POTENTIAL PESTICIDE TRANSPORT IN COLORADO AGRICULTURE: A MODEL COMPARISON

by

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ABSTRACT

Agricultural chemicals (fertilizers and pesticides) leached from the fields of Colorado and other parts of the United States are increasingly attacked as a major source of groundwater pollution. Leaching causes loss of fertilizers from the root zone and may cost the average farmer a significant portion of profits. Farmers and regulatory agencies need a tool to help manage these chemicals. Unfortunately, no such tool has been available until recently.

Opus and PRZM, computer simulation programs, have the potential for assisting the Colorado farmer with chemical management decisions. Although they are written for areas where irrigation is not the main source of a crop's water, this study shows that they can be adapted to fit a sprinkler irrigated, farm.

To evaluate these models, chemicals were applied to an experimental facility, and their movements through the soil root zone (45.7 cm, 18 inches) were monitored. Water was applied as rainfall through an overhead sprinkling system. Soil moisture was monitored along with chemical concentrations. Data gathered from monitoring were compared to results obtained from PRZM and Opus, without model calibration, in order to determine the usefulness of such models in a realistic setting.

Comparisons showed that Opus predicted changes in soil moisture and chemical concentrations, even though it was not able to predict the measured distributions in the soil profile. PRZM predicted some changes in chemical concentrations, but was unable to assess the measured water content trend initially. It too was unable to accurately predict measured profiles of moisture content and chemical concentrations.

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I. INTRODUCTION

A. Problem Description

Groundwater contamination due to the leaching of nutrient and organic pesticides has recently become of utmost concern to the future of United States agriculture. The Environmental Protection Agency (EPA) is adding many pesticides to its priority list of hazardous chemicals. Williams, et al. (1988) reports that 46 different pesticides have been detected in groundwater in 26 states. A primary source of such contaminations has been identified nationally as leaching of pesticides and inorganic fertilizers from cultivated farmland.

The Committee on Groundwater Protection (1986) indicates that pesticides are a major contributor to groundwater contamination in California, Florida, New Jersey, Wisconsin and other states. In 1980, upwards of 178,000 metric tons (360 million pounds) of pesticides were used in California. Farm lands received 90 percent of the total. The committee called for further study to define the scope of the pesticide leaching problem.

According to D'Itre and Wolfson (1987), in 34 states, agricultural non-point source pollution is blamed for the failure of those states to meet water quality goals. They report that 1.1 million metric tons (2.5 billion pounds) of pesticides are output in the United States annually. Forty one out of 101 agricultural organic compounds have been found in groundwaters nationwide. They also suggest that some pesticides invade groundwater even when applied at suggested rates.

According to Holden (1986), the pesticide, aldicarb, has been found extensively in groundwaters of Long Island, Wisconsin and Florida. Twelve out of 45 pesticides monitored in Wisconsin were found in groundwater.

State and federal agencies need tools to aid them in determining potential pesticide pollution of groundwaters. The Environmental Protection Agency's report on nonpoint-source pollution (1989) suggests that hydrologic models be used to predict possible contamination from pesticide use on agricultural sites. Carsel, et al. (1984) proposes that the Pesticide Root Zone Model (PRZM) be used in such a manner. PRZM was created to provide evaluations to aid the user in defining both the risk from leaching of pesticides and the effects of land management schemes on pesticide transport.

Holden (1986) warns that many professionals in California and New York are skeptical about substituting model predictions for field data gathered on pesticides. They claim that most models have not been properly validated under field conditions and that heterogeneity of agricultural soils limits the reliability of model predictions. Wagenet (1987), however, believes that useful models for vadose zone transport do exist if care is taken when using the model. Smith and Ferreira (1987) believe that Opus, a vadose zone transport model, can be an effective tool for predicting the effects of agricultural management practices on nonpoint-source pollution.

Agencies involved in regulating pesticides are not the only people concerned with contamination of groundwater by pesticides. Farmers are also aware of the threat that pesticides can pose if not handled properly. D'Itre and Wolfson (1987) report that over 95 percent of rural inhabitants in the United States rely on groundwater as their main supply of drinking water. Since farmers make up the majority of that 95 percent, they are concerned with the possibility of groundwater contamination. Another aspect that is important to farmers is the cost of agricultural chemicals. Chemicals which stay in the root zone are more beneficial to farmers than those which are leachable.

Both contamination of groundwaters and loss of valuable chemicals due to leaching from farm land can be controlled through management schemes such as improved selection of chemicals, irrigation management, multiple chemical applications over longer periods of time, and better tillage practices. Since the fate of many agricultural chemicals is unknown after application, farmers and agencies such as the Cooperative Extension Service and Soil Conservation Service need a method for choosing the best management decision schemes.

Several computer models are available to simulate the effects of management practices on, and the movement of, agricultural chemicals through the soil. The Pesticide Root Zone Model (PRZM) and Opus are two such models. However, neither of these models have been extensively validated in the field , and neither is in use by farmers or government agencies who provide technical assistance to farmers.

B. Objectives

The objective of this research is to evaluate two pesticide transport models: Opus and PRZM. By evaluation (validation), we do not mean verification. Verification is the process of testing a model by determining how well it responds to input parameters. Evaluation, in this study, is to determine how model predictions compare to measured field data for the transport of water, bromide and atrazine through the vadose zone. When evaluating a model, one must take care not to test models in situations that are not within their scope. Therefore, the models will be evaluated to determine if they perform as they were intended with the available input data. Thus, their use as tools by regulating agencies and farmers will be evaluated.

II. METHODOLOGY

A. Experimental Procedures

1. Description of Rainfall Facility

We chose the outdoor rainfall facility, located at the Engineering Research Center (ERC) of Colorado State University, for the physical simulation site. It was designed and constructed by a team from the USDA-Agricultural Research Service. The site was designed to study surface runoff and erosion phenomena. Saturated groundwater flow through a gravel layer (described below) can be created using a band of injection wells. Although the facility was not designed to study unsaturated flow in the vadose zone, it was used in such a manner.

The facility bridges the gap between laboratory scale and full field scale. The plot has a field area of 0.026ha (0.064ac). Soil was sampled in five locations on the plot, mixed and sent to the Soils Testing Laboratory at Colorado State University for particle size analysis. The results showed that the soil portion of the rainfall facility is a sandy loam. The 14 percent clays present are expansive. The soil has a depth of 45.7cm (18in). Underlying the soil is a permeable geotextile. Supporting the soil and geotextile is a 106.7cm (42in) layer of coarse gravel. Lining the upper end, bottom and sides of the gravel is an impervious rubber membrane. The plot, on a two percent grade, lies under a canopy of supply pipes and electronically operated sprinklers. The area has been divided in half lengthwise creating north and south plots. Funnel-shaped catchment flumes on both north and south plots collect runoff water for flow measurements. The groundwater outflow can be measured using a sharp-crested weir, located in a control house. The control house also holds the circuitry for the operation of the sprinklers. Figures 1 and 2 describe the plot.

2. Overall Description of Experiments

Physical modeling (outdoor experiment) began on June 13th, 1989. The plots (north and south) were rototilled. We planted sweet corn by hand on the north half. The south plot was left fallow. Equal amounts of atrazine (6Kg/ha, (5.4lb/ac) in accordance with label directions) and bromide (234.8Kg/ha (260.0lb/ac) in the form of KBr) were applied to each half using a tractor mounted, automated sprayer on June 14th. During the course of the growing season, we applied water through the overhead sprinkler system in amounts that would not cause runoff. The quantities sprinkled provided enough moisture for plant growth without inducing water stress to the corn. Chemical concentration measurements were taken throughout the summer growing season, by pulling soil cores from six different locations on each plot. Samples were taken 5 different times for bromide and moisture content and 4 different times for atrazine. Dates are shown in figure 3. Data taken on June 13th served as the initial condition for simulation. The physical modeling ended on the 21st of August. PRZM and Opus were then used to model the physical system. Outputs, such as pesticide and water movement through the soil, were compared between model predictions and actual measurements.

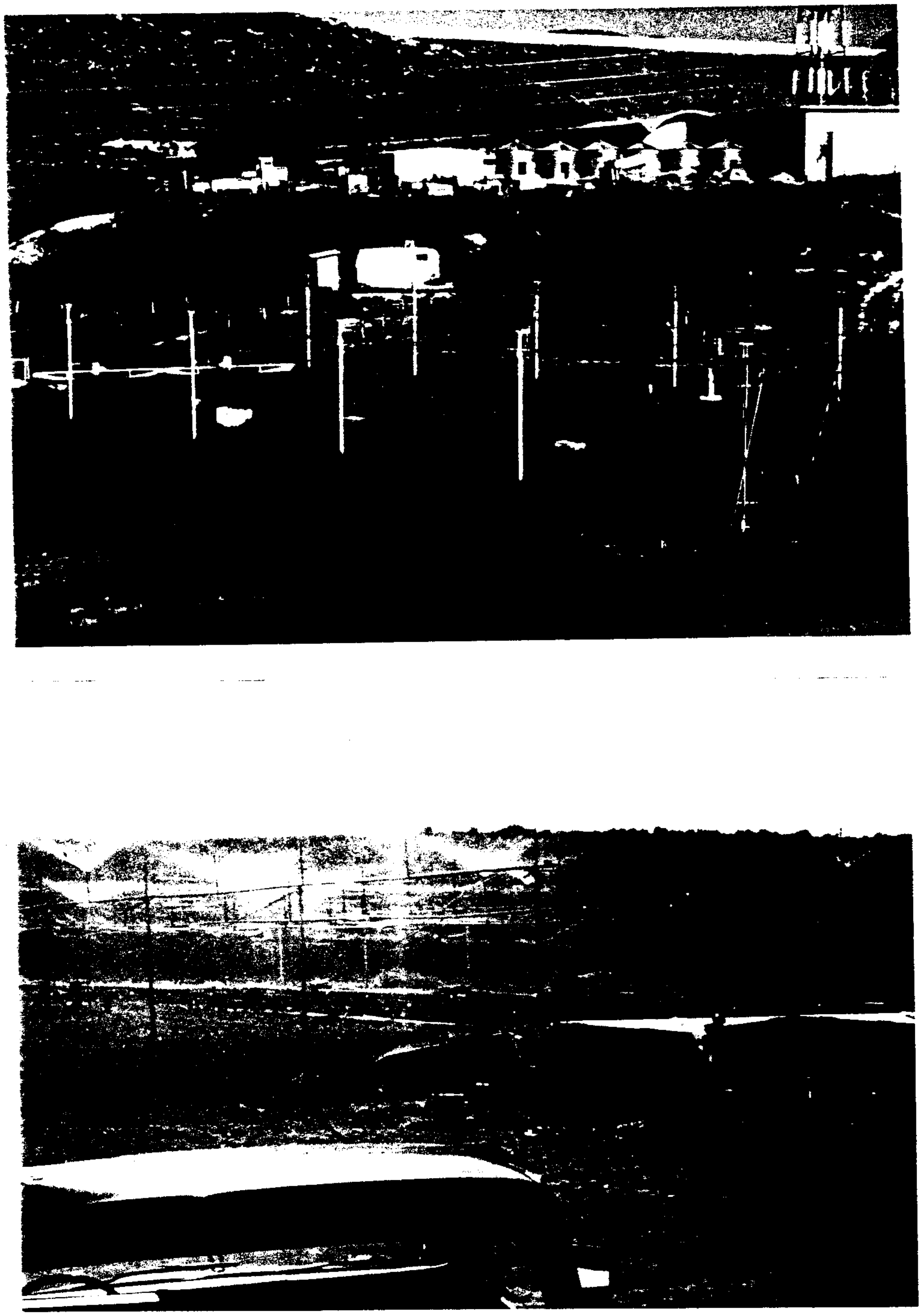


Figure 1

Rainfall Facility during irrigation. (Top)

