOVEMENT IN COARSE-TEXTURED, LEACHING-VULNERABLE SOILS WITHIN ZERO-TENSION COLUMN LYSIMETERS

STUDY 279

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ABSTRACT

Results from field studies utilizing zero-tension column lysimeters that characterize the fate and transport of pesticides in the soil environment have recently been submitted to DPR in support of pesticide registration in California. In Europe, these studies have been routinely submitted in support of pesticide registration, often substituting for studies that require data from monitoring wells when higher tier assessments of pesticide leaching potential have been necessary. Since it remains unclear if data obtained from lysimeters represents pesticide movement in the natural soil environment, this study compared the soil movement of several pre-emergent herbicides and their degradates in soil confined within lysimeters with soil located outside of the lysimeters, denoted from here on as being lysimeter-confined and unconfined soil, respectively. Movement of bromide in soil also was measured because it is a surrogate for the measurement of water movement. Results indicated that in a coarse-textured, leaching vulnerable soil the existence of a saturated zone at the base of the lysimeters retarded the movement of bromide, bromacil and hexazinone through the lysimeter-confined soil compared to the unconfined soil. For diuron, norflurazon, simazine and degradates that did not encounter the saturated zone at the base of the lysimeters, there was no significant difference in their fate and movement in the lysimeter-confined soil compared to the unconfined soil. The HYDRUS-1D computer model was used to investigate the possibility of simulating residues in lysimeters and relating simulated output to the fate and movement of pesticides in the unconfined, natural soil environment. Good agreement occurred between model-simulated and field-recovered residues in lysimeter-confined and unconfined soil under variable water inputs for several pesticides representing diverse levels of soil adsorption potential and degradation rates. Successful simulation of residue fate and transport between either lysimeter-confined or unconfined soil did not require adjustment or manipulation of any pesticide properties or soil hydraulic model input properties. The sole modification required for simulating pesticide residues within lysimeters was changing the soil profile bottom boundary condition from free-draining, which is applicable to the unconfined natural soil environment, to a seepage face boundary condition with the appropriate pressure head.

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INTRODUCTION

Lysimeters are devices incorporated into the soil that are useful for characterizing water or solute movement in soil. They are often used in agricultural settings to account for evapotranspiration losses by determining changes in the soil-water status over time, usually by weight differential. Soil lysimeters also have been utilized to sample drainage water for solute concentration in contaminant transport research. Soil drainage water can be collected by gravitational means at zero tension (zero-tension lysimeter), or by an externally applied pressure into a reservoir at the base of the lysimeter (suction lysimeter), or otherwise by capillary tension into a reservoir through a porous interface with the soil.

Zero-tension soil lysimeters have been utilized by pesticide registrants in parts of Europe for higher tier assessments of pesticide leaching potential to provide data for use in their pesticide registration process (FOCUS, 2009). These lysimeters collect the soil solution into a reservoir located below the soil column by means of free drainage. In the US, capillary tension lysimeters have previously been used by pesticide registrants and by the Department of Pesticide Regulation (DPR) to investigate aspects of pesticide movement in the soil. However, the use of zero-tension lysimeters has recently been introduced into studies conducted by registrants in the US to characterize leaching of water and solute.

Historically, DPR field studies on movement of pesticides in soil have focused on soil coring following pesticide and water applications. In these studies, chemical analyses of soil cores with respect to the depth at which they were collected have been used to characterize the fate and movement of pesticides in soil. However, soil coring alone has limitations in characterizing the fate and movement of leaching residues:

1) In irrigated agriculture, soil-water movement and leaching of residues are dynamic processes, whereas, the process of soil coring is intermittent and sporadic and difficult to coincide exactly with leaching events.
2) Soil coring is resource intensive and is often a limiting factor in the scale and scope of field study design.
3) Soil coring requires prior knowledge of potential residue movement in order to recover leaching residues that might otherwise travel beyond the maximum soil coring depth. The magnitude, intensity and frequency of water applications, duration of study, pesticide physical/chemical properties and soil characteristics all influence movement of residues in soil.

4) Compared to residues in aqueous solution, analytical analysis of soil-bound residues typically involves more complicated extraction processes at the expense of detection sensitivity.
5) Accountability of highly mobile pesticide transformation products is challenging in soil coring studies as they form gradually and leach rapidly thereby temporally and spatially existing at low concentrations relative to their parent products.

Zero-tension column lysimeters with collection reservoirs address the limitations listed above that are inherent with soil coring:

1) Coinciding sampling activities with solute leaching events is less critical with zero-tension lysimeters as all leachate within the confines of a lysimeter is captured irrespective of the magnitude of water applications, potential for residue movement, or soil characteristics.
2) Solution collection from lysimeter reservoirs is cost effective compared to soil sampling; only requiring extraction by pump with the frequency of sampling unrestricted.
3) Little or no prior knowledge of potential residue movement is required with lysimeters as their collection reservoirs remove any possibility of residue loss from leaching below the soil profile.
4) Chemical residues extracted from lysimeter reservoirs are in aqueous solution thereby typically providing for improved detection sensitivity compared to soil-bound residues.
5) Pesticide transformation products that have been elusive in DPR soil coring studies, likely due to their gradual rate of formation and high mobility coupled to constraints associated with analytical limits in soil would accumulate in lysimeter reservoirs.

A further benefit of lysimeters is realized when the base of the lysimeter-confined soil is below the soil evaporative depth and active biota zone. Solute captured in lysimeter reservoirs under these circumstances is a direct measure of residue mass that can potentially leach below the crop root zone because there is a low potential for vertical upward movement of solute towards the soil surface and the rates of metabolic-based degradation are diminished. These measurements provide a direct measure of the leaching potential of a chemical and they can be used to measure the performance of models that predict the amount of residues and drainage water leached.

Utilizing zero-tension column lysimeters to characterize leaching residues would ideally consist of encapsulating an undisturbed soil core whereby the soil's hydrological characteristics have not been significantly modified or influenced by contact with the lysimeter casing. Determining the effect of lysimeters on residue movement in soil by comparing solute extraction from their reservoirs with residues sampled from unconfined soil is problematic, leading to approaches of

indirect comparisons (Kasteel et al., 2010). A common approach has been to compare measured solute concentrations from lysimeter reservoirs to model-simulated solute concentrations from unconfined soils. FOCUS (2009) cited numerous studies investigating this subject with somewhat conflicting results and opinions. Factors that complicate comparisons between these studies are diversity of soil types, lysimeter designs, study methodologies, modeling tools and pesticides used.

Hardy et al. (2008) reported on comparisons between lysimeter studies and model leaching simulations for many pesticides that were assessed as part of a European regulatory decision making process to protect ground water. Many of these comparisons were in agreement (84%) and would have resulted in the same regulatory decisions being made. However, the comparisons were only qualitative in nature being judged as either exceeding or not exceeding a European ground water threshold concentration.

In some studies cited by FOCUS (2009), soil water content measurements and simulation results were compared between lysimeter-confined and unconfined cores. When differences were discovered they were often attributed to a saturated boundary-layer-effect at the base of the soil core within the lysimeter due to discontinuity in soil pore capillarity. Other studies indicated no appreciable difference in soil water content between lysimeter-confined and unconfined soil cores as related to water inputs. Kasteel et al. (2010) observed that transport of two pesticides with contrasting soil adsorption properties arrived at the lysimeter reservoirs (1.2 m deep) simultaneously and much earlier than simulations predicted, implying the existence of preferential flow pathways. The soil used in their study was fine textured, bordering on a silty-clay- to silt-loam, which may have experienced contraction during periods of drying that facilitated formation of cracks and fissures down its profile leading to preferential flow pathways. The authors also speculated that the lysimeter casing could have accelerated the downward movement of the chemicals.

Efforts have been attempted to minimize the potential effect of a saturated soil boundary layer at the base of lysimeter-confined soil cores in order to replicate semi-infinite soil columns (Corwin and LeMert, 1994). The study personnel used a repacked, fine-loam soil and layered various grades of sand and gravel between the base of the soil cores and the solute-collection reservoirs to improve drainage. A minor vacuum pressure also was applied to the base of the lysimeter-confined soil cores to force drainage. As the effect of these modifications was not part of the study objectives, the impact of the drainage material and vacuum pressure on the saturated soil boundary condition was not reported.

This study was conducted to determine whether zero-tension column lysimeters can be successfully implemented in future DPR field studies as reliable indicators for the movement of pesticides in soil. The study objective was to compare movement in soil of chemicals applied to the surface of soil confinement within lysimeters to soil located outside but adjacent to the lysimeters. The column lysimeters were installed in a coarse-textured, leaching vulnerable soil. The study was designed to provide data to:

1) Contrast any differences in pesticide residue movement between lysimeter-confined and unconfined soil.
2) Determine if preferential flow pathways and saturated lower boundary conditions exist in lysimeter-confined soil.
3) Evaluate the ability of a pesticide fate and transport model to predict and relate water and pesticide residue movement between lysimeter-confined and unconfined soil.

MATERIALS AND METHODS

Study Site

The study was conducted at the University of California, Kearney Agricultural Research and Extension Center near Parlier in eastern Fresno County. The USDA Natural Resources Conservation Service taxonomic classification for the soil at the study site was a Hanford fine sandy loam (Coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents). Depth to ground water was approximately 12 m and the surface slope was less than 2%.

Field Study Design and Apparatus

Each of two adjacent study sites, devoid of vegetation, consisted of treatment plots arranged as a completely randomized design where within each site there were two treatments denoted as the presence or absence of lysimeters. Each site contained eight treatment plots with a zero-tension column lysimeter randomly assigned to four of the plots. The remaining four plots were treated as controls where the movement of solute in soil was measured in the natural soil environment. The effect of the amount of water applied was also investigated by applying a different amount of water to each of the two sites thereby producing two levels of percolating water. Plots at each site were configured in a single line with adjacent plot-centers separated by a distance of 3 m (Figure 1). All treatment plots at both sites received an identical application of several chemicals.

The lysimeters and irrigation system were installed nine weeks prior to chemical application to the plots. Irrigation design consisted of a single line of 18 Supernet Jr. #40 (Netafim USA, Fresno, CA) rotary micro-sprinklers oriented down the center-line of each site, parallel with the treatment plots. The micro-sprinklers were elevated 25 cm above ground level and laterally-spaced at 150 cm. In this configuration, each sprinkler was adjacent to the center of a treatment plot by 75 cm with exception to one additional sprinkler located at both ends of the irrigation line (Figure 1). Testing of the irrigation system for water application uniformity and rate of application, and functionality of the lysimeter-solution extraction process was conducted during the nine week period prior to chemical application. Features of the lysimeter design and installation process reflected characteristics that were expected to minimize the potential for development of preferential flow pathways and saturated lower boundary conditions, and maintain structural integrity of the soil core inside the units (Appendix 1). These features included lysimeter-confined cores of undisturbed soil as opposed to repacked soil, and fine sand overlaying coarse sand at the base of the soil cores to enhance drainage and act as a filtration barrier. The soil was coarse textured, which also minimized the potential for preferential flow and saturated lower boundary conditions. After the irrigation system was verified for uniformity of water application, frequent irrigations were conducted across the sites until drainage water extracted from all lysimeter reservoirs confirmed their functionality and standardized the soil-water content between plots.

Chemical Application

The pre-emergent herbicides bromacil, hexazinone, simazine, diuron, and norflurazon were simultaneously applied to each study site at a rate of 3.4 kg ha^{-1} of active ingredient by method of chemigation using an A-100N Flexflo peristaltic pump (Blue-White Industries, Ltd, Huntington Beach, CA). These chemicals were chosen because they have potential for movement in the soil and have been found in California ground water as a result of agricultural use. Potassium bromide also was applied with the pesticides but at a rate of 150 kg ha^{-1}, equating to a bromide (Br) ion application rate of 100 kg ha^{-1}. This compound was used as a tracer for water movement and has been regarded as an ideal hydrologic tracer (Whitmer et.al., 2000). Dimensions of the chemigated area and subsequent water applications at each site were 33 m by 4.5 m. The width was confirmed to be sufficiently wide to ensure that water movement at the center of the unconfined soil plots was not appreciably influenced by the dry soil beyond the irrigated area. HYDRUS-2D computer simulations tested for this effect by simulating the hypothetical movement of Br in the vertical and radial plane perpendicular to the longitudinal direction of the plots and irrigation system (Appendix 2).

The chemigation at each site consisted of a solution application of 3-mm-depth, which was immediately followed by a water application of 7-mm-depth to incorporate the chemical residues into the soil.

Water Applications

Water applied to the study sites was sourced from a nearby irrigation well. Target application rates to the sites were based partially on DPR's standard ground water modeling scenario developed by the Environmental Monitoring (EM) Branch program (Troiano and Clayton, 2009). The modeling scenario simulates pesticide movement in soil using water application efficiencies typical of unpressurized, surface delivery methods such as flood, furrow and border irrigation systems where inputs at 160% of evapotranspirative demand can occur (California Agricultural Technology Institute, 1988; Snyder et al., 1986). Under this scenario, simulated output from DPR's model for a coarse-textured soil in the Fresno and Tulare County area estimated mean deep drainage levels of approximately 20 mm per week during a six-month irrigation season. Accordingly, treatment plots at one study site received weekly water inputs targeted to also produce drainage levels of approximately 20 mm per week, denoted hereafter as the heavy irrigated site. The remaining study site received reduced weekly water inputs producing less percolating water with the anticipation that the majority of chemical residues would be maintained within the 90-cm-deep soil cores. These treatment plots received water applications targeted at approximately 110% of evapotranspirative demand, denoted hereafter as the light irrigated site. Under this scenario, simulated deep drainage from DPR's ground water model approximated 4 mm per week.

Spreadsheet-based water balances based on procedures by Allen et al. (1998) provided estimates for water inputs in order to generate the required drainage levels of 20 mm and 4 mm per week for the respective study sites. Data input to the spreadsheets was indexed to daily reference evapotranspiration (ETo) and rainfall information from CIMIS weather station #39 located on the UC Kearney property, 600 m north of the study sites. The water balance partitions water applications into the components of evaporation, drainage and changes in soil moisture content, and centers on the use of a coefficient to limit evaporation when soil-water content drops below a threshold. Required parameters for the water balance included initial soil moisture content (field measured), volumetric water content at field capacity and at wilting point (Saxton and Rawls, 2005), an adjustment factor relating ETo to soil evaporation, and determination of the threshold to initiate the coefficient for evaporation reduction (Allen et al., 1998).

Field Sampling of Soil, Lysimeter Solution and Irrigation Water

Field sampling consisted of collecting soil, solution from lysimeter reservoir, and irrigation water at several discrete periods during the study:

1) Sample collection for establishing background residues:

A soil core was collected at both study sites one day prior to chemical application to establish background soil concentrations for Br; the pesticides: bromacil, hexazinone, simazine, diuron and norflurazon; the simazine degradates deethylsimazine (ACET) and didealkylated triazine (DACT); and the norflurazon degradate desmethyl norflurazon (DSMN). These soil cores were sampled to a depth of 90 cm at 15-cm increments with a 7.5-cm-diameter bucket auger using methods in soil sampling protocol FSSO002.00 (Garretson, 1999[A]). Upon extraction, each 15-cm soil subsample was split with one partition placed in a sealed jar on dried ice and maintained in frozen storage until chemical analysis for pesticide residues. The remaining soil partition from the split subsample was sealed in a plastic bag and maintained in refrigerated storage until analysis for Br residues. Background pesticide residues were not detected in these soil cores. However, mean background Br concentration was measured at 0.39 (standard error [se] = 0.04) and 0.37 (se = 0.04) ug g^{-1} for the light and heavy irrigated plots, respectively. A t-test at the 95 % confidence interval found no significant difference between study sites for background Br concentration in soil.

A solution sample was collected from each lysimeter reservoir one day prior to chemical application also to establish background concentrations for the above listed chemicals. Sampling from lysimeter reservoirs consisted of extracting all solution from each lysimeter using a 12 VDC peristaltic pump (Eijkelkamp Agrisearch Equipment, Giesbeek, Netherlands). Each extraction was partitioned into two vessels for pesticide and Br analyses. The samples were placed on ice and then transferred to refrigerated storage until chemical analysis. Between each extraction the pump's tubing was cleansed by flushing, first with alcohol and then with DI water. DACT was found in the solution of one lysimeter reservoir at 0.05 ug L^{-1} (analytical limit of quantification [LOQ]). Br was found in the background solution of all lysimeters with a mean concentration of 0.75 (se = 0.06) and 1.00 (se = 0.14) ug mL^{-1} in the light and heavy irrigated sites, respectively. A t-test at the 95 % confidence interval found no significant difference between study sites for background Br concentration in lysimeter reservoir solution.

Finally, a water sample was collected from the irrigation system on the day of chemical application, and at 8 and 19 weeks after chemical application to establish background concentration levels for the chemicals used in this study. ACET, DACT and DSMN were detected on several occasions at a mean concentration of 0.22 (se = 0.02), 0.35 (se = 0.05) and 0.34 (se = 0.07) ug L^{-1}, respectively. Simazine was detected in the irrigation water on one occasion at 0.071 ug L^{-1}. The impact of these detections on the study was inconsequential as the applied mass from the irrigation water was insufficient to result in background detections in soil or lysimeter reservoir solution – the single DACT detection in one lysimeter at the LOQ the exception. For example, the mean DACT detection in the irrigation water of 0.35 ug L^{-1} converts to a soil dry-weight concentration of approximately 0.06 ug kg^{-1} when assuming a θ of 0.30 and soil bulk density of 1.7 kg L^{-1}. The LOQ for these residues in soil was several orders of magnitude higher at 10 ug kg^{-1}. Since the LOQ in solution was much lower at 0.05 ug L^{-1}, the background pesticide residues in the irrigation water likely degraded in the soil to below this level prior to potentially encountering the lysimeter reservoirs. Br concentration in the irrigation water was measured at 0.49 (se = 0.09) ug mL^{-1}.

Relative to the application rate, background Br concentrations in soil, lysimeter solution and irrigation water were considered sufficiently low to not substantially impact the study.

2) <u>Soil sample collection for characterizing soil physical and hydraulic properties:</u>

One day prior to chemical application eight soil cores were obtained from between the study sites for characterizing several soil physical and hydraulic properties – required for establishing computer modeling parameters to simulate residue movement at the study sites. These cores were analyzed for bulk density, textural composition, organic carbon content, hydraulic conductivity, soil water retention, and initial soil moisture content. The eight soil cores were divided into two groups of four cores because specialized sampling equipment was needed for some of the collection and measurement procedures:

Group (1) soil cores: Four 90-cm long soil cores were obtained at 15-cm sub-core increments using a sample-ring-kit designed to collect, encase and support undisturbed soil samples. With these sub-cores, saturated soil hydraulic conductivity was established using methods specified by the ring-kit equipment manufacturer (Eijkelkamp Argrisearch Equipment, Giesbeek, Netherlands). The undisturbed soil sub-cores were then used to establish soil water retention curves

using ceramic pressure plate cells according to methods specified by the pressure plate manufacturer (Soil Moisture Equipment Corp., Santa Barbara, California, USA). While still maintained in their collection rings in an undisturbed condition, final measurements were made on the soil sub-cores of initial moisture content at the time of field sampling using protocol METH001.00 (Garretson, 1999[B]) and soil bulk density using protocol FSSO001.01 (Richardson, 2014). These final two measurements resulted in the destruction of the soil sub-cores.

Group (2) soil cores: Four 90-cm-deep soil cores were sampled with a 7.5-cm-diameter auger at 15-cm increments using soil sampling protocol FSSO002.00 (Garretson, 1999[A]). The 15-cm sub-cores were placed in plastic bags to be later analyzed for textural composition using protocol METH004.01 (Sartori, 2013) and total organic carbon content using protocol METH005.00 (Gunasekara, 2006).

3) Sample collection of chemigation solution for confirmation of chemical application rates:

To confirm chemical application rates a 1 L sample of solution was collected at each study site during chemigation through a port connected to the irrigation system. A 50 mL aliquot was isolated from each sample for Br residue analysis. The remaining sample from each study site was split to produce duplicate samples for pesticide residue analysis. The Br and duplicate pesticide samples from each study site were maintained in cold storage until analytical analysis. Measured Br concentrations from both study sites corresponded well with the theoretical concentration, being within 4% agreement. However, the measured pesticide concentrations were, in some cases, inconsistent with the theoretical concentrations (Figure 2). Only duplicate sample A in the heavy-irrigated site and duplicate sample B in the light-irrigated sites showed some agreement to the theoretical concentration, varying on average by approximately 20%. The source of measurement inconsistency for the remaining duplicate samples is unknown. It is noteworthy that the measured pesticide concentrations between study sites and also between duplicate samples within each site varied by a magnitude of approximately two (Figure 2). Such a coincidence would be consistent with sample dilution errors during their preparation prior to analytical analysis or with related mathematical accounting errors, particularly when considering the discrepancy between the duplicate samples within a study site. Based on this assumption, agreement between some of the measured and theoretical pesticide concentrations including the Br sample analysis, which was

conducted on undiluted aliquots, the theoretical application rate for the pesticides was considered most likely to be accurate.

4) Sample collection of lysimeter reservoir solution (post chemical application):

A solution sample was collected weekly from each lysimeter reservoir beginning one week after chemical application. The last sample was collected 12 weeks after chemical application as hereafter percolating water was not produced at either study site because irrigation to the plots was terminated and rainfall amounts diminished. As with sampling for background residues, post-chemical-application sampling from lysimeter reservoirs similarly consisted of extracting all solution from each lysimeter using the previously mentioned 12 VDC peristaltic pump. Each extraction was measured for total solution volume then partitioned into two vessels for pesticide and Br analyses. The samples were placed on ice then transferred to refrigerated storage until analytical analysis. Between each extraction the pump's tubing was cleansed by flushing, first with alcohol and then with DI water.

During lysimeter solution extraction a field blank was collected weekly from each study site by hand pouring de-ionized (DI) water into a sterile 1 L sampling bottle while adjacent to a randomly selected lysimeter. This procedure tested for potential sample contamination resulting from handling of the lysimeter solution samples. Beginning at week seven, an additional field blank was collected weekly from either of the study sites while adjacent to a randomly selected lysimeter by pumping DI water into a sterile sample bottle through the portable pump used to extract the lysimeter solution. This field blank tested for cross contamination potential between lysimeters during the solution extraction process. This potential existed because a single pump and set of tubing was used for extracting solution from all lysimeters. All field blanks collected during these periods were analyzed for Br and the previously mentioned pesticides and degradates. Br or pesticide residues were not detected in any of these field blanks.

Laboratory blanks (DI samples filled by laboratory staff), fortified samples (fortified with pesticides by laboratory staff) and blind fortified samples (fortified with pesticides unknown to laboratory staff) were analyzed for the pesticides of interest and found to be either non-detects (blank samples) or detected within control limits (fortified samples) specified in the analytical protocols.

5) Soil sample collection for determination of lysimeter effects:

Soil analyzed for pesticide and Br residues from lysimeter-confined and unconfined soil at the conclusion of the field study, which was 16 and 19 weeks after chemical application to the light- and heavy-irrigated study sites, respectively, was sampled following the general methodology in soil sampling protocol FSSO002.00 (Garretson, 1999[A]). These soil cores were sampled to a depth of 90 cm at 15-cm increments. Each 15-cm sub-core was 30 cm in diameter and extracted using post-hole diggers and trowels, and resulted in complete removal of soil from within the lysimeters as their inside diameter also was 30 cm. For the unconfined soil plots, a 30-cm-diameter ring of 5-cm height was inserted into the ground and used as a guide during removal of their 30-cm-diameter soil cores. Sanitizing of the soil extraction equipment between the 15-cm sub-cores was consistent with those methods used for bucket augers as stated in sampling protocol FSSO002.00 (Garretson, 1999[A]). Soil from each 15-cm sub-core was thoroughly mixed inside a large plastic bag and one of two soil subsamples of approximately 500 g transferred to a sealed jar on dry ice and maintained in frozen storage until chemical analysis for pesticide residues. The remaining soil subsample was transferred to a second plastic bag and maintained in cold storage prior to analyses for Br residues.

Chemical Analysis and Quality Control

Pesticide analysis was conducted by the California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry. A multi-analyte analysis was used for water solubilized and soil-bound residues of simazine, atrazine, diuron, bromacil, norflurazon, hexazinone, ACET, DACT and DSMN using analytical methods EMON-SM-62.9 (CDFA, 1999) and EM 29.7 (CDFA, 2002), respectively; the latter was modified to include DSMN. Analytical quality control procedures for these chemicals followed recommendations from chemistry laboratory quality control protocol QAQC001.00 (Segawa, 1995).

Br sample analysis was conducted by DPR personnel. During analytical analysis of the Br-treated soil several untreated soil samples from the study sites were fortified with a known mass of Br to test the Br extraction process and measurement procedure. Duplicate soil and lysimeter reservoir solution samples from the field plots also were analyzed for consistency of Br measurement. In addition, periodic measurement of Br standards was conducted during the soil and lysimeter solution analyses to assess the Br ion-selective electrode transducer for performance stability. Results from all these analyses were within control limits specified in the Br protocol METH007.00 (Pinera-Pasquino, 2008).

Data Analysis and Model Simulations

Two approaches were used to aid in interpretation of the results. One was a statistical comparison of each chemical's soil distribution between the lysimeter-confined and unconfined soil cores. The other approach was use of a computer model to simulate chemical movement in lysimeter-confined and unconfined soil and residue mass accumulation in lysimeter reservoirs. A strength of the modeling approach was that it could provide a physical explanation for differences in chemical distribution between the lysimeter-confined and unconfined soil.

Statistical approach

A generalized linear mixed model was used to statistically test each study site or irrigation level for lysimeter effects on total recovered Br and pesticide mass and distribution of mass in the soil. The SAS software procedure PROC MIXED (Littell et.al., 2006) allowed for modeling the lysimeter and soil depth effects as fixed effects and the soil cores as the random effect. The soil cores were treated as a random effect because their location was arbitrary with respect to the study design and the results would then be relevant to locations other than just the study sites. Configuration of the study design necessitated a repeated measures component in the mixed model. Repeated measures analyses are more commonly associated with correlated measurements on a subject over time, but also can be applicable to spatial measurements where data from adjacent spaces are correlated. For example, autocorrelation would exist if the recovery of residue mass between adjacent depths was more comparable than between non-adjacent depths. Such correlations were evident in this study as residue distribution patterns with respect to soil depth were apparent.

For each of the chemicals used in the study several covariance models were tested with the mixed model to account for this autocorrelation. Littell et al. (2006) stated that selection of an appropriate covariance model is important for deriving accurate conclusions from the covariance structure of repeated measures data, and listed several consequences for using inappropriately simplistic or complex covariance models. In this study the covariance models tested ranged from the simplest independent covariance structure where within-soil-core errors for each pair of adjacent soil depths assumed no correlated structure to the most complex unstructured covariance model where each pair of soil depths had their own unique correlation. Other intermediary-complex models tested included compound symmetry-, autoregressive-, heterogeneous autoregressive- and heterogeneous compound symmetry-assumed structures between adjacent soil depths. The covariance fit statistic given by SAS included -2 times the Residual Log Likelihood (-2 Res Log Like) and three information criteria, namely, Akaike Information Criterion (AIC), a finite-population corrected AIC (AICC) and the Bayesian

Information Criterion (BIC). Littell et al. (2006) recommended that information criteria be used to select the appropriate covariance structure, which corrects for biases related to the -2 Res Log Like fit statistic. They acknowledged studies by others noting the advantages and disadvantages of the various information criteria when used for selecting covariance models. However, in this study all three information criteria returned almost identical fit statistics. Therefore, for illustrative purposes, AIC was chosen to identify the most appropriate fitting covariance structure.

Finally, for actual covariance model selection a Chi-squared (χ^2) test evaluated for significant differences between AIC of competing covariance models. Procedures followed those by Williams et al. (2003) where the χ^2 test statistic was derived as the difference between AIC values for each pair of covariance models. The test statistic was then compared against a χ^2 distribution table for significant differences with the degrees of freedom equal to the difference in the number of fit parameters between the pair of covariance models (Williams et al., 2003). Where differences between AIC were not significant ($P > 0.05$) the simpler covariance model was selected, which related to that model with fewer fit parameters.

Results from the statistical approach will determine if the presence of lysimeters significantly influenced the movement and distribution of chemical residues in the soil. As mentioned previously, Kasteel et al. (2010) indicated that the interface of the lysimeter structure and the confined soil, or its installation procedure, may cause the development of preferential flow pathways within the soil. Development of such pathways diminishes the usefulness of lysimeters in evaluating the relative movement potential of chemicals. In this study, statistical results indicating enhanced movement of chemical residues in lysimeter-confined compared to unconfined soil would intuitively suggest the presence of preferential flow pathways. In addition, little or no differentiation in movement within lysimeters between chemicals of dissimilar soil adsorption capacities would suggest also the existence of preferential flow within the units, as was observed and hypothesized in the study by Kasteel et al. (2010). Conversely, statistical results indicating the restricted movement of chemicals within lysimeter-confined compared to unconfined soil would be evidence of saturated lower boundary conditions as a result of drainage impediment due to capillary discontinuity of the soil at the base of the units. The existence of this condition could be substantiated by observing a saturated lower boundary condition at the base of the lysimeters during soil coring and/or by the modeling optimization process whereby a positive pressure head would be predicted for the lysimeter seepage face.

Modeling approach

HYDRUS-1D (Simunek et.al., 2008) was used to model the fate and transport of chemical residues in the soil. This model simulates variably-saturated flow in soil with the Richard's equation and solute transport in the liquid phase using advection-dispersion equations. HYDRUS-1D also provides the ability to simulate specialized boundary conditions such as saturated conditions encountered at the base of discontinuous soil columns – a feature likely to exist in zero-tension column lysimeters. An important requirement for conducting HYDRUS-1D simulations is establishment of the relationship between soil volumetric water content and soil water potential. This relationship is described by several models including that by Brooks and Corey (1964) and can be implemented in HYDRUS-1D once the model parameter values are provided. The SAS software procedure PROC OPTMODEL allowed for fitting of the Brooks and Corey model to the soil water retention curves that were experimentally derived using the ring-confined soil-core-samples and pressure plates previously mentioned. This approach of experimentally establishing the soil water retention curves was preferred to the alternative approach of relying on HYDRUS-generated curves from pedotransfer functions because the latter has been reported to produce variable results depending on the particular function used, especially at high soil moisture contents (Nemes and Rawls, 2004).

Other necessary parameter values required for HYDRUS-1D simulations that could not be physically measured in this study were tortuosity in the hydraulic conductivity function, longitudinal dispersivity for solute transport, chemical-specific soil adsorption isotherm coefficients (Kd) and first-order rate constants (k). Pressure head at the lysimeter seepage face also is an important parameter if saturated conditions should exist in the base of the lysimeters in spite of measures taken in this study to minimize this effect. Model-Independent Parameter Estimation (PEST) software (Doherty, J., 1998) established the above parameter values utilizing optimization procedures in order to calibrate the HYDRUS-1D model to the study site and simulate fate and transport of the pesticides. PEST's optimization procedure minimized the 'objective function', which in this case was the weighted sum of squared errors (SSEs) between the various field-measured data and those corresponding data predicted by HYDRUS-1D simulations.

When calibrating models for pesticide transport in soil, general consensus is first to calibrate model hydrology to the experimental site and then optimize the solute transport components of the model (Debus et.al., 2002). The authors maintained that model parameters calibrated against soil hydrology should generally be left unchanged during model optimization against measured pesticide data. Therefore, the optimization process in this current study proceeded in two phases.

In the first modeling phase, PEST optimized simultaneously for the hydraulic parameters of tortuosity, longitudinal dispersivity and pressure head at the seepage face of the lysimeters while HYDRUS-1D was sequentially simulating the low and high water application regimes. The objective function was the minimum SSEs between model-simulated and field-measured Br

mass in the lysimeter-confined and unconfined soil sub-cores collected at the end of the field study, and cumulative mass of Br and cumulative depth of solution extracted from lysimeter reservoirs throughout the whole field study. Weighting of the SSEs was applied accordingly to compensate for the large differences in the magnitude of measurement values between the residue mass (mg) and cumulative solution depth (cm) data. Br is a conservative tracer for water; therefore, the chemical-specific parameters of Kd and k were set appropriately to zero.

In the second modeling phase, PEST simultaneously optimized Kd and k for each individual pesticide using the soil hydraulic-related parameter values established during the first optimization phase for Br. The objective function here was the minimum SSEs between model-simulated and field-measured mass of each pesticide in the lysimeter-confined and unconfined soil sub-cores collected at the end of the field study and cumulative total mass extracted from the lysimeter reservoirs throughout the whole field study.