Runoff flumes at the end of each plot. (Bottom)

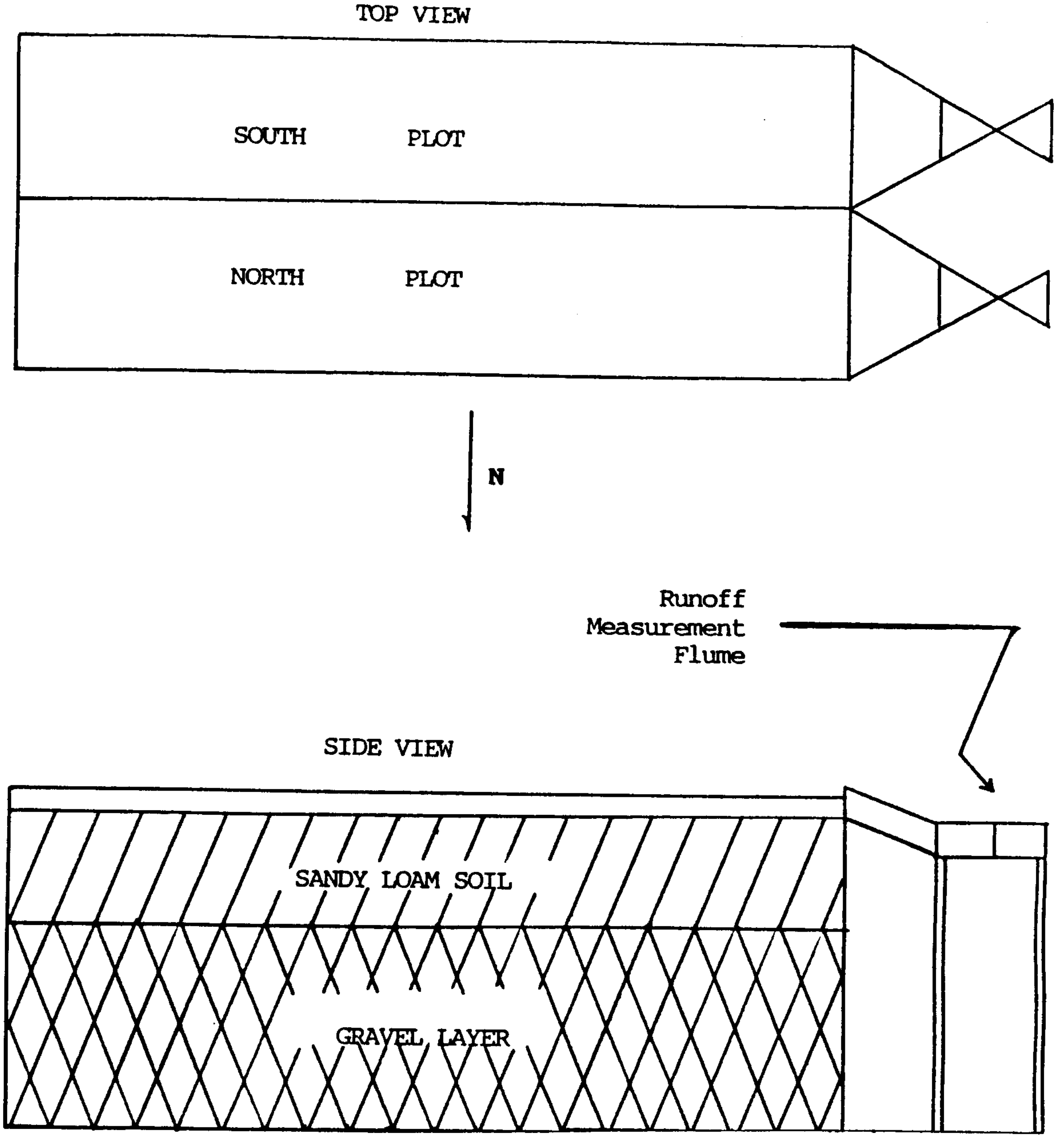


Figure 2

Graphical description of the rainfall facility.

Function	June 13	June 15	June 29	July 17	August 21
Moisture Content	XX XX	XX XX	XX XX	XX XX	XX XX
Bromide Concentration	XX XX	XX XX	XX XX	XX XX	XX XX
Atrazine Concentration	XX XX	XX XX		XX XX	XX XX

Figure 3.
Time table of sampling dates.

The outdoor experiment was the result of a previous study. During the summer of 1988, similar experiments were performed on the facility. The specifics of the 1988 study are included in appendix G. The 1988 study provided great insight and in all likelihood, saved the 1989 experiment.

3. Chemical Descriptions

Bromide is a nonreactive, inorganic chemical often used as a tracer in groundwater studies. It does not adsorb to soil nor will it degrade, although Lindsay (1979) reports that bromide activity may decline if the activity of silver is high and certain soil conditions exist. Natural occurrences of bromide are generally low, according to Smith and Davis (1974), and bromide is not toxic to plants. Its use as a tracer is well documented.

Bohmart (1976) described atrazine as a widely-used, broad-leaf herbicide that controls weeds in corn fields, shelter belts and chemically fallow fields. It is non-flammable, non-corrosive and has a very low toxicity to fish and wildlife (LD_{50} = 3080 mg/Kg). It is mobile in sandy soils and has the ability to cause groundwater contamination as shown by Anderson and Kazemi (1988) and by Smith, et al. (1988). McBride et al. (1988) list atrazine as persistent in high-pH soils and slightly mobile.

4. Data Collection

Hassan, Warrick and Amoozegar-Fard (1983), showed that field sampling variability is reduced by using a large diameter soil sampler. Therefore, all soil cores were gathered with a 5.08cm (2in) diameter soil probe, instead of the more common 1.91cm (3/4in) soil probe. Based on earlier experience with the smaller probe on the same plot, variability in sampling was, in fact, reduced.

We pushed a probe into the soil profile down to a depth of 45.7cm (18in), and extracted a soil core (See figure 4). This core was divided into 7.52cm (3in) segments, bagged or bottled, placed on ice and taken to the laboratory where it was properly stored prior to analysis. Moisture contents were determined using a gravimetric technique.

We determined chemical concentrations using the following procedures. Bromide analysis was carried out as described by Yoder, (1987). The soil sample was oven dried for 24 hours, then ground with a rotary grinder to a fine powder. A 25g (0.88oz) sub-sample was taken from each soil sample. A two to one extraction was carried out using 0.1 M $NaNO_3$ solution as the extracting agent. The solution was mechanically shaken for 20 minutes, then vacuum filtered, using a number one qualitative filter. The filtered solution was placed in a beaker. The potential difference was then measured between a bromide specific electrode and a reference electrode. Measured millivolt readings for each sample tested were used to calculate bromide concentrations based on calibration curves created using standard solutions.

Soil samples were analyzed for atrazine in the Biochemistry Laboratory in the Agricultural and Chemical Engineering department of Colorado State University. A preservative, mercuric chloride, was used to save the samples for analysis. Extraction and detection techniques similar to those described by Gorder and Dahm (1981) were used. Prior to extraction, soil samples were analyzed for oven dry weight. Each soil sample was adjusted to 70 percent dry weight by the addition of distilled water. Acetonitrile, pesticide grade, was adjusted to pH 9.0 with 1 molar ammonium hydroxide and then added to the soil samples in an average ratio of 3.1 to 1, liquid to solid ratio. Samples were extracted overnight and then sonicated for approximately ten minutes. Soil was allowed to settle after sonication. The liquid phase was removed without disturbing the soil and filtered through a Gelman Acrodisc-CR disposable pre-filter assemble, 0.45 micron (0.00011 in) pore size, compatible with acetonitrile. Samples of soil containing a known amount of atrazine were extracted similarly to obtain recovery data.

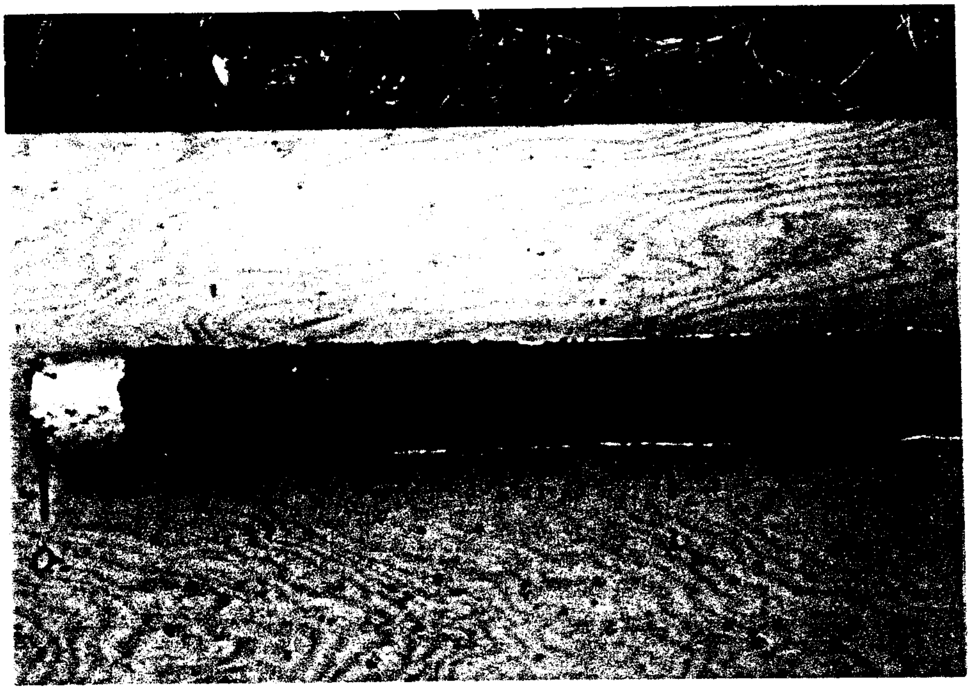


Figure 4

Soil core inside sampler.

Filtrates were analyzed by HPLC. The following are the analysis conditions:

Waters High Performance Chromatograph Model.

Waters UV Detector, Model 440, 254nm., 0.005 AUFS.

Effluent: 25mM phosphoric acid, 65 percent; Acetonitrile, 35 percent.

Flow Rate: 1.5ml/min

Column temperature: Ambient.

Column: Alltech RSil C18, 10 micron, 250mm x 4.6mm.

A disc permeameter (Figure 5), described by Canberra (1989), was used to estimate saturated hydraulic conductivity and saturated moisture content, θ_s . The permeameter required that we measure volume of water infiltrated, time of infiltration, soil moisture content before water application and a final soil moisture content. Soil moisture contents were measured gravimetrically. These data were then used to create plots of cumulative infiltration versus the square root of time.

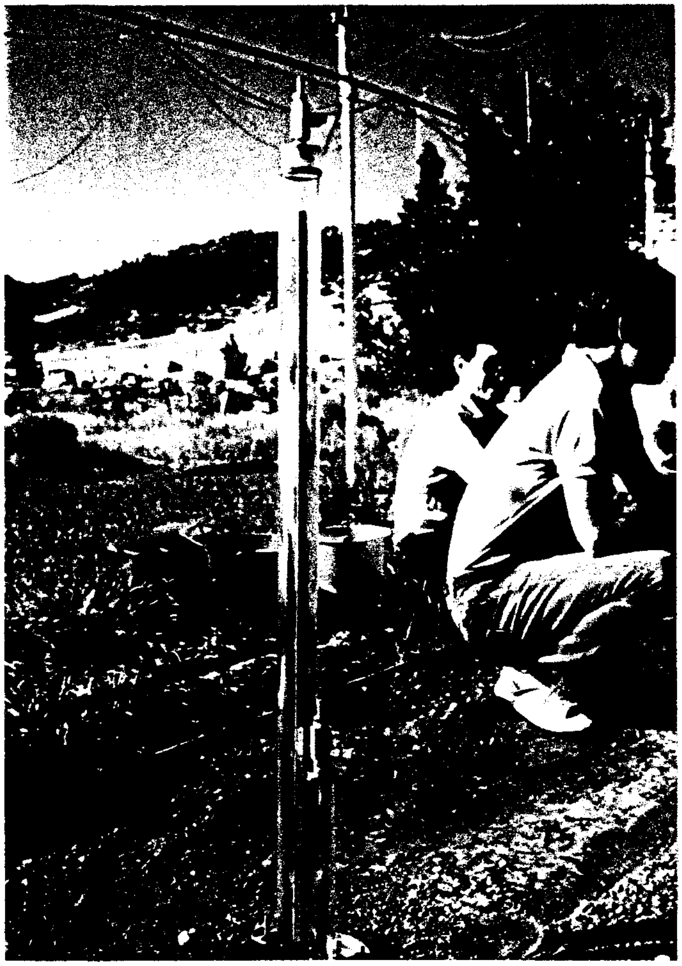


Figure 5

Disc permeameter.

These plots were then used to find sorptivity, which in turn was used to calculate hydraulic conductivity from the following equation:

$$K_0 = q/\pi r_0^2 - (4bS_0^2)/(\pi r_0(\Theta_0 - \Theta_n)) \qquad \text{(Eq. 1)}$$

where

K_0 = the hydraulic conductivity of the soil at the potential at which the infiltration data were collected,

S_0 = the sorptivity calculated from infiltration data,

r_0 = the radius of the ring on the permeameter,

q = the steady state infiltration rate,

Θ_0 = the soil moisture content at the given potential,

Θ_n = the initial soil moisture content,

b = approximately 0.55 (given).

Two flumes and stage recorders were used to keep track of surface runoff from rainfall. We constructed calibration curves on each flume using a bucket and stopwatch. Curves of water flow rate versus stage recorder depth were fit with an empirical equation which was used to calculate measured runoff rates and quantities from the plots. However, during this season, there was no significant runoff.

We used two rain gauges, one recording and one manual, to measure both natural and artificial rainfall rates and quantities. Since only one point on the field was used to measure rainfall, we performed a sprinkler uniformity test (according to Hahn and Rosentreter (1987)) to find the relationship between rain gauge measurements and the average depth of water applied to the field. Rain gauge recordings were found to be approximately 101 percent or 79 percent (depending on which sprinkler setting was being used) of the actual water depth applied to the plot. These deviations were used to alter rainfall data accordingly. We found the rainfall simulator, operating at specified supply rates, to have a coefficient of uniformity equal to 0.78.

We estimated wilting point water content by measuring the soil moisture content when the crop had been showing signs of severe water stress after several days without irrigation. This step was performed after the last measurement for chemical movement. Normally, a pressure cell is used to measure this parameter at 15-bars pressure. We chose to estimate the wilting point in the manner described above because the pressure cell method requires disturbing the sample and may not reflect field soil properties.

B. Computer Models

1. Model Description

a. PRZM

The development of PRZM was funded by the United States Environmental Protection Agency (EPA) and was completed near the end of 1984. The model was designed to simulate chemical and water movement through a field system. This includes runoff, chemical leaching, plant uptake, chemical degradation and erosion.

The model solves a water mass balance on a "compartmentalized" representation of the soil profile, moving water through soil compartments by a volume balance method. PRZM uses the SCS curve number technique to model rainfall runoff. Daily runoff and crop interception are subtracted from total daily rainfall to calculate the volume of water available for infiltration. Infiltration water is added to the uppermost compartment until its capacity is exceeded. Then water is added to the next layer, and so forth. Potential evapotranspiration (ETp) is calculated using one of two methods. If pan evaporation data are available, PRZM estimates ETp by multiplying a pan evaporation factor by the daily values of pan evaporation. The pan evaporation factor, related to geographical area, can be estimated from a figure in the PRZM manual. Thus potential ET is found by:

$$ETp = C_p * PE \qquad \text{(Eq. 4)}$$

where

C_p = the pan evaporation factor and

PE = daily pan evaporation.

The second method calculates ET using air temperatures and the following equation:

$$ETp(cm/d) = 870.8 * L_d^2 * (SVP) /(R_g * T_{abs}) \qquad \text{(Eq. 5)}$$

where

L_d = the possible hours of sunshine per day,

SVP = the saturated vapor pressure at the mean absolute air temperature (mb),

R_g = the dry-air gas constant and

T_{abs} = the absolute mean air temperature (°K).

PRZM modifies the potential ET using the following rules.

$$ETp = ETp \text{ if } SW \geq 0.6\theta_{fc}$$

$$ETp = SMFAC * ETp \text{ if } \theta_{wp} < SW < 0.6\theta_{fc}$$

$$ETp = 0 \text{ if } SW \leq \theta_{wp}$$

where

θ_{fc} = water content at field capacity.

θ_{wp} = water content at wilting point.

SW = total water stored in the profile.

SMFAC = an internally set parameter to linearly reduce ETP.

Total ET is then extracted from crop storage and subsequent soil compartments to meet the crop requirements.

Chemical transport from the soil surface and through the unsaturated zone are determined using a mass balance technique. The mass balance includes chemical application, adsorption, dispersion, advection, plant uptake, removal in runoff, plant wash off, removal on eroded elements and chemical transformation. Chemical movement is based on equilibrium soil adsorption, defined later. Carsel et al. (1984) provide a detailed explanation in the PRZM User's Manual.

b. Opus

Opus was developed (and is still under testing) by the Hydro-ecosystems Research Group from the United States Department of Agriculture, Agricultural Research Service (USDA, ARS). Developed for the purpose of predicting the effects of agricultural management on nonpoint-source pollution, Opus relies on the present understanding of the physical processes that control water movement over and through the soil. It was designed to simulate water movement, sediment transport, soil heat flow, crop growth, nutrient cycling, chemical transport and residue decay. Opus can be used on areas with a single cropping system that have one or two catchment areas. The soil profile may be comprised of up to six different horizons.

Simulations for water transport can be completed by one of two different options. Both use daily weather values (rainfall, solar radiation, temperature), but the two different options manipulate this data differently. The more simple option basically uses daily total values. The more complex option requires a much more complete record of rainfall/duration data. This option is best suited for simulations of short time periods. According to Smith (in press), the complex option requires huge data input files for extended time periods.

Since Opus is a rather detailed model and information gained from the field did not allow for validation of all processes that Opus simulates, we will not include a description of all the theory involved. Instead, a short summary explaining water and chemical transport will be provided. For a more detailed explanation see Volume One of the Opus documentation by Smith (in press).

Infiltration and runoff are the key to any soil transport model. These values control the amount of water available to transport chemicals and are closely related to one another. If one can be calculated, the other can be found from a mass balance between water added (rainfall) and the value calculated. Opus can estimate infiltration from either daily weather values (simple option) or breakpoint rainfall data (complex option). The simple option uses a modified SCS curve number technique to create an expected value of runoff from each rainfall event. It may then optionally distribute the simulated storm runoff about this mean. At this point, the balance of rainfall is available for distribution in the soil profile.

The complex option uses a physical relationship between rainfall intensities and soil infiltration properties to estimate infiltration and runoff. This option was used for our simulations. Relating infiltration into the soil surface with a Darcian approach, Smith (1989) reports the following basic equation.

$$I = \int_{\theta_i}^{\theta_s} (\theta - \theta_i) \frac{D(\theta)}{f-K_s} d\theta \qquad \text{(Eq. 6)}$$

where

I = the depth of infiltration from start of rainfall

f = the rate of infiltration

$D(\theta)$ = the diffusivity

K_s = the saturated hydraulic conductivity

θ = the volumetric water content

θ_i = initial water content.

By making the assumption that $D(\theta)$ is proportional to $dK(\theta)/d\theta$, equation 6 can be integrated, yielding the empirical relationship,

$$I(f) = G(\theta_i) \ln \left[\frac{f}{f-K_s}\right] \qquad \text{(Eq. 7)}$$

where

$$G(\theta_i) = H_c(\theta_s - \theta_i) \qquad \text{(Eq. 8)}$$

$$H_c = \frac{1}{K_s} \int_{-\infty}^{0} K(p_c)\, dp_c \qquad \text{(Eq. 9)}$$

K = the hydraulic conductivity and

p_c = the matric soil water potential.