HYDRUS-1D also supports capabilities to simulate a sequential degradation reaction chain of pesticides coupled to their breakdown products. A reaction chain was simulated in HYDRUS-1D to simultaneously establish values for Kd and k of DSMN – the breakdown product of norflurazon. A triple-chemical reaction chain also was simulated to simultaneously establish values for Kd and k of ACET – the breakdown product of simazine, and then of DACT – the breakdown product of ACET.

These data were used to evaluate the ability of the HYDRUS-1D model to simulate the fate and movement of residues both within lysimeters and in the unconfined, natural soil environment. Graphical comparisons contrasted differences between field-recovered residues from soil and lysimeter reservoirs to model-simulated output for the various chemicals under two contrasting levels of water inputs. Differences between field-measured and simulated output also was statistically quantified using the root mean square error (RMSE).

RESULTS AND DISCUSSION

Soil Characterization

The study site soil-type was identified as moderately coarse-textured soil where sand was predominant, and bordering closely between a USDA defined fine sandy loam and loamy sand classification (Table 1). Soil analysis revealed the texture to be comparatively consistent in composition with depth. Organic carbon content was relatively low, transitioning from 0.39% at

the surface to 0.06% at the 90-cm depth (Table 1). This soil type was considered suitable to meet the objectives of this study as coarse-textured soils low in organic carbon are conducive to movement of water and pesticides (Troiano et.al., 1993). Soil bulk density was lower at the surface compared to the deeper soil layers and measurements were relatively consistent between replications as evident by the low coefficients of variability (Table 2). Fractional volumetric soil moisture content (Theta [θ]) one day prior to chemical application to the plots was consistent with depth, ranging between 0.23 and 0.25 $cm^3\ cm^{-3}$ (Table 2). Theta at saturation, a parameter required for modeling purposes, also was relatively consistent with depth (Table 2).

Saturated soil hydraulic conductivity of each soil layer was measured from four replicate soil cores (Table 3). However, one replicate from the surface soil layer was removed from the analysis as an outlier because its value was exceedingly large compared to values established for the other replicate samples. This sample also exceeded typical hydraulic conductivity values reported by others for this soil type (Rawls et.al., 1982). The median measurement for each soil layer was later utilized for modeling purposes.

Volumetric soil water content at several matric potentials was measured for each soil layer using the same soil samples from the four replicate soil cores used earlier for the saturated hydraulic conductivity measurements. Soil water retention curves were fit to these data (Figure 3) using the model by Brooks and Corey (1964):

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \begin{cases} |\alpha h|^{-n} & h < -1/\alpha \\ 1 & h \geq -1/\alpha \end{cases}$$

where:
- S_e - effective soil water content ($cm^3\ cm^{-3}$)
- θ - soil water content ($cm^3\ cm^{-3}$)
- θ_r - residual soil water content ($cm^3\ cm^{-3}$)
- θ_s - saturated soil water content ($cm^3\ cm^{-3}$)
- h - matric potential (cm)
- α - empirical parameter (cm)
- n - empirical parameter (-)

Estimation of the unknown parameter values for θ_r, α, and n required the derivation of a user-defined objective function for solution with the SAS procedure PROC OPTMODEL. The solution utilized an optimization process with the objective function expressed as the minimum

SSEs between the logs of laboratory-measured- and model-fitted-θ for ten corresponding soil matric potentials within each soil depth (Table 4):

$$obj\ fn\ = min \sum_{i=1}^{n} (log\ \theta_{Model_i} - log\ \theta_{Meas_i})^2$$

Solving for θ_{Model} by the SAS optimization procedure necessitated the rearrangement of the Brooks and Corey equation:

$$\theta_{Model} = (\theta_s - \theta_r)\ |\alpha h|^{-n} + \theta_r$$

Estimates for θ_r, α, and *n* were specific to each soil depth (Table 5), and resulted in an acceptable fit of the Brooks and Corey model to the measured data as evident by visual agreement and the relatively small RMSEs (Figure 3).

The hydraulic conductivity function associated with the Brooks and Corey model contains the tortuosity parameter and its value was later established by optimization procedures in PEST during HYDRUS-1D simulations:

$$K = K_s\ S_e^{\frac{2}{n} + l + 2}$$

where: K - hydraulic conductivity (cm d^{-1})
K_s - saturated hydraulic conductivity (cm d^{-1})
l - tortuosity (-)

Water Application and Measured Drainage

Water was applied to the study sites (Figure 4) with the goal of creating an average depth of drainage solution in the lysimeter reservoirs of 4 mm and 20 mm per week for the light and heavy irrigated sites, respectively. However, rain events and irrigation equipment problems resulted in excess drainage amounts during some weeks. Attempts were made to offset the excess drainage by reducing irrigation applications in subsequent weeks. Irrigation to both sites was ceased 6 weeks after chemical application because of the onset of frequent rain events (Figure 4).

During the field study the depth of drainage solution extracted from the lysimeter reservoirs varied greatly between weeks (Figure 5). Eventually, drainage ceased 11 weeks after chemical application as rainfall intensity declined. However, within each week, drainage amounts were comparatively consistent between lysimeter replicates as evident by the relatively small standard errors (Figure 5). Average depth of weekly drainage extracted from the lysimeter reservoirs during the 11-week monitoring period was 8.7 mm and 20.2 mm in the light and heavy irrigation sites, respectively. Soil coring in the unconfined soil plots and within the lysimeters signified the conclusion of the field component of the study, occurring 16 and 19 weeks following chemical application to the light and heavy irrigated study sites, respectively. This extended period from the final drainage event at week 11 allowed for drying of the soil profile prior to soil coring.

Recovery of Chemical Residues from Lysimeter-confined and Unconfined Soil Plots

Quantification of chemical residues recovered at each sampled depth from lysimeter-confined and unconfined soil, and from lysimeter reservoir solution comprised of four replicate measurements for each chemical and study site (Appendix 3). Reporting of chemical recoveries in subsequent sections relates to the arithmetic mean of the replicates, and where applicable the standard error for the mean is given.

Bromide recovery

A mass balance was conducted for Br residues recovered from the study plots containing the lysimeters-confined soil. Total recovery was 91% and 104% of the theoretical Br application rate for the light and heavy irrigated study sites, respectively (Table 6). In the light irrigated site almost all the Br was recovered from soil whereas in the heavy irrigated site most was recovered from lysimeter reservoirs with the remainder recovered from soil. The balance from the total recoveries with respect to the application rate was the mass balance error of 9% and -4%, respectively (Table 6).

A complete mass balance for Br recovered from the unconfined soil plots was not possible because the movement of mass below the soil sampling depth could not be measured. However, the mass of Br recovery from the unconfined soil at either study site was a relatively small fraction of the application rate (Table 6), suggesting that the majority of Br applied to these plots leached below the soil sampling profile.

Pesticide recovery

Pesticide recovery from laboratory-spiked soil and solution was acceptable, being within the control limits of the analytical methodology. However, the pesticide recovery data from field-based samples could not be used to generate mass balances because the pesticides experienced degradation and this loss was not quantified by direct field measurement. Furthermore, pesticide degradation in the field was considerable as the combined mass of each pesticide recovered from the soil and reservoir solution of lysimeters plots was substantially less than its application rate (Table 7). Residue loss to volatilization was presumed negligible as the volatility potential for the pesticides was low, ranging from 0.003 mPa for simazine to 0.041 mPa for bromacil (median values from studies conducted at 20 - 25 C [DPR Pesticide Properties Database]).

Recovery of the individual pesticides varied between study sites and was likely related to their depth of movement in the soil. All but one chemical had considerably higher recoveries in lysimeter plots of the heavier-irrigated site where pesticide degradation must have been slower as a result of residue movement to greater soil depths. This result is consistent with several studies reporting that the degradation rate of pesticides decreases significantly with depth (Frank and Sirons, 1985; Johnson and Lavy, 1994; Kruger et al., 1993), often correlating with decreasing organic material (Kordel et al, 1995; Miller et al., 1997). However, for plots containing the unconfined soil, the recovery of some chemicals was substantially less in the heavy irrigated site compared to the light irrigated site. This finding almost certainly resulted from disproportionately greater losses of residues to leaching below the soil coring depth over the effects of reduced degradation rates at the heavy-irrigated site. Consistent with this hypothesis, the result was most substantial for those chemicals with the highest potential for soil mobility, namely bromacil, hexazinone and simazine, which have relatively low organic carbon normalized soil adsorption coefficient (Koc) values of 14, 45 and 152 $cm^3 g^{-1}$, respectively; and for Br, which likewise is highly mobile in soil. The result was observed to a lesser extent for diuron and not at all for norflurazon, both of which maintain higher Koc values of 482 and 413 $cm^3 g^{-1}$, respectively (median values [DPR Pesticide Properties Database]).

Effect of Lysimeter on Bromide and Pesticide Distribution in Soil

Figures 6 and 7 illustrate the respective distribution of Br and pesticides recovered from the soil profiles at both study sites. Movement of chemicals with respect to irrigation level occurred to greater soil depths in the more heavily irrigated site, which was consistent for both the lysimeter-confined and unconfined soil as evident by the locations of their center of recovered mass (Table 8). Depth to center of mass for each chemical was calculated as follows:

$$CoMx = \frac{\sum_{i=1}^{n} m_i x_i}{\sum_{i=1}^{n} m_i}$$

where: CoMx - depth to center of residue mass (cm)
m*i* - residue mass recovered from soil core segment *i* (ug cm^{-2})
x*i* - depth to the bottom of soil core segment *i* (cm)

For pesticides and degradates the summation upper-limit notation (*n*) was six – number of soil sampling depths; for Br, *n* was seven, which included also the lysimeter reservoir that was assigned a depth of 90 cm – same as the lowest soil sampling depth. Calculated depth to center of mass for Br included residues recovered from lysimeter reservoirs because, unlike for pesticides, a relatively large amount of Br was recovered from reservoirs of the heavy irrigated site. Br also was the only chemical that approximated a full residue recovery in the plots containing lysimeters. Therefore, Br losses from drainage below the soil profile in the unconfined soil plots, which could not be measured, were estimated by subtracting soil recovered residues from the Br application rate. This was not possible for pesticides in the unconfined soil plots because residue losses from drainage were not distinguishable from losses due to degradation.

Movement of Br, bromacil and hexazinone in both the light and heavy irrigated sites was retarded in lysimeter-confined soil compared to unconfined soil as their recovered residue distributions appeared more proportionally substantial in the higher soil layers of lysimeter plots (Figures 6 and 7). For these chemicals, this result also was evident by the locations of their center of recovered mass, which were calculated at shallower soil depths in the lysimeter-confined soil (Table 8). Lysimeter effects on soil residue movement was not as clearly apparent for the remaining chemicals, which exhibited less overall soil movement and where residues were recovered closer to the soil surface.

With the appropriate covariance structure, as determined by the AIC fit statistic (Table 9), lysimeter effects and lysimeter-with-depth interaction effects between lysimeter-confined and unconfined soil correspondingly tested for differences in total residue mass and the distribution of residue mass within soil cores. As observed in Figures 6 and 7, lysimeters did significantly ($P < 0.05$) retard the movement of Br, bromacil and hexazinone in the soil as indicated by the lysimeter-with-depth interaction effect in Table 10. Significantly higher total mass recoveries for these chemicals occurred also in lysimeter-confined soil of the heavy irrigated site, undoubtedly due to greater leaching of residues in the unconfined soil to below the soil sampling depth. However, compared to the unconfined soil, total residue recovery of bromacil ($P < 0.05$) and

hexazinone (P = 0.12) was lower in the lysimeter-confined soil of the light irrigated site, which as discussed previously was likely due to enhanced degradation because of their closer proximity to the soil surface and active biological zone. In contrast, Br residue recovery was higher in lysimeters of the light irrigated site, likely due to a combination of greater residue leaching in the unconfined soil to below the soil sampling depth and because Br was not susceptible to biological degradation, unlike bromacil and hexazinone.

Diuron and norflurazon experienced comparatively less soil movement with residues confined almost entirely to within 45 cm of the soil surface (Figure 7). The statistical analysis determined that lysimeters had no significant effect on the total mass or movement of these chemicals under either light or heavy irrigation regimes (Table 10).

For simazine, residue recovery at both study sites was mostly confined to near the soil surface, but some residue movement was observed to the lowest soil coring depths in the heavy irrigated site (Figure 7). Residues recovered from the soil surface of the unconfined soil were somewhat variable compared to the other chemicals as illustrated by simazine's large standard errors relative to mean recovered mass (Figure 7). As such, the large apparent difference in total recovered simazine between lysimeter-confined and unconfined soil (Table 7) was not statistically significant at either study site (Table 10). There was, however, a statistically significant interaction effect between lysimeter and soil depth for simazine, but only in the light irrigated site.

Statistical analyses were not conducted for lysimeter effects on the movement in soil of DSMN, ACET and DACT because such results would be coupled to movement effects from their parent chemicals and consequently would not be interpretable. However, it would appear that the pattern of soil residue distribution for these degradation products was similar to their parent compounds (Figure 7).

Modeling Bromide and Pesticide Distribution in Soil

The second main goal of this study was to evaluate the potential to simulate residue movement in lysimeter-confined soil and identify model parameter adjustments necessary to differentiate this movement from that in soil outside the confines of lysimeters. Rationale for this goal was to relate pesticide movement observed in lysimeters utilized in field studies conducted by DPR or submitted to DPR by registrants in support of their product registrations, to that in the natural, unconfined soil environment.

Simulation of Br in lysimeter-confined and unconfined soil for model calibration

Modeling pesticide fate and movement in this study required a two-step process. The first step involved calibration of the HYDRUS-1D model using the Br data. Soil hydrology-related parameters not previously characterized in this report by methods of experimentation or model fitting to experimental data, but required for model simulations were established by optimization procedures in HYDRUS-1D. These parameters included longitudinal dispersivity, tortuosity in the Brooks and Corey hydraulic conductivity equation, and pressure head at the lysimeter seepage face. Utilizing PEST as the control environment for HYDRUS-1D, optimization was achieved by simultaneous manipulation of these parameter values during successive automated simulations predicting Br mass distribution in soil, and cumulative Br mass and depth of drainage solution in lysimeter reservoirs whereby simulated predictions agreed most closely with field-measured data. The objective function for the optimization procedure was the minimum SSE between predicted and corresponding field-measured values. Single dispersivity and tortuosity estimates were universally applicable to all soil depths of the lysimeter-confined and unconfined soil at both study sites because they are correlated to soil texture and bulk density which were relatively homogeneous with depth throughout the soil profile (Tables 1 and 2) . The pressure head estimate at the lysimeter seepage face was only relevant to the lysimeter-confined soil and because it also is correlated to soil texture and bulk density, a single parameter value was applicable to both irrigated sites.

For laboratory studies utilizing packed soil columns, longitudinal dispersivity values are typically 0.5 – 2 cm (Jury and Horten, 2004). Since longitudinal dispersivity is dependent on measurement scale, intact soil columns in larger field studies are usually higher ranging from 5 – 20 cm (Radcliffe and Simunek, 2010). However, the relatively small-sized lysimeters used in this study could be analogous to laboratory packed soil columns, and considering that soil coring occurred to a depth of only 90 cm, an optimized longitudinal dispersivity value of 1.61 cm was consistent with literature-cited values. The 95% confidence limits around this estimate, established during the optimization procedure was relatively narrow (0.91 – 2.31 cm) providing additional confidence in the stability of the estimate.

Tortuosity is related to the connectivity of capillary tubes and soil pores and has been reported to be very sensitive to hydraulic conductivity estimates in the Brooks and Corey model (Assouline and Tartakovsky, 2001). Kawamoto et al. (2006) cited several studies with conflicting estimates for tortuosity in Campbell's hydraulic conductivity model. Others also have similarly cited sources with conflicting estimates for tortuosity, including estimates with both positive and negative signs, and commented that there is little consensus as to a suitable approximation for

this parameter (Simunek et al., 2008). The authors noted that optimization of tortuosity is useful for well-defined experimental data, such as those with multistep outflow and evaporation procedures, both of which were factors in this study. Therefore, for the purposes of this study, tortuosity in the Brooks and Corey model was treated as a 'fitting parameter' thereby providing an additional degree of freedom for model calibration purposes. The optimized tortuosity value and its relatively well confined 95% confidence limits were estimated at -3.00 (-) and -3.73 – -2.27 (-), respectively.