The model also allows for changes in infiltration due to soil surface crusting, based on work by Smith.

Infiltrated water is available for distribution throughout the soil profile. Unlike PRZM, Opus redistributes water in the root zone with an approach based on physical theory. Opus uses Richards' equation to model water flow in the unsaturated zone:

$$\frac{\delta\Theta}{\delta t} + \frac{\delta q}{\delta z} = e \qquad \text{(Eq. 10)}$$

where

Θ = the volumetric water content

t = time

z = the depth from the surface

q = the flux described by Darcy's law:

$$q = -K(\Theta)\frac{\delta h}{\delta z} \qquad \text{(Eq. 11)}$$

h = the total potential (having gravitational and capillary components)

e = local inflow.

A problem results when trying to solve equation 10 numerically. It is difficult to characterize the local value of hydraulic conductivity between layers. Therefore, the Separable Flux method (Smith, in press) is used. Total flux is divided between gravitational and diffusive flow, which allows for two separate estimates of the local hydraulic conductivity.

To find K and h for a soil, Opus uses a relationship derived by Brooks and Corey (1964). This equation relates soil moisture content to matric potential:

$$\Omega = [1 + (p_c/p_{cb})^{\mu/c}]^{-c} \qquad \text{(Eq. 12)}$$

where

Ω = the normalized volumetric water content,

defined as $\Omega = (\theta - \theta_r)/(\theta_s - \theta_r)$. (Eq. 13)

p_c = the matric soil water potential

p_{cb} = the air entry potential

c = a curve shaping coefficient

μ = a pore size distribution parameter

θ = the volumetric water content

The subscripts r and s stand for residual and saturated, respectively.

The hydraulic conductivity is then determined from

$$K(\theta) = K_s \Omega^{\varepsilon}. \qquad \text{(Eq. 14)}$$

ε is approximated by

$$\varepsilon = (2 + 3\mu)/\mu.$$

Opus estimates soil water transport by coupling these relationships.

Chemical transport is predicted using one of two adsorption models. The first adsorption model assumes instantaneous equilibrium. That is to say, the ratio of solute adsorbed on the soil to that in solution remains constant. The second adsorption model is kinematic in nature. It assumes that solute transfer between the adsorbed and solution phase is proportional to the magnitude between the existing ratio and the equilibrium ratio. These two models use the adsorption assumptions above in a mass balance equation to calculate chemical transport. (For a more detailed explanation, see Smith (in press)).

Potential ET (PET) is found by Opus from a Penman type equation in a scheme derived by Ritchie.

$$PET = (1. + f_w)\ DH_o/(D + 0.68)$$

where

fw = a coefficient related to wind and humidity
D = the slope of the saturation vapor pressure curve at the mean air temperature
$H_o = R_i(1. - \alpha)/58.3$
R_i = the incoming solar radiation
α = the soil surface albedo.

The actual ET is divided between surface evaporation and transpiration. Transpiration is taken from the soil profile in a fashion that is related to matric potential. The higher the matric potential, the less water is taken from that layer of soil.

2. Model Application

Each model incorporates several variables in its input stream which are used for calculation of chemical and water transport. To use a model, appropriate input parameters must be determined. Some parameters are well understood and easily determined from field experiments or laboratory analysis. Some, however, are intangible and may not have any physical meaning. When estimating these variables, modeling becomes a difficult task.

Rao et al. (1979) used a calibration technique to estimate several variables for the models used in their study. They adjusted input variables until model output matched (in a least squares sense) measured data. These "best fit" variables were used as input for the models in different situations. They found that this technique does not always work.

Another method of variable input requires actual measurement of the variable in the field. This method is tedious and often impossible to undertake. Referencing literature is another method of finding approximate variable values. In the present study, both of these methods were used.

We measured field variables that are commonly obtained from field experiments, for example, bulk density, particle size distribution and hydraulic conductivity. The balance of the variable inputs needed for the models were found from literature, mainly the user manuals. This method of determining input information is that most likely to be used by farmers or regulatory agencies who use the models.

The approach is, therefore, realistic. If a farmer or regulatory agency were to employ these models in a particular situation, it is unlikely that the experience or the information would be available to calibrate a model. This approach allows for a comparison of models under a "true" field situation and is intended to show whether or not the models can be useful tools to farmers and regulatory agencies. Relative performance of the models could be different if both were calibrated for a specific situation.

I initially ran PRZM with input parameters that were measured in the field or obtained from literature. I felt that these values may be typical of what a farmer or regulatory agency would use for a similar situation.

After an initial run of PRZM using the above approach, the model was run a second time, adjusting some parameters that influence ET calculations. The parameter initially chosen for adjustment was ANETD. It corresponds to a yearly minimum water depth which is extracted by ET The initial value used was 20cm (7.9in), found from the user's manual. For this geographical area (and for corn) the value seemed too low. Therefore, I increased the value of ANETD to 60cm (23.6in). The output from PRZM did not change.

Carsel et al. (1984) explains that there exists an internally set parameter in PRZM which reduces calculated ET. In order to overcome this internal limitation, calculated daily ET values from the second Opus run were used instead of temperature data. I then adjusted two factors that influenced ET predictions; the pan evaporation coefficient, discussed earlier, and ANETD. By severely altering these parameters, the calculated ET was adjusted to more closely match the estimated potential ET.

Like the initial run of PRZM, I used input parameters that had been measured in the field or obtained from the literature. Opus does not allow for initial conditions to be input for each individual soil layer, but, instead, uses an average value for the whole profile. Therefore, for Opus, I had to simulate conditions prior to the actual measured time period to reproduce the conditions which existed on June

13th. As can be seen from the soil profile plots of moisture content (figure C1), initial conditions were only approximated. This makes it difficult to look at the measured range verses time because the initial condition does not lie within it.

Because Opus does not allow for each individual soil layer to be given initial chemical concentrations, I attempted to simulate the total background mass of bromide present in the profile by applying the initial measured amount to the soil surface before starting the simulation, creating initial conditions which did not fall into the respective measured range.

For a second run of Opus, improvements in model parameter values were suggested by Dr. Roger Smith (member of the Hydro-ecosystems Research Group). Ferreira and Smith (in press) provide a table which gives average values for p_{cb} and μ. Dr. Smith also suggested that we use small values of p_{cb} and larger values of μ (-1mm (0.041in) and 1, respectively) for the gravel layer. So, using arithmetic averaged values from the user's manual (-302mm (-12.33in) for p_{cb} and .378 for μ compared to -99mm (-4.04in) and 0.362 for these same parameters found from a regression equation in the model), Opus simulated the situation again. Initially, Opus overestimated ET, but, for the second run, adjustments were made to the ET parameters in the input file to correct the discrepancy between measured potential and Opus estimated ET.

C. Data Analysis Procedures

When comparing model output to measured data, care must be taken to insure that model output is not compared to data from a situation that the model was not developed to simulate. Both Opus and PRZM were developed to model chemical movement from the surface and through the vadose zone. Both provide outputs of concentration versus depth. Since both models simulate pesticide and water movement through the vadose zone, we chose to compare model output of chemical concentration distribution in the soil to that which was measured. A question arises on how to qualitatively compare measured results with model output.

Martinec and Rango (1989) list three statistical criteria for evaluating model performance. The first is the Nash-Sutcliffe Coefficient, R^2.

$$R^2 = \frac{\sum_{i=1}^{n} (Q_i - Q_i')^2}{\sum_{i=1}^{n} (Q_i - Q_m)^2} \qquad \text{(Eq. 2)}$$

where

Q_i = the measured daily discharge

Q_i' = the computed daily discharge

Q_m = the average measured discharge and

n = the number of daily discharges.

R^2 is also known as the coefficient of determination. The second criterion is the Coefficient of Gain from daily means, DG. The formula is similar to that of R^2, except that Q_m is replaced by Q_{im}. Q_{im} is defined as the average measured discharge from past years for each day of the period. The third criterion is the percent deviation of runoff volumes, D_v, given by:

$$D_v = \frac{V - V'}{V} * 100 \qquad \text{(Eq. 3)}$$

where

V = the measured runoff and

V' = the calculated runoff.

Smith and Ferreira (1988) used graphical techniques when comparing models to one another. They also compared actual numbers output from one model to similar output of another model.

Rao et al. (1979) employed a least squares curve fitting procedure to evaluate the performance of two conceptual models. They measured breakthrough curves in soil columns for two pesticides (2,4-D and Atrazine). This procedure is similar to the first criterion as described by Martinec and Rango (1989) above.

Since the statistical criteria listed by Martinec and Rango (1989) were not designed to evaluate vadose zone transport models, modifications were made to suit our needs. Rename D_v and call it percent difference. Then, let V be the total measured and V' be the total predicted depth of water held in the profile. Total pesticide mass removed from the soil profile and total water stored in the profile were also used for model evaluation. These analyses yielded a quantitative evaluation of the models.

Total chemical mass removed from the soil profile is another way to obtain a qualitative analysis. The total mass lost from the profile can be compared to mass that the model predicts lost. Using the center of mass (com) movement as a guide to the direction of solute movement will allow us to assume which processes are controlling mass loss from the soil profile. Given a hypothetical graph of chemical concentration versus depth (figure 6), the com can be found from the discrete equation

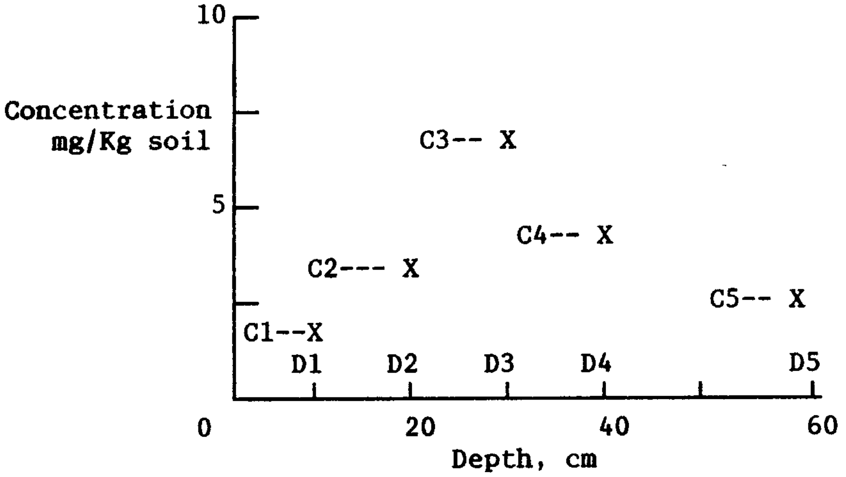
$$\text{com} = \frac{\sum_{1}^{n} D_i C_i}{\sum_{1}^{n} C_i}$$

where

C_i = concentration in layer i

D_i = depth of layer i.