Seepage face pressure head is a phenomenon applicable to finite soil columns experiencing gravity drainage where the bottom boundary layer is exposed to the atmosphere. The condition assumes that the boundary flux will remain zero as long as the pressure head is negative or below the effect of capillary action. This type of boundary condition is often applicable to laboratory soil columns, but can occur also in field-based column lysimeters experiencing gravity drainage (Simunek et al., 2008). Physical measurement of seepage face pressure head was not feasible in this study because priority was given to maintaining undisturbed soil conditions within the lysimeters. Optimization procedures provided a seepage face pressure head estimate of 7.95 cm with 95% confidence limits of 6.07 – 9.84 cm. This estimate was consistent with the depth of saturated soil conditions observed in the base of the lysimeters during soil coring at completion of the field study, despite cessation of water applications several weeks prior. In contrast to the lysimeter-confined soil, the entire soil profile in the unconfined soil appeared relatively dry during soil coring.

Simultaneous optimization of multiple parameter values, as was described above can be problematic particularly if the parameters are correlated. Under these circumstances, pairs or groupings of parameter estimates may fluctuate in unison during the optimization process leading to unrealistic values despite the process achieving a satisfactory objective function. However, dependability in the three parameter values optimized in this study was supported by their relatively narrow 95% confidence limits, consistency with values reported in the literature or conditions observed in the field, and lack of any substantial correlation in PEST's correlation coefficient matrix (Table 11). Therefore, the HYDRUS-1D model was considered satisfactorily calibrated based on these data and the visual agreement between the simulated fit with field measurements for Br mass in the lysimeter-confined and unconfined soil, and cumulative Br mass and depth of solution in lysimeter reservoirs (Figure 8). Agreement between the simulations and field measurements also was statistically supported by the relatively small RMSEs, which were approximately an order of magnitude or more below the range of their corresponding Br concentrations (Figure 8).

Simulation of pesticides and degradates in lysimeter-confined and unconfined soil

Development of the calibrated HYDRUS-1D input files (Appendix 4) provided the basis for the final two-step modeling process of simulating the fate and movement of pesticides and degradates in lysimeter-confined and unconfined soil.

Chemical-specific parameters required for modeling the pesticides and degradates in HYDRUS-1D included molecular diffusion coefficients in air and water, Henry's law constant, soil adsorption isotherm coefficients and first-order rate constants for dissolved, solid and gas phases. The molecular diffusion coefficients and Henry's law constants were obtained from physiochemical databases (Table 12). Chemical-specific values for soil adsorption isotherm coefficients and first-order rate constants are generally more variable than those of molecular diffusion coefficients and Henry's law constant because the former are association with soil; rate constants also may be influenced by changing climatic conditions if derived from field studies. In general, median coefficients of variation for soil adsorption coefficients and rate constants or half-lives have been reported for most pesticides to approximate 0.50 or greater (Spurlock, 2008). Therefore, parameterization of these physiochemical properties by optimization in PEST would provide estimates related more to the soil type and climatic conditions of the study location.

Physiochemical databases do not typically contain data discriminating between rate constants for pesticides in the dissolved, solid and gas phases. More often, reported rate constants are representative of the collective or simultaneous dissipation of residues in all three phases. Consistent with the reporting of these data, and to avoid potential issues with 'over parameterizing' the optimization process, the rate constants for each chemical required by HYDRUS-1D for the dissolved, solid and gas phases were optimized as a single lumped parameter. For each pesticide, attempts were made to optimize depth-specific rate constants for the six soil depths sampled in this study. However, the optimized rate constants were highly variable between adjacent soil depths, often transitioning between extreme nonsensical values. The PEST-generated correlation coefficient matrix revealed high correlations between many of these rate constants (data not shown), thereby accounting for their instability. The optimization process was therefore configured to return only a single, pesticide-specific lumped rate constant for the entire soil column.

The PEST optimization process was then configured to simultaneously parameterize a pesticide-specific adsorption isotherm coefficient for each specific soil segment depth where chemical residues were found. For example, residue movement for bromacil, hexazinone and simazine was to the full soil coring depth. Therefore, for each of these pesticides the optimization process

parameterized seven variables – a single lumped rate constant for the entire soil profile and a unique adsorption isotherm coefficient for each of the six soil depths (Table 13). For each pesticide, the six optimized depth-specific adsorption isotherm coefficients were reasonably consistent between adjacent soil depths, maintained relatively narrow confidence limits and were largely uncorrelated (Appendix 5), indicating stability in their estimation. In the case of diuron and norflurazon where residues were maintained predominantly in the upper soil layer, only two variables were parameterized for each pesticide – a single lumped rate constant and a single adsorption isotherm coefficient, each of which was applied to the entire soil column (Table 13).

Overall confidence in the PEST-optimized rate constants and adsorption isotherm coefficients was supported by their general agreement with median values reported from DPR's Pesticide Chemistry Database (Table 14), despite the potential magnitude in variability expected of such reported values (Spurlock, 2008). Also, as mentioned previously, the 95% confidence limits around the parameter estimates, and coefficients from PEST's correlation matrix were, overall, within an acceptable range as to provide additional confidence in the optimized estimates (Appendix 5).

HYDRUS-1D supports capabilities to simulate transformation reaction chains, synchronizing the decay and formation of parent compounds to their breakdown products. In this study, two separate transformation reaction chains were established in HYDRUS-1D:

1) Norflurazon → DSMN.
2) Simazine → ACET → DACT.

The process first involved establishing, by optimization in PEST, the rate constant and soil adsorption isotherm coefficients for each parent pesticide as described previously. The PEST optimization process was then assigned to the reaction chain whereby the rate constant and adsorption isotherm coefficients were parameterized for the degradate. For simazine, parameterization of the second sequential degradate DACT occurred after initially establishing parameter estimates for ACET. This stepwise process was preferable to parameterizing the parent and degradates simultaneously as optimization of an inordinate number of parameters would undoubtedly be problematic. Despite using the stepwise procedure, and in contrast to DSMN, the optimization process was not successful for ACET and DACT. Soil adsorption isotherm coefficient estimates for these degradates varied by orders of magnitude between adjacent depths with some estimates appearing nonsensical (Appendix 5). Furthermore, many of the 95% confidence intervals around these estimates were the largest computed for any chemical; and reasonably strong correlations, some in excess of 0.7 existed between several adjacent parameters estimates in PEST's correlation coefficient matrix output (Appendix 5). Thus, the

optimized parameter estimates for ACET and DACT lacked stability and were considered unreliable (Table 13).

Overall, pesticide simulation results compared favorably to the field recovered residues for almost all chemicals, attesting to the general success of the optimization procedure and potential to simulate pesticide fate and movement within lysimeter-confined and unconfined soil under variable levels of water input (Figure 9). However, the model fit to field recoveries of simazine in the light irrigated site was relatively poor and asserted the largest RMSEs relative to the mass of residues recovered. This was almost certainly related to the large discrepancy in field-recovered simazine between the lysimeter-confined and unconfined soil plots (Figure 7). In contrast, diuron, norflurazon and DSMN, each of which also maintained residues predominantly in the soil surface layer had comparable residue recoveries between lysimeter-confined and unconfined soil. This inconsistency for simazine suggests the presence of a sampling-related or residue analysis artifact, particularly since the magnitude of this discrepancy was not imparted to the field recoveries of the simazine degradates ACET and DACT (Figure 7). Since the modeling of degradates in HYDRUS-1D requires a synchronized reaction chain linked to the parent pesticide the unstable parameterization of ACET and DACT was possibly related to the poor simulated fit to field-recovered simazine, particularly in the light irrigated study site.

CONCLUSIONS

For diuron, norflurazon and simazine there was no significant difference in their residue movement in soil between lysimeter-confined and unconfined soil. These pesticides maintained the highest soil adsorption capacity of all six chemicals used in this study and subsequently their residues were largely confined to the upper soil layers. The design, installation process, and functionality of the lysimeters, therefore, did not significantly affect the characteristics of their confined soil with respect to chemical movement in the upper regions of the units. However, for Br, bromacil and hexazinone where some proportion of their mass encountered the base of the lysimeters, downward residue movement in lysimeter-confined soil significantly lagged behind those same residues in the unconfined soil, indicating that lysimeters did impact the soil or hydrological conditions at the base of the units. Despite this condition, the unique movement characteristics observed in lysimeters for the various chemicals used in this study suggests that these devices could be used to access the relative leaching potential between two or more pesticides.

Results from this study contradict some reports suggesting the existence of preferential flow pathways in soil confined within lysimeters as it was demonstrated that residue movement was either unaffected or actually retarded in lysimeter-confined soil compared to unconfined soil. The soil type in this present study was unstructured and coarse-textured and therefore not conducive to the development of cracks and fissures during wetting and drying cycles, which for some soil types has otherwise been speculated to occur at the interface of the soil and lysimeter wall leading to development of preferential flow pathways (Kasteel et al., 2010). However, our study did confirm the existence of a saturated lower boundary condition in the base of the lysimeters. This condition was observed inside the units during soil coring and predicted by computer modeling when optimization procedures quantified a seepage face pressure head at the base of the lysimeter-confined soil core.

In this study the HYDRUS-1D model successfully simulated the fate and transport of five pesticides, three degradates and a solute tracer, each with unique soil adsorption and degradation characteristics, in lysimeter-confined and unconfined soil under combinations of light and heavy water inputs. More notably, simulating residue fate and transport in lysimeter-confined soil compared to the unconfined soil required no special adjustments to existing model input parameter values such as degradation rate constants or adsorption isotherm coefficients. The process only necessitated changing the soil core lower boundary condition from 'free draining' – used for an unconfined soil core in the natural soil environment, to a 'seepage face' with the appropriate pressure head for a lysimeter-confined soil core with an atmospheric interface at its base.

The successful simulations of several chemicals in both lysimeter-confined and unconfined soil under diverse modeling scenarios with minimal use of specialized modeling parameters attests to the functionality of lysimeters for future studies in coarse textured, leaching vulnerable soils. This study indicated also that the fate and movement of pesticides measured in the drainage solution and confined soil of lysimeters can potentially be extrapolated to the natural or unconfined soil environment using HYDRUS-1D computer simulations.

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TABLES

Table 1. Measurements of mean (n=4) and coefficient of variation (CV) for sand, silt, clay, and organic carbon content of soil. Textural classification corresponds to mean values for the texture constituents.

Soil depth (cm)	Sand (%)	CV (%)	Silt (%)	CV (%)	Clay (%)	CV (%)	Textural classification[Z]	Organic Carbon (%)	CV (%)
0-15	71.3	2	24.6	4	4.1	13	Sandy loam	0.39	55
15-30	71.4	2	24.4	6	4.3	11	Sandy loam	0.13	22
30-45	73.2	6	23.0	18	3.7	12	Sandy loam	0.09	18
45-60	74.1	7	22.5	21	3.4	12	Loamy sand	0.07	15
60-75	74.2	7	22.2	24	3.6	13	Loamy sand	0.07	25
75-90	74.8	7	22.0	23	3.2	12	Loamy sand	0.06	24

[Z] Classification according to USDA Natural Resources Conservation Service, Soil texture calculator: <http://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey/?cid=nrcs142p2_054167>.

Table 2. Measurements of mean (n=4) and coefficient of variation (CV) for soil bulk density, and soil moisture content one day prior to chemical application (initial) and at saturation.

Soil depth (cm)	Bulk density ($g\ cm^{-3}$)	CV (%)	θ Initial ($cm^3\ cm^{-3}$)	CV (%)	θ Saturation ($cm^3\ cm^{-3}$)	CV (%)
0-15	1.64	4	0.23	8	0.39	7
15-30	1.73	3	0.23	5	0.37	5
30-45	1.77	2	0.25	8	0.39	3
45-60	1.76	3	0.25	8	0.39	4
60-75	1.78	2	0.23	7	0.39	2
75-90	1.77	3	0.23	8	0.40	3

Table 3. Measurements of soil hydraulic conductivity (cm d^{-1}) at saturation.

Soil depth (cm)	Core 1	Core 2	Core 3	Core 4	Median
0-15	106.0[Z]	56.1	10.9	11.8	11.8
15-30	12.9	54.1	8.5	5.0	10.7
30-45	13.4	28.1	11.9	3.1	13.0
45-60	8.3	30.5	17.0	9.0	18.9
60-75	13.0	34.6	24.8	8.3	15.6
75-90	13.3	47.5	17.9	11.0	13.8

[Z] Value considered an outlier and excluded from hydraulic conductivity median.

Table 4. Measurements of mean soil water retention (θ) at several matric potentials.

Matric potential (kPa) / Soil depth (cm)	-3.2	-5.2	-7.1	-10.1	-20.2	-40.2	-80	-120	-160	-232
0-15	0.348	0.323	0.285	0.248	0.180	0.135	0.101	0.096	0.086	0.073
15-30	0.336	0.316	0.285	0.250	0.182	0.139	0.104	0.094	0.085	0.073
30-45	0.356	0.336	0.300	0.268	0.196	0.142	0.098	0.088	0.080	0.065
45-60	0.352	0.331	0.309	0.274	0.189	0.131	0.089	0.080	0.072	0.061
60-75	0.347	0.323	0.298	0.262	0.184	0.128	0.087	0.082	0.074	0.062
75-90	0.353	0.328	0.312	0.274	0.186	0.124	0.082	0.077	0.066	0.057

Table 5. Estimates of the Brooks and Corey soil hydraulic parameters by fitting of their model to measured soil water retention data.

Soil depth (cm)	α (cm)	*n* (-)	θ_r (cm^3 cm^{-3})
0-15	0.344	0.409	9.72e-03
15-30	0.309	0.377	2.05e-05
30-45	0.295	0.419	1.19e-05
45-60	0.281	0.445	1.09e-08
60-75	0.306	0.434	6.47e-06
75-90	0.285	0.467	1.17e-08

Table 6. Mass balance (mg cm^{-2}) for Br recovered from lysimeter-confined and unconfined soil and lysimeter reservoirs at each study site. Br leached below the soil sampling profile in the unconfined soil plots could not be measured.

	Light irrigated site		Heavy irrigated site	
	Unconfined soil	Lysimeter-confined soil	Unconfined soil	Lysimeter-confined soil
Application rate	1.00	1.00	1.00	1.00
Soil recovery	0.33	0.90	0.07	0.50
Lysimeter reservoir recovery	NA[Z]	0.01	NA	0.54
Total recovery	0.33	0.91	0.07	1.04
Mass balance error	NA	0.09	NA	-0.04

[Z] Not applicable (NA).

Table 7. Mass (ug cm^{-2}) of pesticides and degradates recovered from lysimeter-confined and unconfined soil and lysimeter reservoirs at each study site. Application rate for all pesticides was 33.682 ug cm^{-2}.

Chemical	Light irrigated site			Heavy irrigated site		
	Unconfined soil	Lysimeter-confined soil		Unconfined soil	Lysimeter-confined soil	
	Soil	Soil	Reservoir	Soil	Soil	Reservoir
Bromacil	25.612	12.135	0.000	4.339	17.380	1.961
Hexazinone	15.275	7.531	0.000	1.001	12.473	1.755
Diuron	17.138	12.669	0.000	14.648	9.992	0.000
Norflurazon	15.840	9.840	0.000	17.304	14.975	0.000
Simazine	13.111	1.922	0.000	8.106	2.538	0.001
DSMN	3.459	2.124	0.000	3.313	3.150	0.000
ACET	1.302	0.750	0.000	3.314	1.756	0.001
DACT	1.152	0.488	0.000	0.680	0.753	0.000

Table 8. Soil depth (cm) from surface to center of mass for Br, pesticides and degradates recovered from lysimeter-confined and unconfined soil.

Chemical	Unconfined soil		Lysimeter-confined soil	
	Light irrigated site	Heavy irrigated site	Light irrigated site	Heavy irrigated site
Bromide	81.7	87.3	51.4	83.0
Bromacil	44.8	64.0	25.9	55.2
Hexazinone	55.1	85.1	30.7	65.8
Diuron	15.6	18.8	16.3	19.1
Norflurazon	15.6	20.9	16.4	19.7
Simazine	16.6	40.0	16.1	38.9
DSMN	15.4	19.1	15.6	17.2
ACET	21.9	49.5	20.0	37.9
DACT	20.7	25.3	15.0	21.2

Table 9. AIC fit statistics generated for Br and the pesticides. Model selection for each chemical and irrigated site was determined from the smallest significant AIC value, which is denoted in bold. Where differences between AIC were insignificant the simplest model having the least parameters was selected.

Covariance model structure	Model parameters	Light irrigated site AIC	Heavy irrigated site AIC
---------- Bromide ----------			
Independent	2	389.1	316.3
Compound symmetry (CS)	3	391.1	315.4
Autoregressive (AR)	3	**380.1**	313.0
Heterogeneous AR	8	NR[Z]	**280.6**
Heterogeneous CS	8	384.0	NR
Unstructured	22	521.8	NR
---------- Bromacil ----------			
Independent	2	165.2	106.7
Compound symmetry (CS)	3	167.2	110.4
Autoregressive (AR)	3	**152.2**	95.0
Heterogeneous AR	8	146.0	**78.4**
Heterogeneous CS	8	163.5	NR
Unstructured		NR	NR
---------- Hexazinone ----------			
Independent	2	155.2	85
Compound symmetry (CS)	3	157.2	87
Autoregressive (AR)	3	**145.2**	**66.8**
Heterogeneous AR	8	145.2	60.9

Heterogeneous CS	8	159.7	75.8
Unstructured		NR	NR
---------- Diuron ----------			
Independent	2	**135.6**	90.4
Compound symmetry (CS)	3	139.6	92.4
Autoregressive (AR)	3	139.6	92.4
Heterogeneous AR		NR	NR
Heterogeneous CS	5	NR	**65.2**
Unstructured		NR	NR
---------- Norflurazon ----------			
Independent	2	**117.6**	123.5
Compound symmetry (CS)	3	121.6	125.5
Autoregressive (AR)	3	119.6	124.3
Heterogeneous AR	7	NR	**49.1**
Heterogeneous CS	7	NR	49.2
Unstructured		NR	NR
---------- Simazine ----------			
Independent	2	142.6	**127.0**
Compound symmetry (CS)	3	144.6	129.0
Autoregressive (AR)	3	144.6	129.0
Heterogeneous AR		NR	NR
Heterogeneous CS		NR	NR
Unstructured	11	**35.6**	NR

[z] No result returned – could not be computed.

Table 10. Repeated measures, mixed model test results for lysimeter effects, soil depth effects, and lysimeter with soil depth interaction effects with respect to Br and pesticides recovered from the soil of the light and heavy irrigated sites.

Effect	Numerator degrees of freedom	Denominator degrees of freedom	Light irrigated site		Heavy irrigated site	
			F value	*P* > F	F value	*P* > F
---------- Bromide ----------						
Soil depth	5	30	2.60	*0.045*	15.16	*<0.001*
Lysimeter	1	6	7.12	*0.037*	55.27	*<0.001*
Lysimeter x soil depth	5	30	5.03	*0.002*	17.55	*<0.001*
---------- Bromacil ----------						
Soil depth	5	30	7.08	*<0.001*	2.46	*0.055*
Lysimeter	1	6	6.95	*0.039*	27.60	*0.002*
Lysimeter x soil depth	5	30	6.79	*<0.001*	2.35	*0.065*
---------- Hexazinone ----------						
Soil depth	5	30	1.30	*0.289*	9.13	*<0.001*
Lysimeter	1	6	3.21	*0.124*	30.68	*0.002*
Lysimeter x soil depth	5	30	2.87	*0.031*	7.49	*<0.001*
---------- Diuron ----------						
Soil depth	2	12	8.09	*0.006*	45.00	*<0.001*
Lysimeter	1	6	0.22	*0.659*	2.05	*0.203*
Lysimeter x soil depth	2	12	0.25	*0.781*	1.32	*0.303*
---------- Norflurazon ----------						
Soil depth	2 / 4[Z]	12 / 24	16.47	*<0.001*	24.24	*<0.001*
Lysimeter	1	6	1.06	*0.343*	0.43	*0.539*
Lysimeter x soil depth	2 / 4	12 / 24	1.15	*0.349*	0.42	*0.793*
---------- Simazine ----------						
Soil depth	3 / 5	18 / 30	17.90	*<0.001*	4.60	*0.003*
Lysimeter	1	6	4.58	*0.076*	5.45	*0.058*
Lysimeter x soil depth	3 / 5	18 / 30	7.83	*0.002*	1.38	*0.260*

[Z] Degrees of freedom for some chemicals varied between irrigated sites due to differences in size of datasets between the sites. Successive numbers represent light and heavy irrigated sites, respectively.

Table 11. PEST-generated correlation coefficient matrix output for hydrological parameters optimized during HYDRUS-1D simulations of Br.

Optimized parameter	Longitudinal dispersivity (cm)	Seepage face pressure head (cm)
Tortuosity (-)	-0.070	0.007
Longitudinal dispersivity (cm)		0.238

Table 12. Database sourced chemical-specific parameter values used for HYDRUS-1D modeling of pesticides and degradates.

Chemical	Molecular diffusion coefficient in air ($cm^2\ d^{-1}$) [Z]	Molecular diffusion coefficient in water ($cm^2\ d^{-1}$) [Z]	Henry's constant (-) [Y]
Bromacil	4692	0.50	5.39e-09
Hexazinone	4390	0.44	8.30e-11
Diuron	4667	0.46	2.06e-08
Norflurazon	4234	0.40	1.42e-08
Simazine	4234	0.55	1.30e-08
DSMN [X]	4234	0.55	1.42e-08
ACET [X]	4234	0.55	1.30e-08
DACT [X]	4234	0.55	1.30e-08

[Z] Source – GSI Environmental chemical database. Available at: http://www.gsi-net.com/en/publications/gsi-chemical-database.html (Verified August 12, 2015).

[Y] Source - University of Hertfordshire (2013).

[X] Physiochemical information not available – parent value substituted for degradate.

Table 13. Pest-optimized chemical-specific parameter values used for HYDRUS-1D modeling of pesticides and degradates.

Chemical	Lumped first-order rate constant (d^{-1})	Adsorption isotherm coefficient ($cm^3\ mg^{-1}$)					
		---------- Soil depth (cm) ----------					
		15	30	45	60	75	90
Bromacil	5.54e-3	1.31e-4	4.67e-5	4.33e-5	4.88e-5	4.09e-5	2.75e-5
Hexazinone	9.05e-3	6.46e-5	3.49e-5	2.59e-5	1.85e-5	6.81e-5	4.75e-5
Diuron	7.65e-3	1.30e-3	1.30e-3	1.30e-3	1.30e-3	1.30e-3	1.30e-3
Norflurazon	7.65e-3	1.51e-3	1.51e-3	1.51e-3	1.51e-3	1.51e-3	1.51e-3
Simazine	1.34e-2	6.43e-4	2.20e-5	1.01e-4	1.76e-4	2.73e-4	1.76e-3
DSMN	4.23e-2	2.65e-4	2.65e-4	2.65e-4	2.65e-4	2.65e-4	2.65e-4
ACET	U[Z]	U	U	U	U	U	U
DACT	U	U	U	U	U	U	U

[Z] Optimized values were considered unreliable (U).

Table 14. Comparison of PEST-optimized chemical-specific parameter values with median values from DPR's Pesticide Chemistry Database.

Chemical	Degradation half-life (days)		KOC (cm^3 g^{-1})	
	Optimized[Z]	DPR Pestchem Database	Optimized[Y]	DPR Pestchem Database
Bromacil	125	146	29	14
Hexazinone	77	138	29	45
Diuron	91	114	157	482
Norflurazon	91	180	182	413
Simazine	52	83	114	152

[Z] Half-lives calculated from PEST-optimized rate constants using $t_{0.5} = \ln(2) / k$.

[Y] PEST-optimized adsorption isotherm coefficients were normalized for soil organic carbon content (KOC) and averaged across the soil profile depth.

FIGURES

Figure 1. Randomized layout of lysimeter-confined and unconfined soil plots and configuration of irrigation sprinklers.

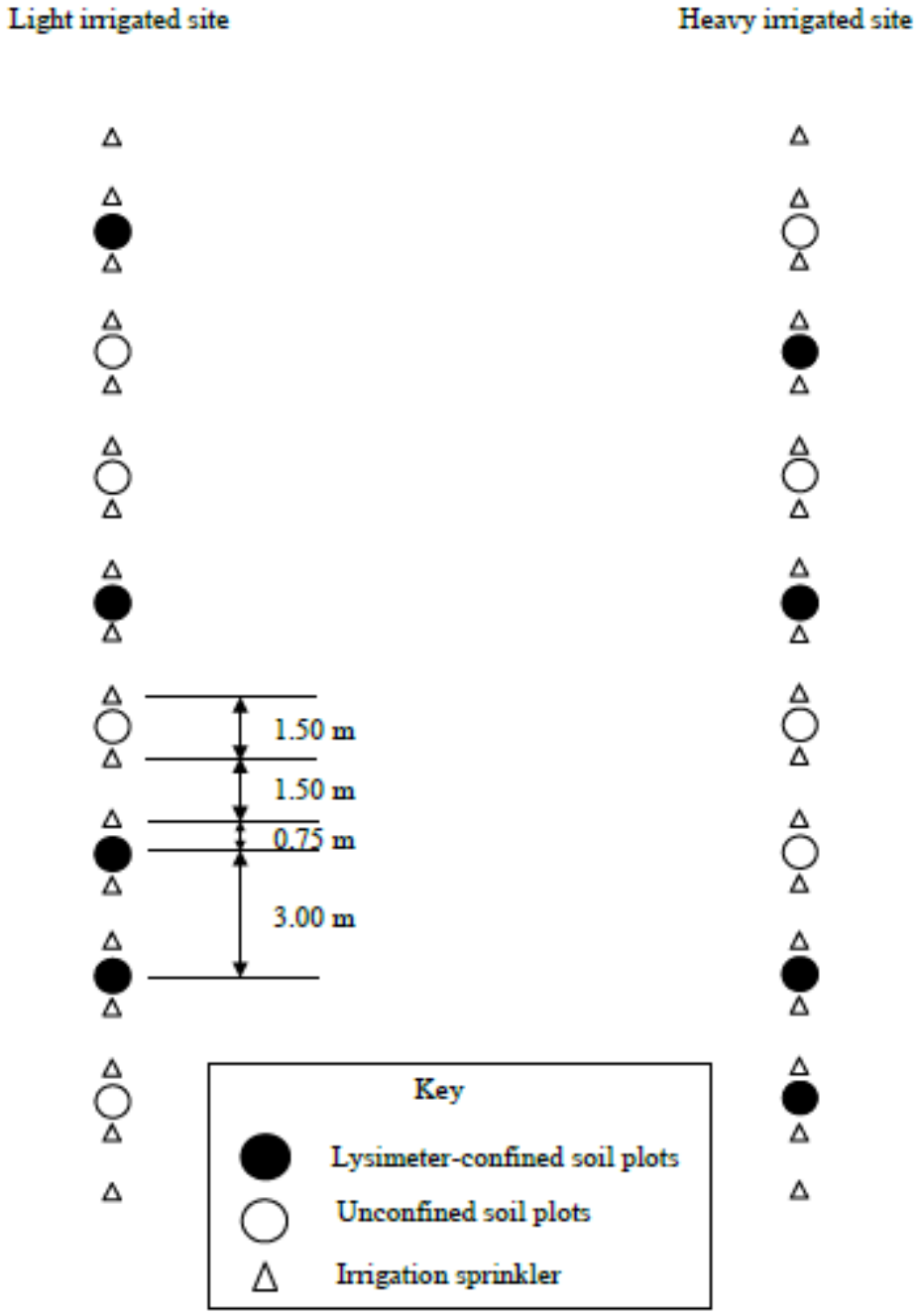


Figure 2. Measured and theoretical pesticide concentrations in chemigation solution during chemical application to the light and heavy irrigated study sites.

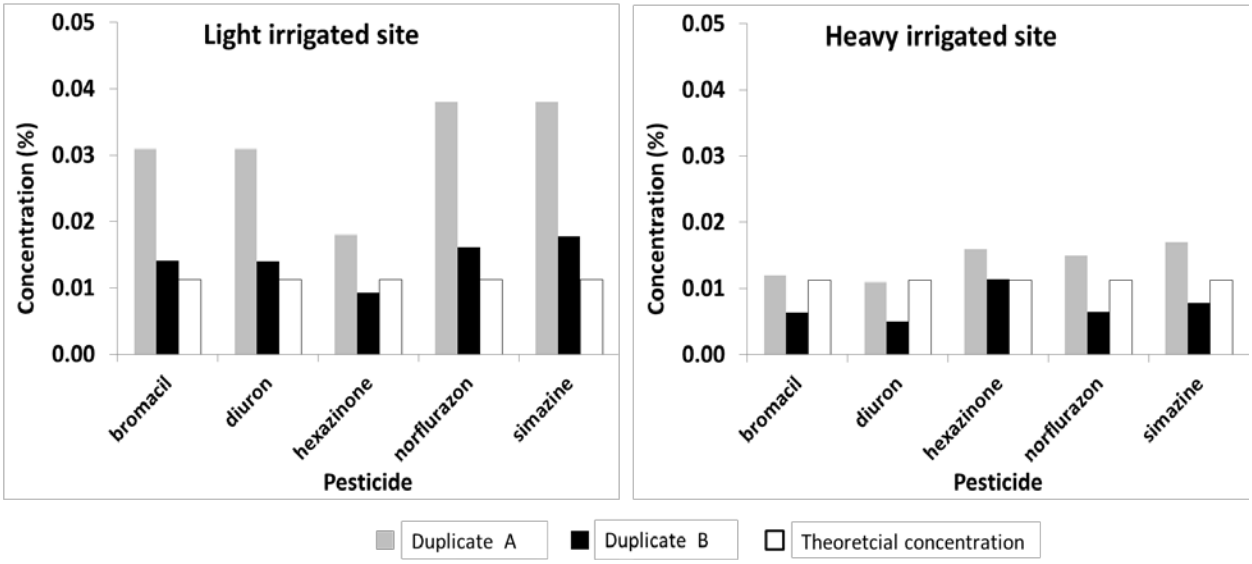


Figure 3. Fit of the Brooks and Corey model to mean soil water retention data measured from soil samples collected at various depths. Goodness of fit is indicated by RMSE.

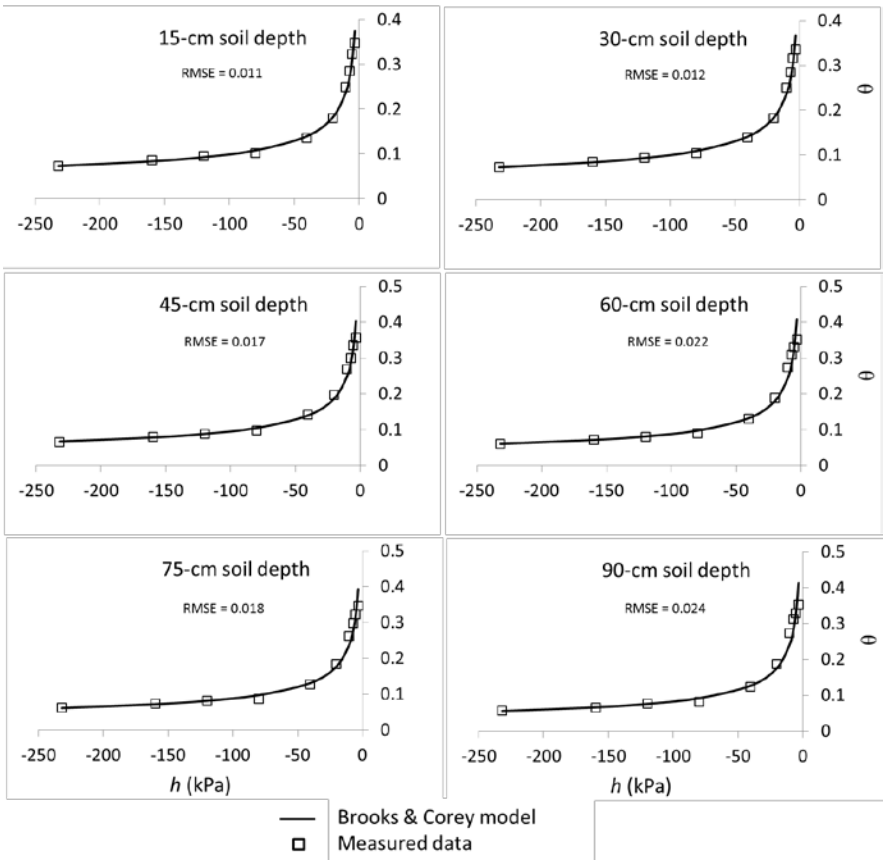


Figure 4. Depth of applied irrigation water and rain to the light and heavy irrigated study sites.