Figure 6: Hypothetical graph of concentration versus depth.



Graphs, as used by Smith and Ferreira (1988), seemed most appropriate for a qualitative analysis. Due to the high variability between measurements taken at different points in the field, it is almost impossible to compare results from the computer models to those from the physical simulation without using statistical descriptions such as a measured range.

III. RESULTS AND DISCUSSION

In this section, measured soil moisture and chemical concentrations are reported and discussed. Results from the initial and second runs of the models are also discussed. Figures are used to illustrate qualitative comparisons between measured data and model results in the soil profile. Table A2 shows D_v for each run.

A. Field Measurements

1. Water Contents

Water content measurements showed little spatial variance. The average value of the coefficient of variation, as defined by Devore (1982), was calculated to be 0.1 for the fifth sampling event. Thus, we are confident that individual measured values adequately represent the true site situation. Median values of measured water content data are listed in table A1.

The total potential ET on both plots was estimated from a water balance on this data. Since water contents in the gravel could not be monitored, we were not able to distinguish between ET and water leached.

2. Bromide

Bromide measurements displayed more spatial variability than moisture measurements. Averaged over the fifth sampling event, the coefficients of variation (spatial) were 0.5 and 0.7 for the north and south plots, respectively. The total bromide mass in the north and south plots varied with time. Table A1 shows the expected mass increase in both plots on June 15th from the bromide application. The table also shows that bromide mass increased in both plots on June 29th and July 17th. The data on these days may be the result of measuring "hot spots" in the field. A hot spot is an area of higher than average concentration. Many processes may cause hot spots, for example, uneven chemical applications or residual chemicals left in the field from previous studies. By August 21st, both plots show a bromide mass loss. We can give a higher degree of reliability to the measured data on this day because more samples at different points on each plot were taken. Since the mass increase between June 13th and 15th shows the bromide application, we can assume the data on these days are reliable. Therefore, we can assume that mass change over the growing season is reasonable (1.2Kg (2.71bs) and 2.3Kg (5.01bs) on the north and south plots respectively).

It is difficult to determine the processes that govern bromide mass loss in this study. Since bromide does not degrade, leaching and plant uptake are the only two processes in which bromide may be removed from the system. Plant uptake on the south plot is not an option, Therefore, all mass lost on the south plot can be attributed to leaching. Bromide concentrations in the corn plants were not determined and bromide concentrations in the gravel layer could not be measured. Center of mass movements were small and yielded little information as to the controlling process of mass loss. Thus, it is impossible to tell which process controls mass loss.

3. Atrazine

Spatially averaged coefficients of variation between atrazine soil samples were 0.3 for the north and 0.5 for the south. Sampling was limited to four, instead of five, occasions due to time and cost of analysis. Four time steps were adequate for the desired comparisons. Table A1 shows measured median concentration of atrazine as a function of time and depth.

Mass of atrazine lost from the north and south plots was 26.5g (0.93oz) and 19.3g (0.68oz), respectively. The com movements of the atrazine profiles were very small. Since no concentration increase was seen at the lower depths, it is assumed that plant uptake and pesticide degradation can be blamed for mass loss.

B. Initial PRZM Run

1. Water

Volumetric water contents are plotted in figures B1 and B4 for the north and south plots, respectively. Since all soil sampling was performed in the morning and the models outputs are for the end of each day (midnight), the previous day's outputs from the model are plotted. Previous day values resemble the actual time of sampling more closely than do the current day model output. PRZM was able to predict the moisture content distribution only on the 15th of June (not plotted). The predicted moisture contents at the lower depths fall into the measured range on June 29th and July 17th, but by August 21st, predictions are well above measured values. The predicted moisture content increases over time, while the measured decreases. This shows that PRZM was unable to estimate the soil moisture trend over the summer.

The percent difference (D_v) between measured and predicted water contents increases in magnitude with time (see table A2 and figure A1). PRZM predicted that more water is stored than measured (211 percent on the north plot and 51 percent on the south plot).

The calculation of ET may be the cause for such large differences. The potential maximum ET for both plots was calculated by subtracting the total depth of water in the profile at the end of the summer from the sum of the initial depth of water in the profile and the total depth of water applied (a water balance). These values are 34.2cm (13.5in) for the north plot and 28.7cm (11.3in) for the south. This initial run of PRZM estimated ET to be 13.9cm (5.5in) and 18.9cm (7.4in) for the north and south plots, respectively. Notice that PRZM estimated higher ET for the fallow (south) plot than for the corn (north) plot. This is contrary to measured values. Intuitively, one would expect higher ET values on the north plot than on the south plot since ET is directly related to crop growth.

2. Bromide

Because the water movement through the vadose zone is not predicted accurately, it follows that chemical transport will not be correctly estimated. Figures B3 and B6 show bromide concentrations as a function of depth and time for measured values and PRZM estimations.

Bromide estimations on the north plot follow measured values up to June 29th. PRZM predicted that most of the bromide moves through the profile, while measured data indicated that bromide stayed in the upper portions of the profile. These assumptions are based on the amount of mass removed from the soil profile, the movement of the com (figure A2 and table A4) and the bromide concentration profile in the soil (figure B3). Estimations on the south plot deteriorate before June 29th. Water movement controls chemical movement. If the water predictions are incorrect, the chemical transport should also be incorrect.

In quantitative terms, measured data show that around 1.2Kg (2.6lbs) bromide were lost from the north plot profile between June 15th and August 21st. PRZM predicted that 1.6Kg (3.52lbs) were removed from the system. Though the estimate is within the range of measured data, the concentration profile is not. The center of bromide mass moved down 2.5cm (1in) between June 15th and August 21st. Calculated com movement from PRZM output suggests that the com moved 12.5cm (4.9in) downward. Table A3 reports the calculated location of the com from PRZM and Opus output as well as from measured data at the various sampling dates. Table A4 shows the respective movements of the com.

Measurements on the south plot show a 2.3Kg (5.0lbs) bromide mass loss between June 15th and August 21st. PRZM predicted that 2.5Kg (5.5lbs) of bromide were lost from the south plot. PRZM's prediction is very close to measured values.

3. Atrazine

Measured values of atrazine in both profiles show that the pesticide stayed in the top 15cm (6in) of the soil. PRZM predicted that the pesticide moved to depths of 30cm (11.8in) (figures B2 and B5) on both plots. This excess movement may have been caused by dispersion and retardation parameters involved in the chemical transport equations.

Measured atrazine lost from the north plot profile was 26.5g (0.93oz). Losses can be attributed to plant uptake and chemical degradation. The data from the south plot indicate that 19.3g (0.63oz) were removed from the soil profile. PRZM predicted 42.5g (1.38oz) and 41.2g (1.45oz) lost from the north and south plots respectively. Again, predicted values are out of the range of measured data. PRZM also predicted that the com moves down 6.2cm (2.4in) and 6.3cm (2.5in) on the north and south plots respectively while measured data indicated very little movement at all. We can not be certain which process (plant uptake or pesticide degradation) in PRZM caused the mass loss.

C. Second PRZM Run

1. Water

Figures D1 and D4 display moisture content versus depth for the second run of PRZM which used adjustments describe earlier. Predictions still do not stay within the measured range as time goes on. Figure A1 shows the percent difference as a function of time. PRZM predictions of total water stored in the profile on the north plot are good until July 17th. On August 21st, PRZM predicted that 59.3 percent more water stored in the profile than measured data indicate. This is an improvement over the 211 percent calculated from the initial run. The percent differences on the south plot grow at a slower rate for the second run compared to the first because of the improved ET estimates, but PRZM still predicts too much water stored.

One would expect predictions and measurements of the total water stored on August 21st to be similar because the altered variables were such that the ET values calculated would closely resemble those estimated from measured water content data. On the north plot, 0.4cm (0.16in) more ET was predicted by PRZM than measured values indicated. The only difference in total water stored on August 21st should be 0.4cm (0.16in). Instead, 2.9cm (1.2in) more water is predicted stored by PRZM. This information tells us that something else is going on in the PRZM water balance. With ET close to the highest potential ET, there should not be sufficient water available for PRZM to predict the high water contents that it does. One would expect PRZM to report a water balance error, but it does not.

2. Bromide

Chemical distribution predictions on the south plot should remain the same as those from the first run of PRZM since there was no change in water movement. Instead, the com was predicted to move down 22.2cm (8.7in). This predicted distance moved is larger than the 14.4cm (5.7in) from the initial PRZM run. Bromide concentrations on the north plot are estimated more closely during the second run. The predicted curve falls in the measured range through June 29th and remains close to the measured minimum throughout the rest of the summer. More bromide was predicted to remain in the upper part of the soil profile than the first run indicated (see figure D3). No concentration increases were seen in the gravel layer from PRZM predictions. Thus, removal of all bromide can be attributed to plant uptake during this run. The predicted com movement was close to the prediction from the first run. Calculated bromide mass removed from the north plot is 2.2Kg (4.8lbs). This value is slightly higher than the PRZM prediction from the first run. Since ET was increased over the first run, this increased mass loss can be assumed to be caused by plant uptake.

3. Atrazine

Mass of atrazine PRZM estimated to be removed from the north plot is 44.3g (1.6oz), up slightly from the first run's prediction of 42.5g (1.5oz), but still out of the measured range. We can see that the pesticide is not lost from leaching (lower depths show no concentration increase and com movement is small, 4.8cm (1.9in)). Evapotransporation increased by twice the value over the initial run. Since plant uptake is proportional to ET in PRZM, one would expect the loss of atrazine to double if plant uptake were the dominant process of atrazine loss. Thus, pesticide degradation can be assumed to be the controlling process of atrazine loss. This inaccuracy could be corrected by adjusting the pesticide decay rate parameter in the input file. I used a half life of 70 days given by Bohmart (1976) which was probably too high for atrazine in soil under the test conditions.

D. Initial Opus Run

1. Water

Figures C1 and C4 describe the relationship between soil depth and volumetric water content for the north and south plots. While the initial condition on the north plot (figure C1) was estimated slightly lower than measured, the percent difference of total water stored ,D_v , is only 10.8 percent (table A2). Opus predicted that the water content in the soil profile decreased with time and at a rate faster than measured (figure C1). By the 21st of August, 14.7 percent difference (0.9cm (0.3in)) can be found between Opus predictions of soil moisture contents and measured median values. The ET prediction from Opus provides a possible reason why the percentage is so low. Total ET estimated by Opus for the north plot is 37.3cm (14.7in), a value 3.1cm (1.2in) higher than the total potential ET (34.2cm (13.5in)) estimated from measured data. Since there was no runoff predicted by Opus, the remaining water was assumed to move upward from the gravel layer below.

Before the initial Opus run was performed for the south plot, we looked at the data from the north plot and noticed that the shape of the soil moisture profile predicted by Opus was not correct. It was too "flat" at the lower depths (see figure C1). The regression represented the particle size distribution that we input into the model but was not accurate for a gravel. So, before the simulation on the south plot was performed, I changed the values of ρ_b and μ for the gravel. This change means that comparisons between management practices on the north and south plot cannot be compared because the two gravel profiles were different. I chose not to re-do the initial run on the north plot to show the effect of the gravel layer on output.

Soil moisture distributions from measured data (south) and Opus simulations are shown in figure C4. They show the same traits as the north plot except that the shape is more correct at greater depths as the end of the growing season approaches. Opus estimated that initial water stored is 10.7 percent less than measured. This percent difference grows over time, but at a slower rate than on the north plot (figure A1). By the end of the growing season, D_r has grown to 18.3 percent. The ET estimated for the south plot is 29.4 cm compared to the potential ET from measured data of 28.7 cm. This and the initial difference accounts for the D_r in total water stored.

Water movement predictions from Opus display the correct trends with measured data. ET predictions are reasonable and correct in relation to one another. In other words, there was less ET from the south plot than from the north.

2. Bromide

In order to test how well the model performs on bromide transport, we will look at the mass of bromide removed from the soil profile and the com movement from the time of application (June 14th) until the end of the season (August 21st).

Opus predicted that -218g (-7.7oz) and 241g (8.5oz) of bromide were removed from the soil profiles of the north and south plot respectively. The negative value indicates a mass gain between June 15th and August 21st. Values are not within the measured range. As can be seen from figures C3 and A2, and table A3, the predicted concentration of bromide on the north plot increases at lower depths and the com in the soil profile moves down 16.7cm (6.6in) to a depth of 24.3cm (9.6in). Bromide on the south plot moves very little (9cm (3.5in)). Since Opus does not simulate plant uptake, the bromide is assumed lost from leaching on the south plot. The mass gain on the north plot was caused by water movement upward from the gravel. Bromide was stored by the model in the gravel layer when the initial conditions were being simulated.

3. Atrazine

Atrazine transport estimates by Opus are shown in figure C2 and C5. Opus was unable to predict the atrazine profile on the north plot. It's predictions on the south plot remained close to the upper confidence interval on the south plot. The graphs show that no atrazine was leached out through the gravel in the actual field or by Opus predictions. Opus predicted concentration profiles show very little com movement (4.1cm (1.6in) and 2.3cm (0.9in) on the north and south plots respectively). We can assume that Opus predicted that atrazine was lost from the profile by pesticide degradation. Opus did transport atrazine to a greater depth on the north plot than measured data indicate.

Quantitatively, 26.7g (0.94oz) of atrazine were transported out of the north plot soil profile. Opus predicted that 28.4g (1oz) were removed. Even though the value is very close to measured data, we are unsure whether or not plant uptake or pesticide degradation is the cause of actual mass loss on the north plot. Opus predicted that 32.2g (1.1oz) of atrazine were lost from the south plot. This value is higher than measured data indicate. Since there are no plants growing on the south plot and there is no leaching, actual pesticide mass loss is due to degradation. With an adjustment of the pesticide decay factor in the model, improved estimates might be obtained.

E. Second Opus Run

1. Water

For the second run, more representative values of p_{cb} and μ were used. The soil albedo and wind coefficient (discussed previously) were adjusted to correct ET estimates. Figure E1 and E4 display the relationship between measured and Opus predicted moisture content profiles. Predicted water content distributions for the north plot were improved over the first run. They tend to remain closer to the measured range. The south plot distributions were similar to the first run. Table A2 shows that by the end of the season the difference between measurements and predictions of total water stored in the profile is approximately 12.2 and 22.9 percent for the north and south plots respectively. These D_v's are comparable to the D_v's from the first run. Since predicted ET's are reasonable, the larger percent difference on the south plot can be attributed to the use of a slightly larger μ value. This value, μ, has a strong effect on the storage capacity of a soil. The higher the magnitude of μ, the less water is stored. The improved D_v on the north plot is a result of a better ET estimate.

2. Bromide

Opus predicted a mass loss on the north plot of 173g (6.1oz), instead of the 218g (7.7oz) gain it predicted in the first run. In this run, no bromide was present in the gravel layer prior to June 15th, so, none was available for movement into the soil profile. The capillary barrier between the soil and gravel was better represented in the second run, which restricted movement between layers. Even though movement of bromide was more restricted, the com moved farther down in the profile. Bromide was also accumulating at the interface between the soil and gravel (see figure E3). The Opus prediction is still not within the measured range of bromide lost from the north plot. Opus does not simulate plant uptake, which could be the cause for the discrepancy between measured and predicted mass loss.

Estimated mass loss and com movement on the south plot increased when compared to the initial run. Measured data indicate that bromide was leached out of the soil profile. Obviously, the capillary barrier in the model is too restrictive. The values of p_{cb} and μ used for the gravel may be too extreme. Because it is next to impossible to measure these parameters for a gravel, they are not usually found in the literature.

3. Atrazine

Figures E2 and E5 show Opus predictions and measured ranges of atrazine concentrations as a function of depth. On the north plot, the predicted concentration profile remains close to the measured range until August 21st. Opus showed that atrazine is transported to a depth of 30cm (11.8in) while measured data indicate that it stays in the top 15 cm. The predicted profile for the south plot stays within the measured range and remains close to it through August 21st.

For the north and south plots respectively, 20.7g (0.73oz) and 33.5g (1.18oz) were lost. Neither value is within the measured range. Opus uses a relationship that is dependent on soil moisture content, organic matter content and soil temperature, to name a few, to estimate pesticide degradation. With the change in ET, moisture contents and soil temperature also change. This is the reason for the difference in atrazine loss between the first and second runs.

IV. CONCLUSIONS

A. Summary

Once again, the main purpose of this study was to determine whether PRZM and Opus could be used as a tool by farmers and the by agencies who provide them technical assistance, as well as regulatory agencies. To reduce the number of complicating factors during field experiments, several steps were ignored that a farmer would normally perform (ie. cultivation and aeration of the soil). We applied slightly less water to the plots than a typical farmer would have. Overall, however, the physical simulation of a real field was accomplished. Corn was grown and harvested. Chemical movement through the soil was measured over the course of a growing season. Input variables used by Opus and PRZM to simulate water and chemical transport through the vadose zone were measured values or those referenced from a convenient source.

Assumptions were made that allowed for a mass balance of the measured chemical concentrations. The total mass stored on June 15th was subtracted from the total mass stored on August 21st. The change in mass was attributed to plant uptake, chemical degradation (in the case of atrazine) and leaching. We hoped to use the com movement to distinguish the main processes controlling mass loss. Unfortunately, the com movement was so small that it provided no insight to the governing mass loss processes. Chemical movement processes simulated by the models were assumed using the output of concentration increases in the gravel layer. If increases were seen in the gravel, leaching in the model could be determined. The models did not provide output to show the mass loss due to pesticide decay or plant uptake (in the case of PRZM).

Both models correctly predicted that no runoff would occur. PRZM incorrectly estimated water and chemical movement through the unsaturated zone when no correction of the evapotranspiration parameters was made. ET predictions for the north plot were low, and they were higher for the south plot where no crop was grown. After correcting for ET, the water balance in PRZM was improved but PRZM still showed percent differences in depth of water stored at various times throughout the growing season for the north plot ranging from 14.0 percent less to 59.3 percent more. A range of 3.4 less to 51 greater percent difference on the south plot was found from predicted values. The model correctly predicted that no atrazine was leached out of the root zone but over predicted the amount of atrazine that was lost. Even when ET was adjusted, PRZM did not estimate the mass of bromide lost from either plot to be within the measured range.

Opus' initial run also used literature and measured values for input. The initial results were comparable to those of the second run using adjusted soil hydraulic and ET parameters. Opus' water balance was reasonable. Percent differences between estimated and measured depth of water stored ranged from 13.1 percent more to 19.8 percent less for the north plot, and from 20.9 percent more to 30.6 percent less for the south plot over the growing season. Evapotranspiration was predicted to be higher on the north plot than on the south. Predicted bromide mass removed from the plots was not within the measured range, but Opus was able to predict that more bromide was lost from the south plot. No atrazine was estimated to be leached from the soil profile, but the mass removed from the plots was not representative of measured values probably due to unrepresentative decay rate values.

Computer model predictions were not always close to measured values at individual depths. The mass of chemicals removed from the north and south plot were not always representative. Possibly, new parameters could be found to allow for better predictions. For example, Brooks and Corey (1964) claim that a fine sand has a p_{cb} equal to -410 mm (-16.73 in) and a μ of 0.37. We used values (for a sandy loam) of p_{cb} equal to -301 mm (-12.29 in) and a μ equal to 0.386, obtained from the Opus User's Manual. If we were to rely on the information from Brooks and Corey, p_{cb} would be larger and μ would be smaller [(-750 mm (-30.61 in) < p_{cb} <-410 mm (-16.73 in)) and ($0.182 < \mu < 0.37$)]. As we have explained before, a smaller μ would allow for more storage. This might improve Opus water results. An analysis with this type of information is included in Appendix F. I did not include it in this text because it involves calibration.

Opus claims that it can show the differences between management practices. PRZM also claims this, as well as several other prediction capabilities. When the appropriate parameters were selected, both models were able to show a correct relationship between ET and management practices (plant growth). Comparing the amount of water stored in the two different plots, both were able to predict that more water was stored in the south soil profile than the north. Measured data indicates that more atrazine was lost from the north plot than from the south, probably due to plant uptake. PRZM showed the same trend. Opus showed the opposite trend, mainly because it does not estimate plant uptake. Because there were no plants on the south plot (thus higher temperatures and more water), Opus predicted pesticide decay to be higher than on the north plot. Measured bromide transport from the south plot was higher than the north plot, most likely due to leaching. Opus and PRZM showed this trend in both runs. Even though they did show the correct trend, it is not possible to determine if the controlling processes for mass removal were correct.