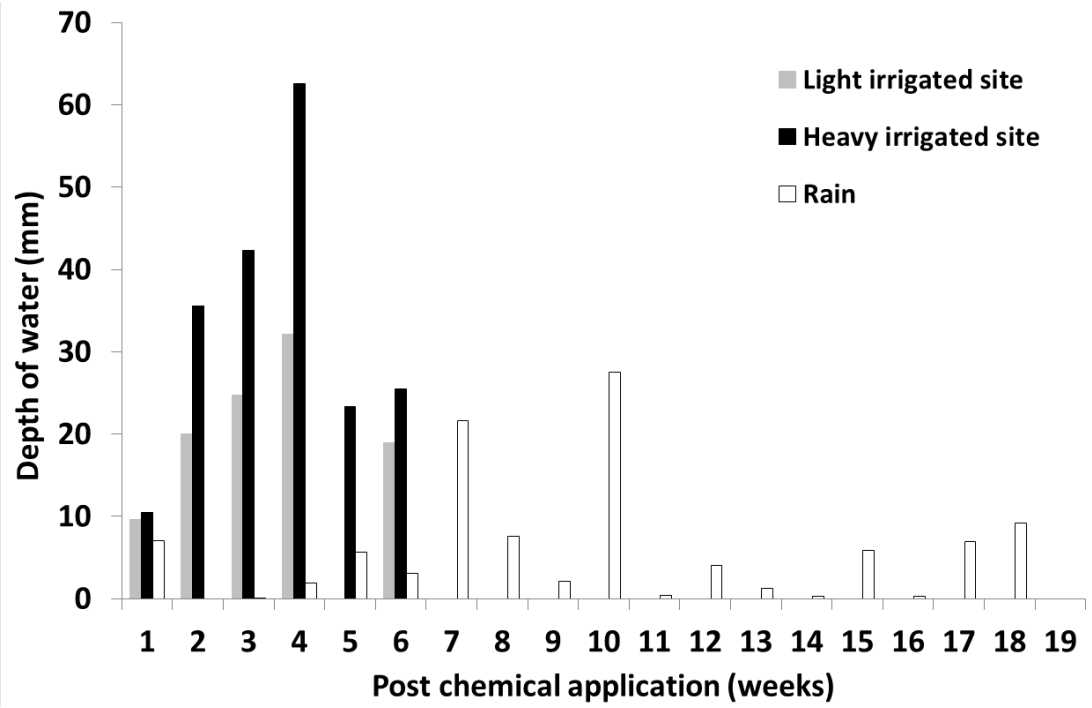


Figure 5. Depth of drainage solution extracted from lysimeter reservoirs in the light and heavy irrigated study sites. Standard error bars shown.

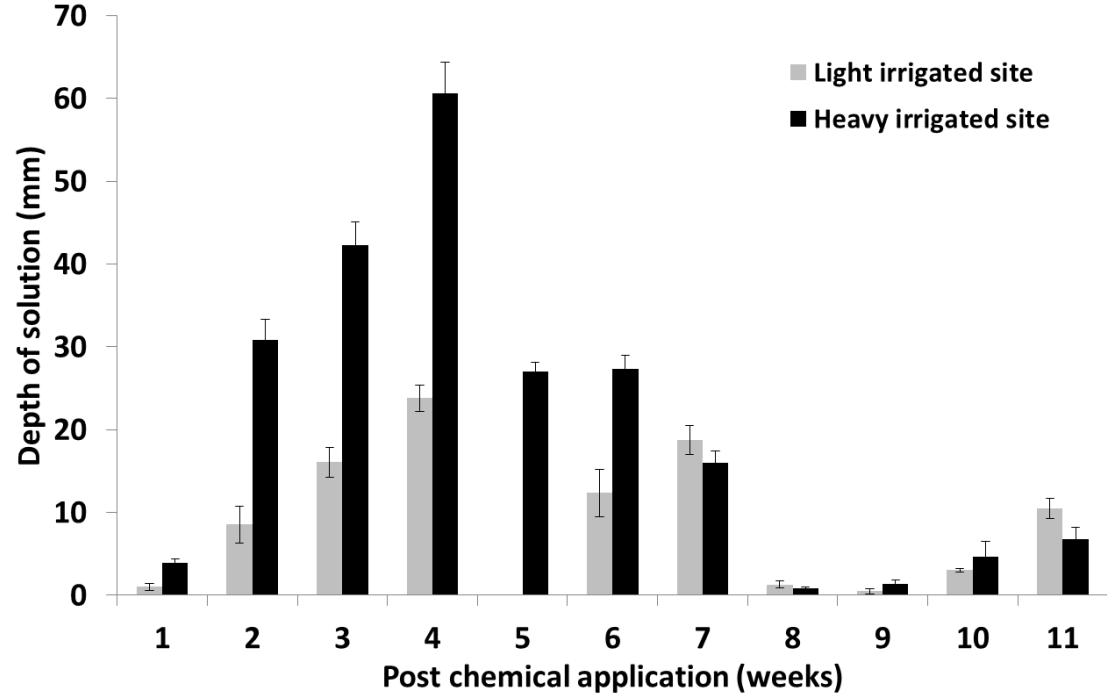


Figure 6. Distribution of Br mass recovered from soil profile within the lysimeter-confined and unconfined soil of the light and heavy irrigated study sites. Standard error bars shown.

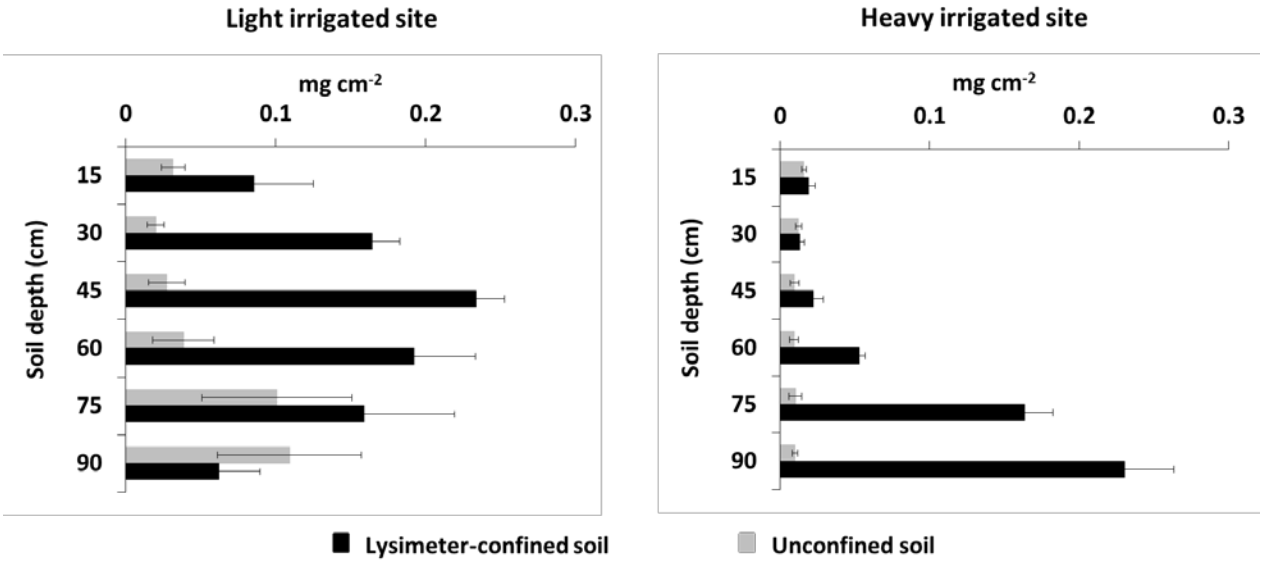


Figure 7. Distribution of pesticide and degradate mass recovered from soil profile within lysimeter-confined and unconfined soil of the light and heavy irrigated study sites. Standard error bars shown.

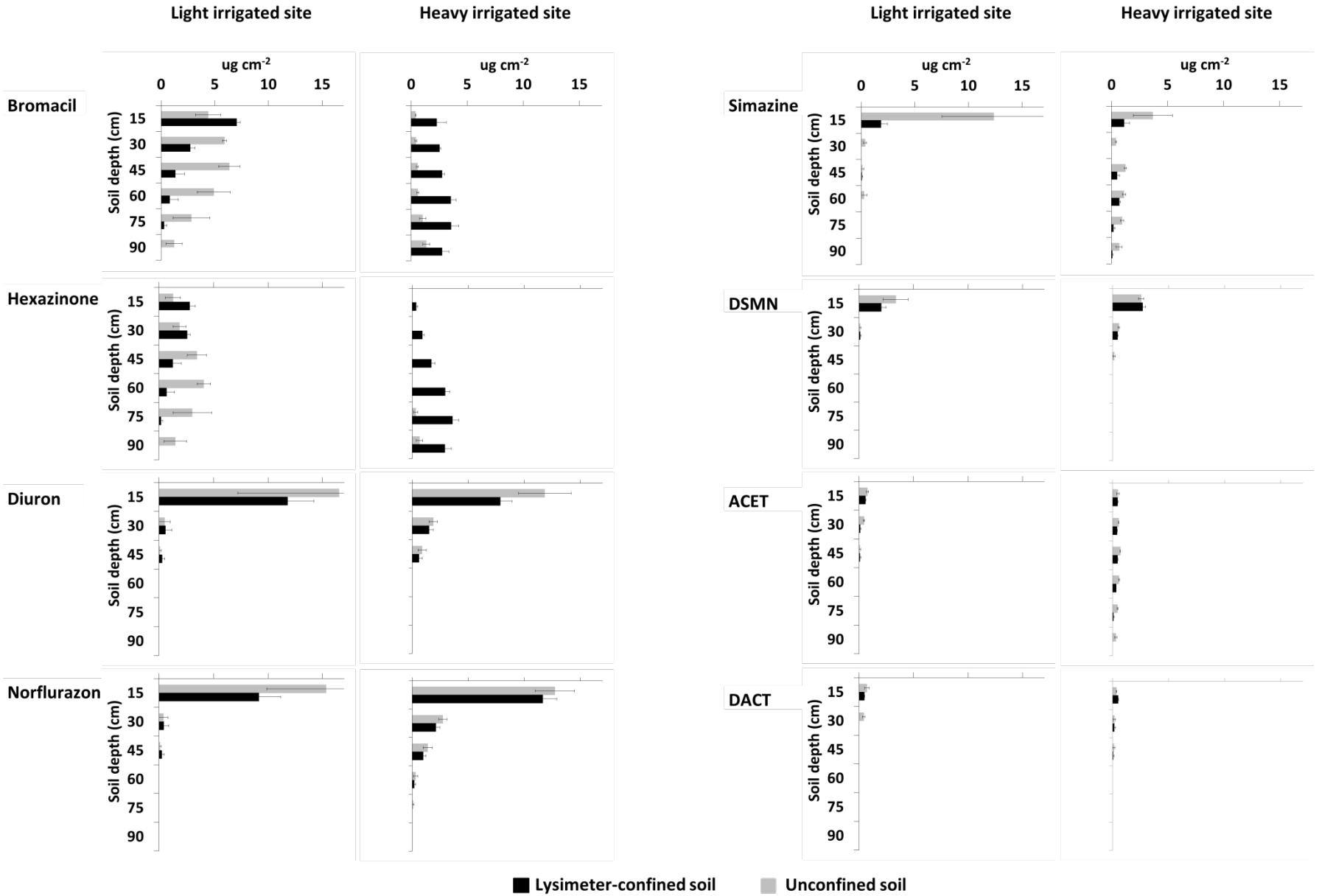


Figure 8. HYDRUS-1D-simulated and field-measured Br mass in lysimeter-confined and unconfined soil, and cumulative total from lysimeter reservoir solution at conclusion of the field study. Br mass in drainage water of the unconfined soil categorized as 'estimate drainage (Field)', formatted in the figure as unfilled bars, was approximated from the difference between the theoretical application rate of Br and that recovered from the unconfined soil. This assumed that total Br recovery in the lysimeter-confined soil, which approximated 100%, would similarly be expected in the unconfined soil had their drainage solute been measureable. Plots also compare simulated and field-measured cumulative depth of solution collected in lysimeter reservoirs. Goodness of fit is given by the RMSE.

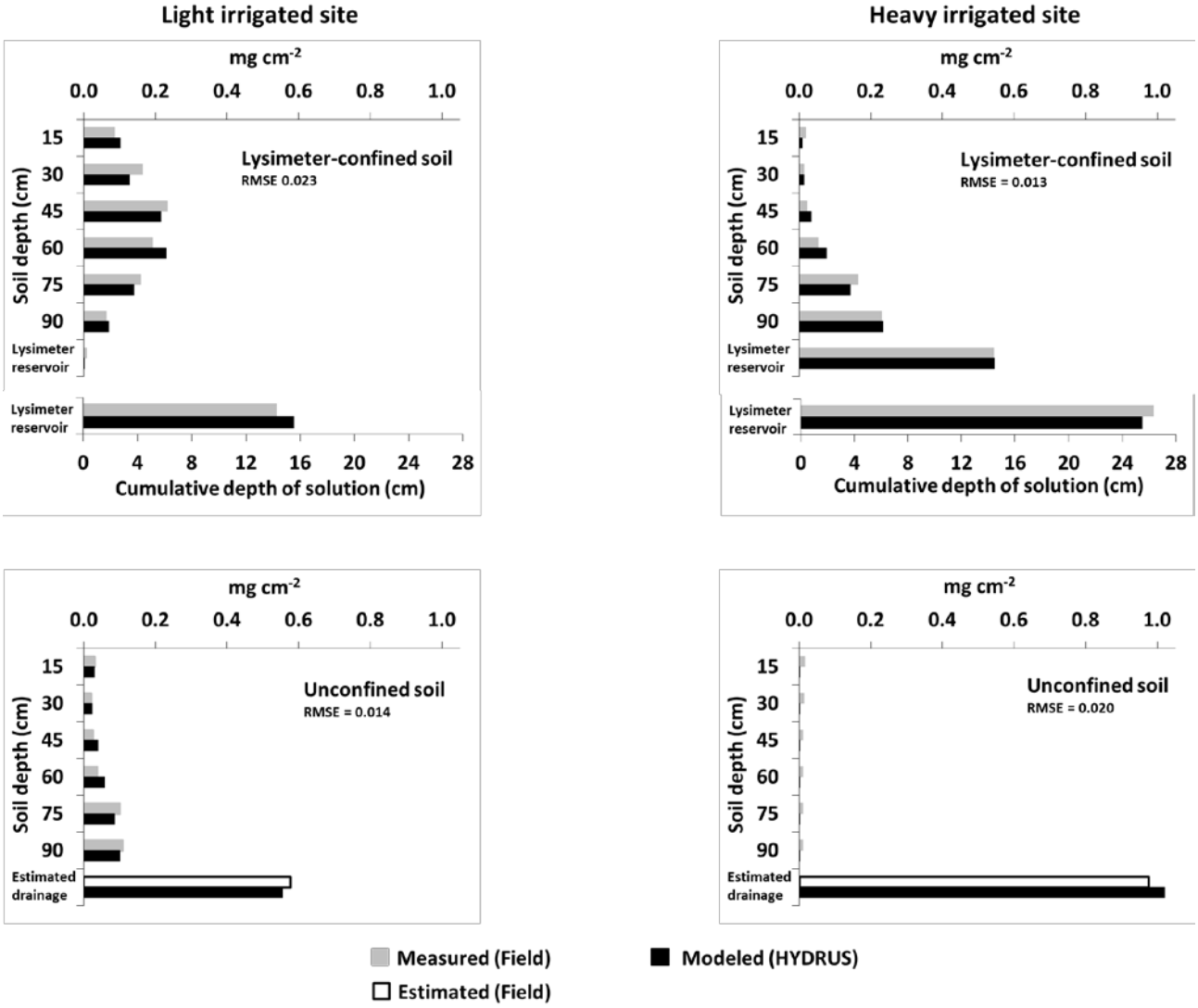


Figure 9. HYDRUS-1D-simulated and field-measured pesticide and degradate mass in lysimeter-confined and unconfined soil, and cumulative total mass from lysimeter reservoir solution at conclusion of the field study. Goodness of fit is given by the RMSE.

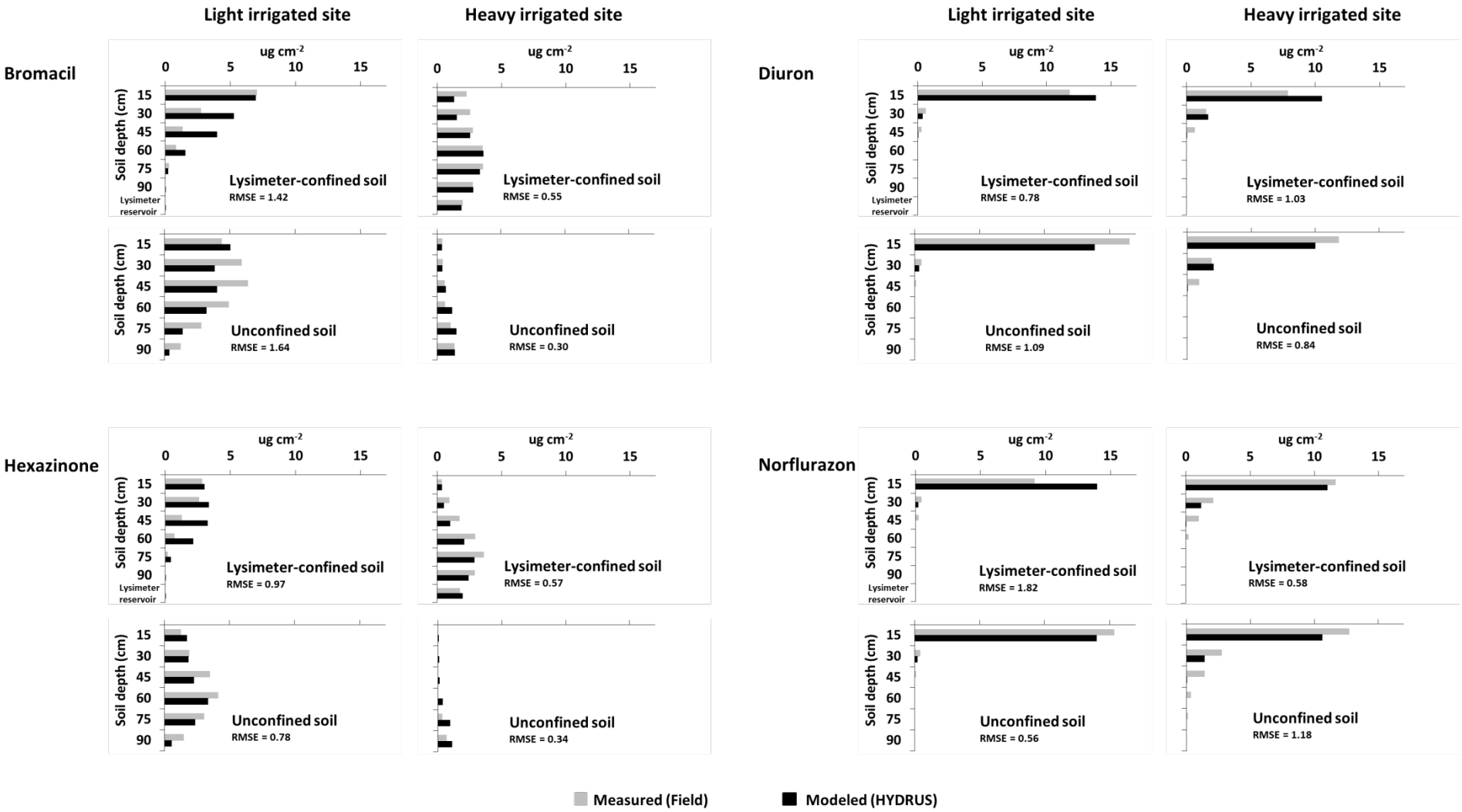
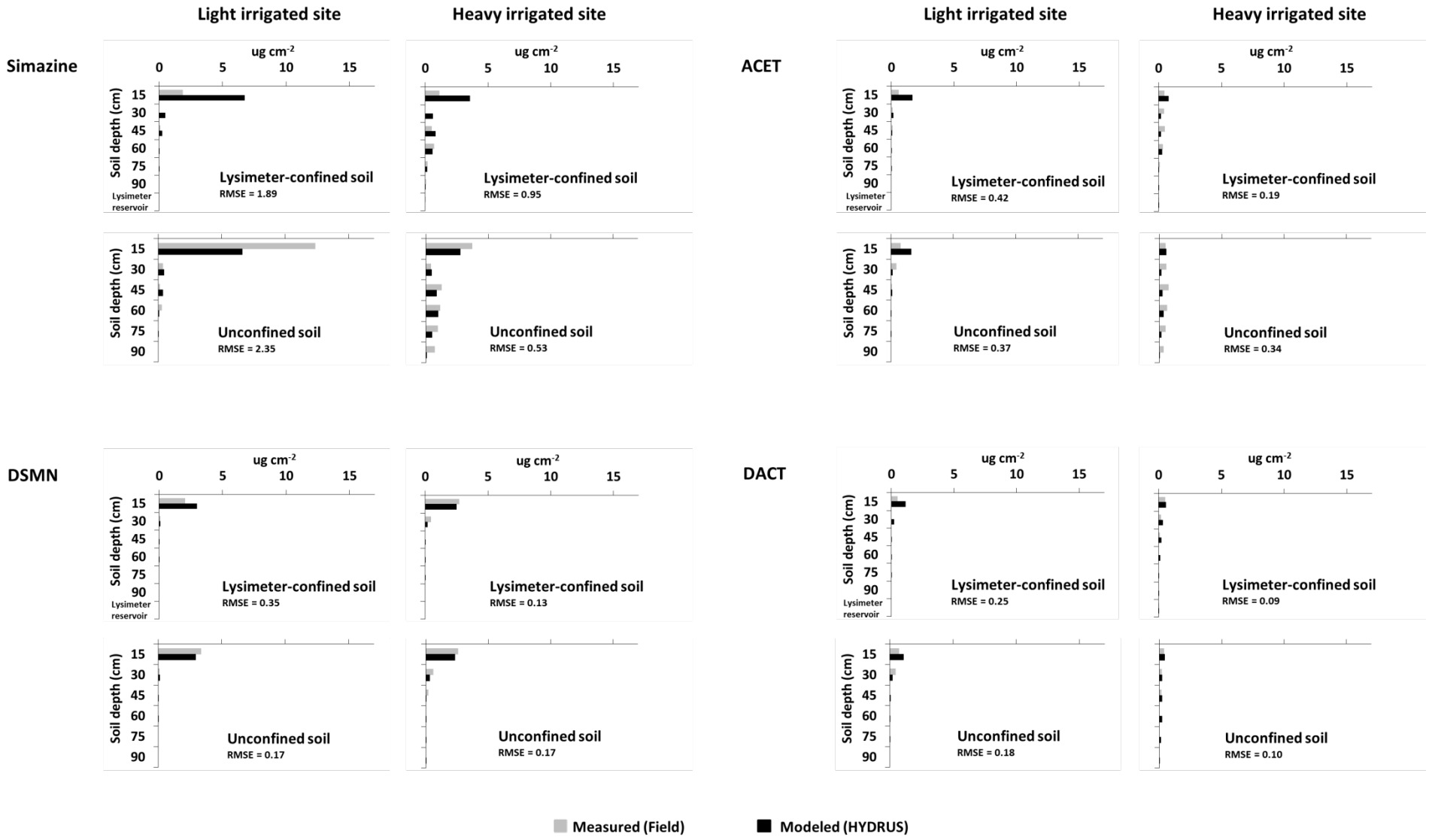


Figure 9 cont.



APPENDIX 1. Lysimeter construction and installation procedure.

Lysimeter casings were constructed of Schedule 80 polyvinyl chloride piping of 12-inch nominal diameter and 1.2-m length. The entire rim at the base of each pipe was beveled to form a chisel-type edge. To obtain a sample of undisturbed soil, an excavator with a hydraulic bucket attachment applied force to a wooden block on top of each lysimeter casing pressing it vertically into the soil to its full length (1.2 m). The chiseled edge at the base of the casings was shaped to displace soil directly below the rim to the outer edge during insertion into the ground, thereby leaving the confined soil in an undisturbed state. The procedure for extraction of the lysimeter casings and confined soil involved:

1. Removing the soil around the outer edge of each casing to expose the base,
2. Horizontally inserting blades from two hoes just below the chiseled edge on opposing sides of each casing to support the base of the soil core,
3. Attaching the handle of the hoes to the outside of the casing with tape or screws, and
4. Removal of the casing and soil core from the ground with a hydraulic forklift using a chain with its ends affixed to screw-pin chain shackles, each secured to two previously drilled holes located near the top of each lysimeter casing.

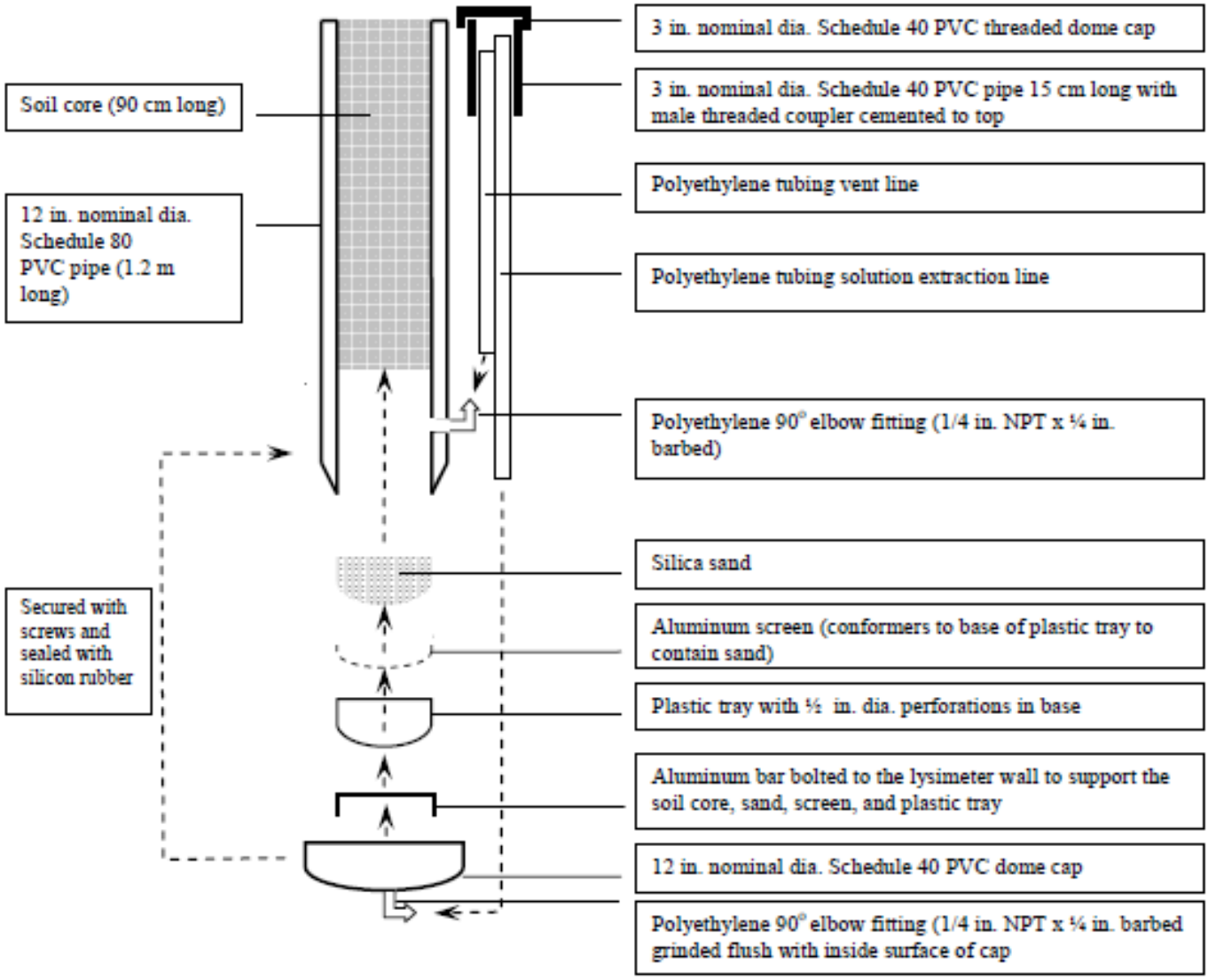
After enclosing the top of each lysimeter casing with a wooden disc the units were inverted for final assembly, which involved:

1. Removing the hoes that were supporting the base of the soil core,
2. Extracting and discarding a 30-cm length soil core from the base of the casing,
3. Layering 5-cm thick strata of fine sand followed by coarse sand to interface with the base of the soil core to act as a filter and enhance drainage,
4. Insertion of a fine stainless steel screen to retain the coarse sand,
5. Insertion of a shallow plastic tray with drainage holes that borders tightly with the inside surface of the lysimeter casing wall to act as a retainer for the soil core, sand filter and stainless steel screen,
6. Mounting of two perpendicular-affixed aluminum bars bolted through tab extensions to the lysimeter casing to support the weight of the lysimeter contents,
7. Fitting of a polyvinyl chloride dome cap of 12-inch nominal diameter to provide the base of the lysimeter reservoir, secured with screws to the sides of the lysimeter casing and sealed with silicone rubber,
8. Installation of a threaded, 90-degree brass fitting with barbed tube connection into the base of the dome cap for solution extraction and another into the lysimeter wall near the

top of the lysimeter reservoir for air pressure equilibration during solution extraction, and finally,

9. Attachment of polyethylene tubing, secured with hose clamps to the barbed connectors of the 90-degree brass fittings, with enough length to extent to the surface to enable solution extraction and air pressure equilibration.

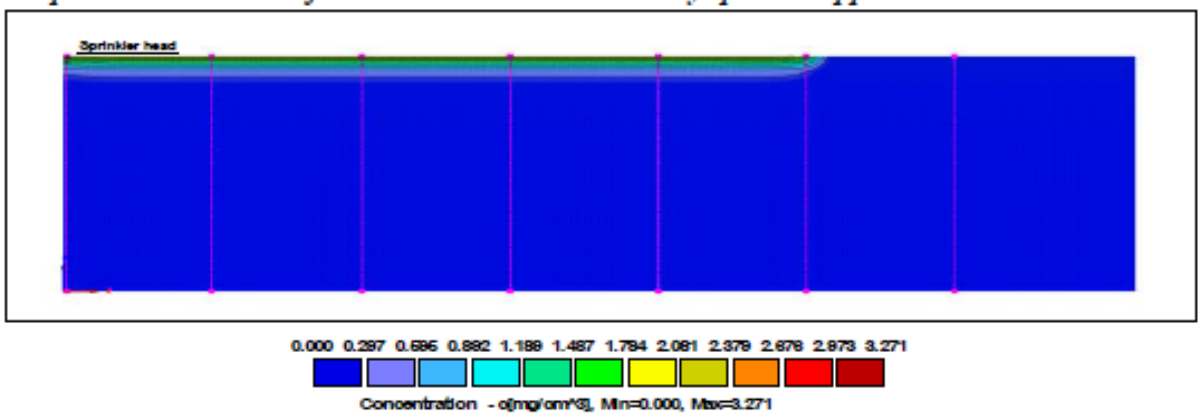
Once assembled in the inverted position and righted, the wooden disc enclosing the soil at the top of each casing was removed and the lysimeter returned to the cavity from where the soil core was obtained. The cavity was deepened approximately 20 cm to accommodate the additional length of the dome cap, and adjustments were made to ensure the top of the lysimeter and the soil core were flush with the soil surface. Soil was returned to the area around the lysimeter to support the unit in the ground. The polyethylene solute extraction and air equilibrium tubing was extended approximately 50 cm away from the lysimeter casing with the ends coiled within a 4-in nominal diameter polyvinyl chloride casing of 30-cm length. A threaded cap enclosed the casing to protect the tubing within. Schematic below:


3 in. nominal dia. Schedule 40 PVC threaded dome cap
3 in. nominal dia. Schedule 40 PVC pipe 15 cm long with male threaded coupler cemented to top
Soil core (90 cm long)
Polyethylene tubing vent line
12 in. nominal dia. Schedule 80 PVC pipe (1.2 m long)
Polyethylene tubing solution extraction line
Polyethylene 90° elbow fitting (1/4 in. NPT x ¼ in. barbed)
Silica sand
Secured with screws and sealed with silicon rubber
Aluminum screen (conformers to base of plastic tray to contain sand)
Plastic tray with ½ in. dia. perforations in base
Aluminum bar bolted to the lysimeter wall to support the soil core, sand, screen, and plastic tray
12 in. nominal dia. Schedule 40 PVC dome cap
Polyethylene 90° elbow fitting (1/4 in. NPT x ¼ in. barbed grinded flush with inside surface of cap

APPENDIX 2. Preliminary HYDRUS-2D simulations.