Opus is not ready to be distributed as a modeling package yet. The manual and program are still in the organizational stages. The model and accompanying documentation will be sent to Washington, D.C. for review and publishing in the near future. PRZM is available through the U.S. EPA and has been used by individuals for research purposes. The manual is written comprehensively and is readable, although it does not explain the ET variable requirements well.

B. Conclusion

These results show that in no way are models going to predict exactly what happens in every field situation. They sometimes yield results that are representative and at other times may produce results which do not represent the true system response. Models should not be relied upon to predict reality.

As far as being used as a tool by the farmer and regulatory agencies, both models are fairly easy to run, but, easy operation of a model does not necessarily mean that the results it provides are useful. Modeling should be left to experts who have an excellent understanding of all processes involved in the vadose zone. This includes soil physics, plant development and chemical processes. A person with an average understanding might get the model to run, but the reliability in the results to predict actual processes will be low. However, these models did show the differences of management practices on water storage, evapotranspiration and bromide loss. In this capacity, they may assist a farmer or regulator.

It was mentioned in the introduction that some people are considering the use of models to determine potential groundwater pesticide contamination. At least in this situation, the models were only able to predict the relative movement between the two chemicals. That is to say, they predicted that bromide is much more mobile in the soil than atrazine. They were not able to correctly predict the movement (magnitude and/or direction) of the corn. These results raise doubts in the models' abilities to predict actual field events. A particular model may unjustly predict the leaching hazards of a pesticide. A more reasonable approach would be to use models in conjunction with measured data. In this capacity, models may be useful to regulatory agencies.

C. Recommendations

In the future, the following suggestions may help. Measure all the physical parameters required for the input file. Measure chemical concentrations in a manner that will allow the determination of the mass loss processes. Given some of the measured input variables, have another person who has no knowledge of the measured results run the models . Have "experts" do the same and compare the results. Perform the same type of study on an actual field for a longer period of time.

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APPENDIX A.

This section contains tables of measured data, percent differences between measured soil moisture contents and model predictions, center of mass locations and center of mass movements.

Table A1: Measured values of water content (cm^3/cm^3), atrazine concentration (mg/Kg soil) and bromide concentration (mg/Kg soil) related to depth and time.

North Plot June 13, 1989

Depth cm From	to	Water Cont. cm^3/cm^3	Atrazine Soil Conc. mg/Kg soil	Bromide Soil Conc. mg/Kg soil
0.0	7.6	20.8	0.0	7.4
7.6	15.2	25.2	0.0	12.1
15.2	22.9	28.2	0.0	8.7
22.9	30.5	31.2	NM	10.5
30.5	38.1	30.6	NM	18.4
38.1	45.7	29.5	NM	43.1
Total stored		12.6cm	0.0g	1401.4g

North Plot June 15, 1989

Depth cm From	to	Water Cont. cm^3/cm^3	Atrazine Soil Conc. mg/Kg soil	Bromide Soil Conc. mg/Kg soil
0.0	7.6	15.4	3.4	87.9
7.6	15.2	32.2	0.9	35.0
15.2	22.9	29.0	0.0	19.8
22.9	30.5	27.2	0.0	33.3
30.5	38.1	29.5	NM	45.3
38.1	45.7	27.7	NM	80.3
Total Stored		12.3cm	60.1g	4217.1g

Table A1 continued.

North Plot June 29, 1989

Depth cm		Water Cont.	Atrazine Soil Conc.	Bromide Soil Conc.
From	to	cm^3/cm^3	mg/Kg soil	mg/Kg soil
0.0	7.6	20.5	NM	54.4
7.6	15.2	27.5	NM	52.7
15.2	22.9	30.6	NM	12.5
22.9	30.5	25.4	NM	14.0
30.5	38.1	29.3	NM	31.9
38.1	45.7	27.7	NM	73.2
Total Stored		12.3cm		3338.4g

North Plot July 17, 1989

Depth cm		Water Cont.	Atrazine Soil Conc.	Bromide Soil Conc.
From	to	cm^3/cm^3	mg/Kg soil	mg/Kg soil
0.0	7.6	17.2	2.9	117.7
7.6	15.2	19.3	0.0	97.6
15.2	22.9	22.1	0.0	65.9
22.9	30.5	20.8	0.0	34.9
30.5	38.1	26.2	0.0	34.1
38.1	45.7	29.9	0.0	71.5
Total Stored		10.3cm	39.9g	5897.8g

North Plot August 21, 1989

Depth cm		Water Cont.	Atrazine Soil Conc.	Bromide Soil Conc.
From	to	cm^3/cm^3	mg/Kg soil	mg/Kg soil
0.0	7.6	15.7	2.4	6.4
7.6	15.2	9.4	0.0	68.5
15.2	22.9	11.3	0.0	32.5
22.9	30.5	8.0	0.0	5.7
30.5	38.1	13.9	0.0	48.2
38.1	45.7	17.3	NM	53.2
Total Stored		5.8cm	33.6g	2999.9g

Table A1 continued.

South Plot June 13, 1989

Depth cm From	to	Water Cont. cm^3/cm^3	Atrazine Soil Conc. mg/Kg soil	Bromide Soil Conc. mg/Kg soil
0.0	7.6	19.0	0.0	8.3
7.6	15.2	28.6	0.0	8.7
15.2	22.9	31.6	0.0	12.6
22.9	30.5	31.5	0.0	15.5
30.5	38.1	30.6	0.0	19.5
38.1	45.7	31.4	0.0	46.7
Total Stored		13.2cm	0.0g	1556.6g

South Plot June 15, 1989

Depth cm From	to	Water Cont. cm^3/cm^3	Atrazine Soil Conc. mg/Kg soil	Bromide Soil Conc. mg/Kg soil
0.0	7.6	13.8	2.9	127.5
7.6	15.2	20.4	0.9	28.4
15.2	22.9	28.3	0.0	21.2
22.9	30.5	28.3	0.0	25.4
30.5	38.1	30.1	0.0	47.5
38.1	45.7	29.0	0.0	88.2
Total Stored		11.4cm	52.4g	4730.0g

South Plot June 29, 1989

Depth cm From	to	Water Cont. cm^3/cm^3	Atrazine Soil Conc. mg/Kg soil	Bromide Soil Conc. mg/Kg soil
0.0	7.6	21.8	NM	122.8
7.6	15.2	20.4	NM	81.0
15.2	22.9	28.3	NM	32.4
22.9	30.5	28.3	NM	30.0
30.5	38.1	30.1	NM	53.4
38.1	45.7	29.0	NM	99.5
Total Stored		12.0cm		5861.4g

Table A1 continued.

South Plot July 17, 1989

Depth cm From	to	Water Cont. cm^3/cm^3	Atrazine Soil Conc. mg/Kg soil	Bromide Soil Conc. mg/Kg soil
0.0	7.6	15.9	2.7	139.7
7.6	15.2	22.9	0.0	53.0
15.2	22.9	29.6	0.0	25.7
22.9	30.5	30.7	0.0	34.0
30.5	38.1	30.7	0.0	59.5
38.1	45.7	28.7	0.0	66.1
Total Stored		12.1cm	37.8g	5286.6g

South Plot August 21, 1989

Depth cm From	to	Water Cont. cm^3/cm^3	Atrazine Soil Conc. mg/Kg soil	Bromide Soil Conc. mg/Kg soil
0.0	7.6	17.6	1.8	18.8
7.6	15.2	20.9	0.6	44.1
15.2	22.9	27.4	0.0	54.0
22.9	30.5	30.2	0.0	30.3
30.5	38.1	28.6	0.0	19.2
38.1	45.7	31.0	0.0	9.6
Total Stored		11.9cm	33.1g	2461.5g

Table A2: Percent difference between measured moisture contents and predicted moisture contents.

Results from the initial run on north plot.

	PRZM		Opus	
Date	Previous	Current	Previous	Current
06/13/89	2.5	4.0	10.8	13.3
06/15/89	2.7	4.0	18.2	25.8
06/29/89	-31.8	-32.0	36.5	38.1
07/17/89	-56.0	-52.3	60.6	65.0
08/21/89	-211.1	-211.1	14.7	10.9

Table A2 continued.

Results from the initial run on south plot.

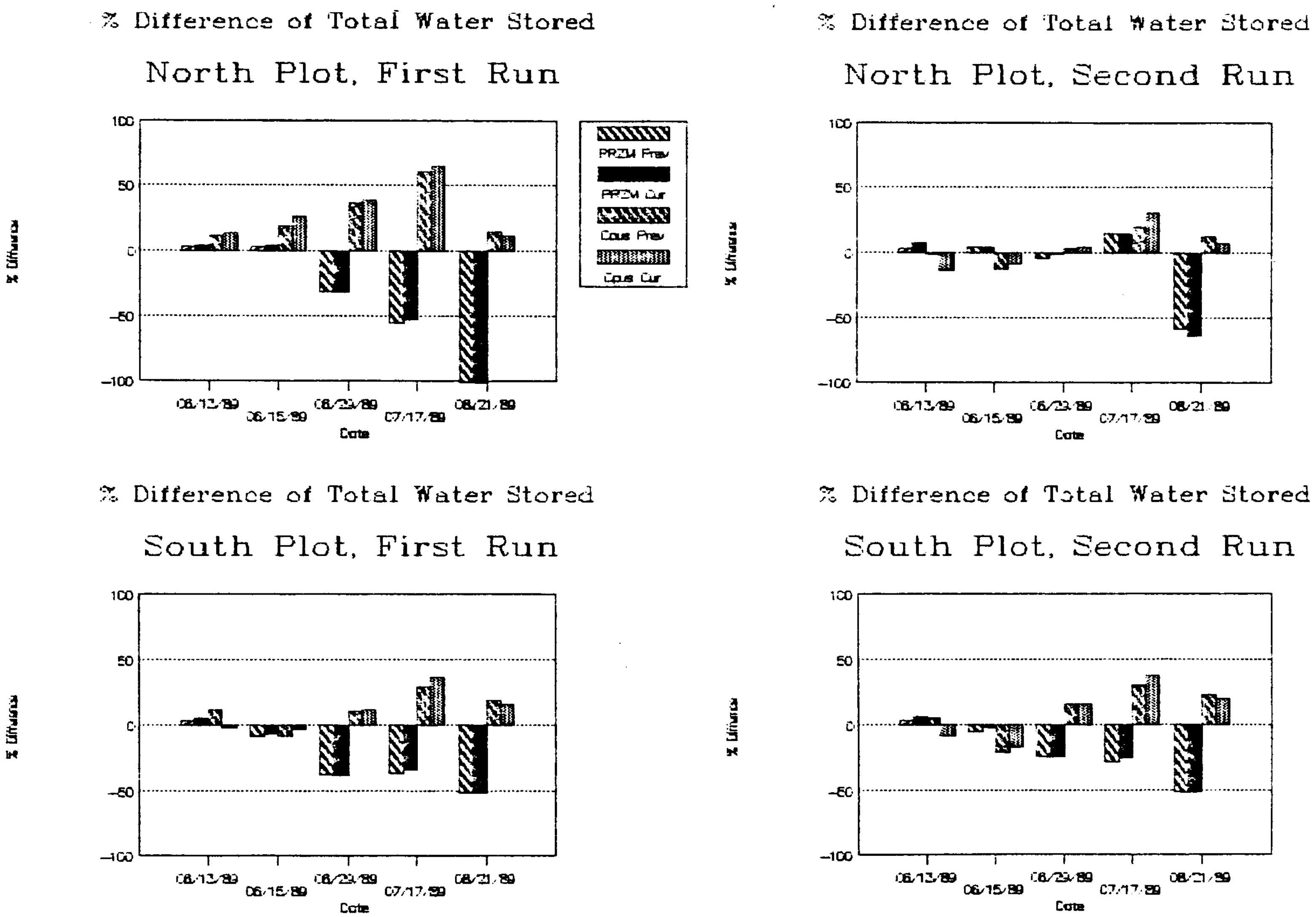
	PRZM		Opus	
Date	Previous	Current	Previous	Current
06/13/89	3.4	4.7	10.7	-2.2
06/15/89	-8.5	-7.0	-8.5	-3.7
06/29/89	-38.1	-38.4	10.1	10.8
07/17/89	-37.2	-33.9	29.6	36.7
08/21/89	-51.1	-51.1	18.3	15.2