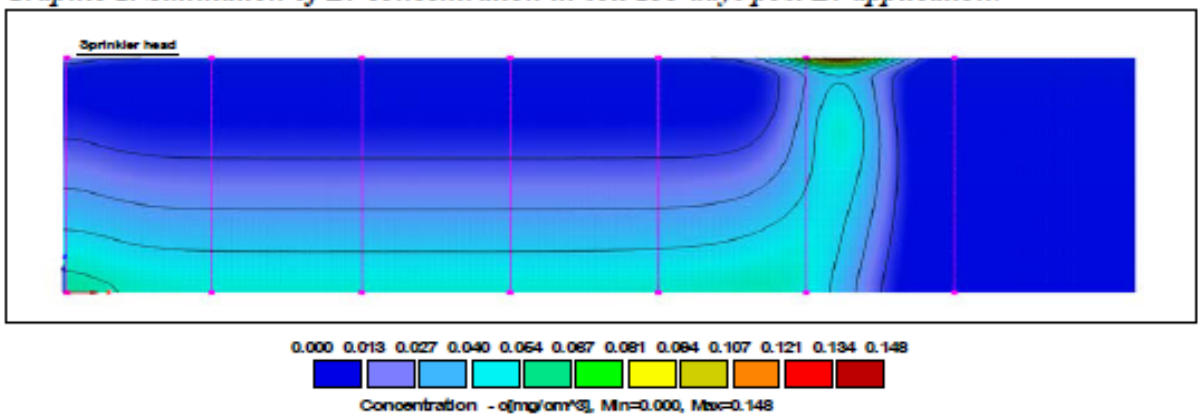
Two dimensional HYDRUS simulations were conducted prior to the field study to investigate suitable chemigation and irrigation application widths for the unconfined soil plots. Simulated results are of Br soil concentration in the vertical and horizontal radial planes perpendicular to the longitudinal direction of the field plots and irrigation sprinkler line. Model inputs included soil analysis data from the field sites, a hypothetical irrigation regime that generated percolating water, climatic conditions for the study site, and HYDRUS-2D default values for soil hydraulic properties relating to the field-study soil-type because field-measured values were not available at the time. Graphics illustrate an axial-symmetrical view of the simulation output with the sprinkler head located at the axis. Graphic 1 illustrates sprinkler reach and Br treatment area. Graphic 2 illustrates the extent of Br movement, most notably in the horizontal radial plane beyond the application area, likely resulting from capillary tension in the dry soil beyond the sprinkler reach. The magnitude of this movement was not evident near the sprinkler head.

Graphic 1. Simulation of Br concentration in soil 3 days post Br application.



Project b160gEx4 - study279-controlplot-partial heavy irrig plot
Results, Concentration, Time 4 - 20.0 days

Graphic 2. Simulation of Br concentration in soil 133 days post Br application.



Project b160gEx4 - study279-controlplot-partial heavy irrig plot
Results, Concentration, Time 30 - 150.0 days

APPENDIX 3. Bromide and pesticides recovered from soil and lysimeter reservoirs.

Bromide (mg cm^{-2}):

Soil depth (cm)	Unconfined soil plots				Lysimeter-confined soil plots			
Replication	1	2	3	4	1	2	3	4
	Light irrigated site							
15	0.052	0.015	0.028	0.032	0.032	0.050	0.204	0.058
30	0.035	0.007	0.017	0.023	0.114	0.177	0.203	0.163
45	0.062	0.026	0.011	0.011	0.186	0.238	0.233	0.279
60	0.096	0.039	0.008	0.012	0.243	0.083	0.266	0.178
75	0.132	0.228	0.017	0.026	0.228	0.030	0.290	0.088
90	0.137	0.233	0.029	0.039	0.079	0.018	0.132	0.020
Lysimeter reservoir	NA[Z]	NA	NA	NA	0.012	0.005	0.008	0.007
	Heavy irrigated site							
15	0.012	0.016	0.018	0.019	0.022	0.030	0.009	0.015
30	0.013	0.007	0.016	0.015	0.008	0.022	0.013	0.009
45	0.005	0.006	0.011	0.017	0.007	0.033	0.033	0.015
60	0.004	0.016	0.013	0.004	0.045	0.055	0.064	0.047
75	0.023	0.005	0.004	0.009	0.164	0.164	0.210	0.117
90	0.006	0.008	0.012	0.014	0.211	0.183	0.198	0.328
Lysimeter reservoir	NA	NA	NA	NA	0.636	0.462	0.389	0.684

[Z]Not applicable

Bromacil (ug cm^{-2}):

Soil depth (cm)	Unconfined soil plots				Lysimeter-confined soil plots			
Replication	1	2	3	4	1	2	3	4
	Light irrigated site							
15	7.0797	5.3347	1.6328	3.4651	7.6531	6.9052	7.4287	6.1574
30	5.8212	6.4534	5.6631	5.6895	3.1081	2.4707	3.6876	1.6120
45	4.0951	5.9709	6.4729	8.9300	0.8375	ND	3.9102	0.4888
60	4.0429	1.5556	8.9425	5.0871	ND	ND	3.2129	ND
75	2.1062	ND[y]	7.8125	1.3830	ND	ND	1.0689	ND
90	1.1613	ND	3.3926	0.3549	ND	ND	ND	ND
Lysimeter reservoir	NA[Z]	NA	NA	NA	ND	ND	ND	ND
	Heavy irrigated site							
15	0.3764	0.3665	0.3939	0.4587	1.3461	4.7364	1.9918	1.0395
30	0.5531	0.2976	0.2634	0.5400	2.5576	2.3970	2.8184	2.3548
45	0.7133	0.4359	0.3567	0.7213	2.9062	2.2034	3.1968	2.7213
60	0.8300	0.7256	0.3802	0.4418	4.2035	2.2865	3.2396	4.3374
75	1.2273	1.7446	0.4672	0.6546	4.6980	2.1273	2.6657	4.6980
90	1.3570	2.2182	0.7568	1.0778	3.0794	1.7302	1.8529	4.3321
Lysimeter reservoir	NA	NA	NA	NA	1.4715	1.2615	1.1569	3.9541

[Z]Not applicable

[Y]Non detect

Hexazinone (ug cm^{-2}):

Soil depth (cm)	Unconfined soil plots				Lysimeter-confined soil plots			
Replication	1	2	3	4	1	2	3	4
	Light irrigated site							
15	3.3155	0.8052	0.3266	0.6432	2.2486	1.7924	4.1631	3.0413
30	2.5708	3.1608	1.0062	0.7823	2.6156	2.5339	3.2398	1.9334
45	3.1176	5.9974	1.8970	2.9062	0.9062	ND	3.4875	0.6764
60	4.0696	2.4578	5.3280	4.5783	ND	ND	2.8113	ND
75	2.0429	ND[y]	8.1820	1.9690	ND	ND	0.6730	ND
90	0.9369	ND	4.5147	0.4906	ND	ND	ND	ND
Lysimeter reservoir	NA[Z]	NA	NA	NA	ND	ND	ND	ND
	Heavy irrigated site							
15	ND	ND	ND	ND	0.2792	0.7877	0.3789	ND
30	ND	ND	ND	ND	0.6401	0.9957	1.3486	0.7112
45	ND	ND	ND	ND	1.3104	1.3712	2.6420	1.5746
60	ND	ND	ND	ND	3.1058	1.7590	3.0790	3.8287
75	0.5358	0.7839	ND	ND	4.5397	2.1484	3.2200	4.4869
90	0.7438	1.3701	ND	0.5689	3.1055	2.0355	2.0564	4.4886
Lysimeter reservoir	NA	NA	NA	NA	1.3023	1.1939	1.1605	3.3616

[Z]Not applicable

[Y]Non detect

Diuron (ug cm^{-2}):

Soil depth (cm)	Unconfined soil plots				Lysimeter-confined soil plots			
Replication	1	2	3	4	1	2	3	4
	Light irrigated site							
15	7.7528	7.3540	44.3979	6.5812	16.7521	7.2792	15.0818	8.1018
30	2.0730	ND	ND	ND	ND	ND	2.3654	ND
45	0.3937	ND	ND	ND	ND	ND	1.0964	ND
60	ND[y]	ND	ND	ND	ND	ND	ND	ND
75	ND	ND	ND	ND	ND	ND	ND	ND
90	ND	ND	ND	ND	ND	ND	ND	ND
Lysimeter reservoir	NA[Z]	NA	NA	NA	ND	ND	ND	ND
	Heavy irrigated site							
15	6.4067	9.6972	16.8767	14.4088	9.7222	5.5342	6.5812	9.5975
30	1.0246	1.6436	2.7657	2.1546	0.3740	1.7622	1.6963	2.1994
45	0.2853	0.3012	1.6909	1.3369	ND	0.7530	0.3857	1.3606
60	ND	ND	ND	ND	ND	ND	ND	ND
75	ND	ND	ND	ND	ND	ND	ND	ND
90	ND	ND	ND	ND	ND	ND	ND	ND
Lysimeter reservoir	NA	NA	NA	NA	ND	ND	ND	ND

[Z]Not applicable

[Y]Non detect

Norflurazon (ug cm^{-2}):

Soil depth (cm)	Unconfined soil plots				Lysimeter-confined soil plots			
Replication	1	2	3	4	1	2	3	4
	Light irrigated site							
15	10.1709	8.1766	31.5597	11.4173	14.2093	6.5064	10.4950	5.4095
30	1.6331	ND	ND	ND	ND	ND	1.7806	ND
45	0.4042	ND	ND	ND	ND	ND	0.9590	ND
60	ND[y]	ND	ND	ND	ND	ND	ND	ND
75	ND	ND	ND	ND	ND	ND	ND	ND
90	ND	ND	ND	ND	ND	ND	ND	ND
Lysimeter reservoir	NA[Z]	NA	NA	NA	ND	ND	ND	ND
	Heavy irrigated site							
15	8.3511	11.7663	16.5277	14.3090	14.7328	9.0740	10.1958	12.6139
30	1.9228	2.6604	3.6613	2.7921	1.4224	1.8069	2.2205	3.0555
45	0.7503	0.6182	2.1585	2.0872	0.5548	0.9089	0.8375	1.7067
60	ND	ND	0.7149	0.5569	ND	ND	0.2838	0.4846
75	ND	ND	0.3378	ND	ND	ND	ND	ND
90	ND	ND	ND	ND	ND	ND	ND	ND
Lysimeter reservoir	NA	NA	NA	NA	ND	ND	ND	ND

[Z]Not applicable

[Y]Non detect

Simazine (ug cm^{-2}):

Soil depth (cm)	Unconfined soil plots				Lysimeter-confined soil plots			
Replication	1	2	3	4	1	2	3	4
	Light irrigated site							
15	7.8775	8.9992	26.7235	5.8333	0.4786	3.0912	1.1891	2.6424
30	0.3029	0.5294	0.6348	ND	ND	ND	ND	ND
45	0.4676	ND	ND	ND	ND	ND	0.2853	ND
60	ND[y]	ND	1.0763	ND	ND	ND	ND	ND
75	ND	ND	ND	ND	ND	ND	ND	ND
90	ND	ND	ND	ND	ND	ND	ND	ND
Lysimeter reservoir	NA[Z]	NA	NA	NA	ND	ND	ND	ND
	Heavy irrigated site							
15	1.1392	0.5036	7.8525	5.2599	1.4708	0.3091	0.3665	2.3383
30	0.4715	0.3503	0.3609	0.4188	ND	ND	ND	ND
45	1.0542	1.2100	1.2180	1.5377	ND	0.4808	1.0225	0.5020
60	1.1834	1.0683	1.4619	0.7845	0.4793	0.6158	0.7925	0.8782
75	0.9818	0.5516	1.2827	0.9845	ND	ND	ND	0.6334
90	0.5898	ND	1.2057	0.9525	ND	ND	ND	0.2610
Lysimeter reservoir	NA	NA	NA	NA	0.0002	0.0012	0.0003	0.0005

[Z]Not applicable

[Y]Non detect

DSMN (ug cm^{-2}):

Soil depth (cm)	Unconfined soil plots				Lysimeter-confined soil plots			
Replication	1	2	3	4	1	2	3	4
	Light irrigated site							
15	1.6154	1.6303	6.5064	3.7144	3.0912	1.3038	2.3508	1.3985
30	0.3688	ND	ND	ND	ND	ND	0.3503	ND
45	ND[y]	ND	ND	ND	ND	ND	ND	ND
60	ND	ND	ND	ND	ND	ND	ND	ND
75	ND	ND	ND	ND	ND	ND	ND	ND
90	ND	ND	ND	ND	ND	ND	ND	ND
Lysimeter reservoir	NA[z]	NA	NA	NA	ND	ND	ND	ND
	Heavy irrigated site							
15	1.9120	2.9665	2.9167	2.4630	3.4651	2.4555	2.0641	2.7671
30	0.5084	0.5742	0.7586	0.4978	0.3635	0.4451	0.4346	0.6032
45	ND	ND	0.3593	0.2959	ND	ND	ND	ND
60	ND	ND	ND	ND	ND	ND	ND	ND
75	ND	ND	ND	ND	ND	ND	ND	ND
90	ND	ND	ND	ND	ND	ND	ND	ND
Lysimeter reservoir	NA	NA	NA	NA	0.0002	0.0012	0.0003	0.0005

[z]Not applicable

[y]Non detect

ACET (ug cm^{-2}):

Soil depth (cm)	Unconfined soil plots				Lysimeter-confined soil plots			
Replication	1	2	3	4	1	2	3	4
	Light irrigated site							
15	0.6058	0.6382	0.8326	1.0445	0.6830	0.4462	0.7030	0.4911
30	0.4241	0.4004	0.6453	0.3134	ND	ND	0.3503	ND
45	0.3038	ND	ND	ND	ND	ND	0.3250	ND
60	ND[y]	ND	ND	ND	ND	ND	ND	ND
75	ND	ND	ND	ND	ND	ND	ND	ND
90	ND	ND	ND	ND	ND	ND	ND	ND
Lysimeter reservoir	NA[z]	NA	NA	NA	ND	ND	ND	ND
	Heavy irrigated site							
15	0.3016	0.3340	0.5335	0.7952	0.4038	0.3989	0.6457	0.3839
30	0.5874	0.5005	0.5426	0.5874	0.3661	0.3793	0.4214	0.5005
45	0.7398	0.7107	0.6711	0.7239	0.4333	0.4306	0.5310	0.4650
60	0.6747	0.5756	0.6426	0.4900	0.3695	0.3079	0.2999	0.3534
75	0.5595	0.3510	0.5490	0.4197	ND	ND	ND	0.3326
90	0.3680	ND	0.5115	0.3680	ND	ND	ND	ND
Lysimeter reservoir	NA	NA	NA	NA	0.0002	0.0010	0.0003	0.0027

[z]Not applicable

[y]Non detect

DACT (ug cm^{-2}):

Soil depth (cm)	Unconfined soil plots				Lysimeter-confined soil plots			
Replication	1	2	3	4	1	2	3	4
	---------- *Light irrigated site* ----------							
15	0.3490	0.6083	0.5783	1.3337	0.5559	0.4662	0.4238	0.5061
30	0.2450	0.2845	0.4873	0.7217	ND	ND	ND	ND
45	ND[y]	ND	ND	ND	ND	ND	ND	ND
60	ND	ND	ND	ND	ND	ND	ND	ND
75	ND	ND	ND	ND	ND	ND	ND	ND
90	ND	ND	ND	ND	ND	ND	ND	ND
Lysimeter reservoir	NA[Z]	NA	NA	NA	ND	ND	ND	ND
	---------- *Heavy irrigated site* ----------							
15	0.3340	0.3241	0.3490	0.4188	0.5584	0.4437	0.5734	0.4811
30	0.4030	0.3108	ND	ND	0.3951	ND	ND	0.2766
45	0.3170	0.2642	ND	ND	0.2827	ND	ND	ND
60	ND	ND	ND	ND	ND	ND	ND	ND
75	ND	ND	ND	ND	ND	ND	ND	ND
90	ND	ND	ND	ND	ND	ND	ND	ND
Lysimeter reservoir	NA	NA	NA	NA	ND	ND	ND	ND

[Z]Not applicable

[Y]Non detect

Contact GWPP@cdpr.ca.gov for a copy of Appendix 4. Calibrated HYDRUS-1D input files and for references not currently available on the web.