Results from the second run on the north plot.

	PRZM		Opus	
Date	Previous	Current	Previous	Current
06/13/89	2.5	6.8	-1.5	-14.2
06/15/89	4.2	4.2	-13.1	-9.1
06/29/89	-4.5	-1.7	2.6	3.7
07/17/89	14.0	14.0	19.8	29.7
08/21/89	-59.3	-63.9	12.2	7.0

Results from the second run on the south plot.

	PRZM		Opus	
	Previous	Current	Previous	Current
06/13/89	3.4	5.8	4.5	-8.1
06/15/89	-5.6	-2.7	-20.9	-17.2
06/29/89	-24.1	-23.9	15.1	15.4
07/17/89	-28.2	-25.7	30.6	37.7
08/21/89	-51.0	-51.1	22.9	19.7



% Difference of Total Water Stored

North Plot, First Run

% Difference of Total Water Stored

North Plot, Second Run

% Difference of Total Water Stored

South Plot, First Run

% Difference of Total Water Stored

South Plot, Second Run

Figure A1: Calculated percent differences between measured average moisture stored and moisture stored as calculated from model predictions. Prev stands for the previous day's output and Cur stands for the current day's output.

Table A3: Center of mass locations from measured mass averages and predicted atrazine and bromide soil concentrations.

Location (cm from surface) of the center of mass of bromide and atrazine on the north plot. The number 1 signifies results from the initial run while the number two represents the second run.

	Bromide 1			Bromide 2		
Date	PRZM	Meas	Opus	PRZM	Meas	Opus
06/15/89	-16.8	-26.8	-7.6	-16.8	-26.8	-10.2
06/29/89	-21.8	-27.2	-11.1	-22.2	-27.2	-21
07/17/89	-23.5	-22.6	-17.9	-23.9	-22.6	-31.8
08/21/89	-31.2	-29.3	-24.3	-30.3	-29.3	-37.6

	Atrazine 1			Atrazine 2		
Date	PRZM	Meas	Opus	PRZM	Meas	Opus
06/15/89	-7.6	-9.3	-7.6	-7.6	-9.3	-7.6
07/17/89	-10.3	-7.6	-8.7	-10.6	-7.6	-9.1
08/21/89	-13.8	-7.6	-11.7	-12.4	-7.6	-12

Location (cm from surface) of the center of mass of bromide and atrazine on the south plot. The number 1 signifies results from the initial run while the number two represents the second run.

	Bromide 1			Bromide 2		
Date	PRZM	Meas	Opus	PRZM	Meas	Opus
06/15/89	-17.7	-25.1	-13.4	-17.7	-25.1	-10.8
06/29/89	-32.2	-24.8	-18.5	-31.1	-24.8	-23.8
07/17/89	-32.5	-23.2	-14.9	-34.4	-23.2	-19.9
08/21/89	-35.6	-23.5	-22.4	-39.9	-23.5	-26.4

	Atrazine 1			Atrazine 2		
Date	PRZM	Meas	Opus	PRZM	Meas	Opus
06/15/89	-7.6	-9.4	-7.6	-7.6	-9	-7.6
07/17/89	-10.5	-7.6	-8.4	-12.9	-7.6	-9.8
08/21/89	-13.9	-9.6	-9.9	-18.8	-9.5	-11.8

Table A4: Distance moved (cm) by the center of mass from June 15, 1989 to August 21, 1989. Positive numbers indicate downward movement while negative numbers indicate upward movement.

	Bromide 1			Bromide 2		
	PRZM	Meas	Opus	PRZM	Meas	Opus
North Plot	-14.4	-2.5	-16.7	-13.5	-2.5	-27.4
South Plot	-17.9	1.6	-9.0	-22.2	1.6	-15.6

	Atrazine 1			Atrazine 2		
	PRZM	Meas	Opus	PRZM	Meas	Opus
North Plot	-6.2	1.7	-4.1	-4.8	1.7	-4.4
South Plot	-6.3	-0.2	-2.3	-11.2	-0.5	-4.2

Table A5: Water balance data from model predictions and measured data. All values are in cm of water. The numbers 1 and 2 siginify the first run and second runs, respectively.

	PRZM				Measured		Opus			
cm of	N1	N2	S1	S2	N	S	N1	N2	S1	S2
Total Water Applied	28.2	28.2	28.2	28.2	28.2	28.2	28.2	31.7	28.2	31.2
Est. ET	13.9	34.6	18.9	27.7	34.2	28.7	37.3	34.7	29.4	27.6
Stored 6/13/89	12.3	12.3	12.7	12.7	12.3	12.7	11.2	12.8	11.7	12.6
Stored 8/21/89	17.9	9.2	17.9	17.9	6.3	12.2	4.9	5.1	9.7	9.1
Balance	8.7	-3.3	4.1	-4.7	0.0	0.0	-2.8	4.7	0.8	7.1

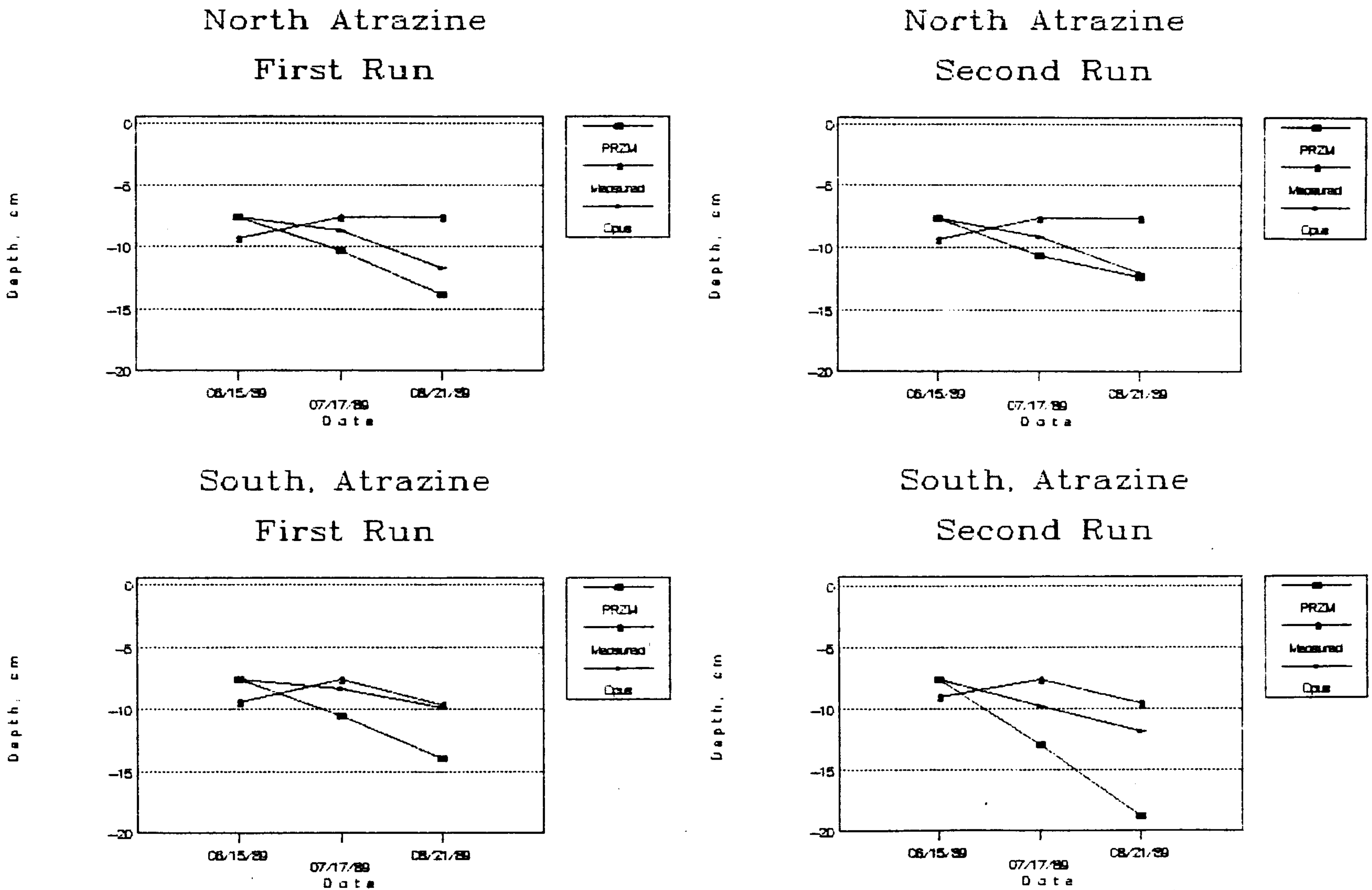


Figure A2: Calculated depth of the center of atrazine mass as a function of time from Opus, PRZM and measured data for the first and second runs.

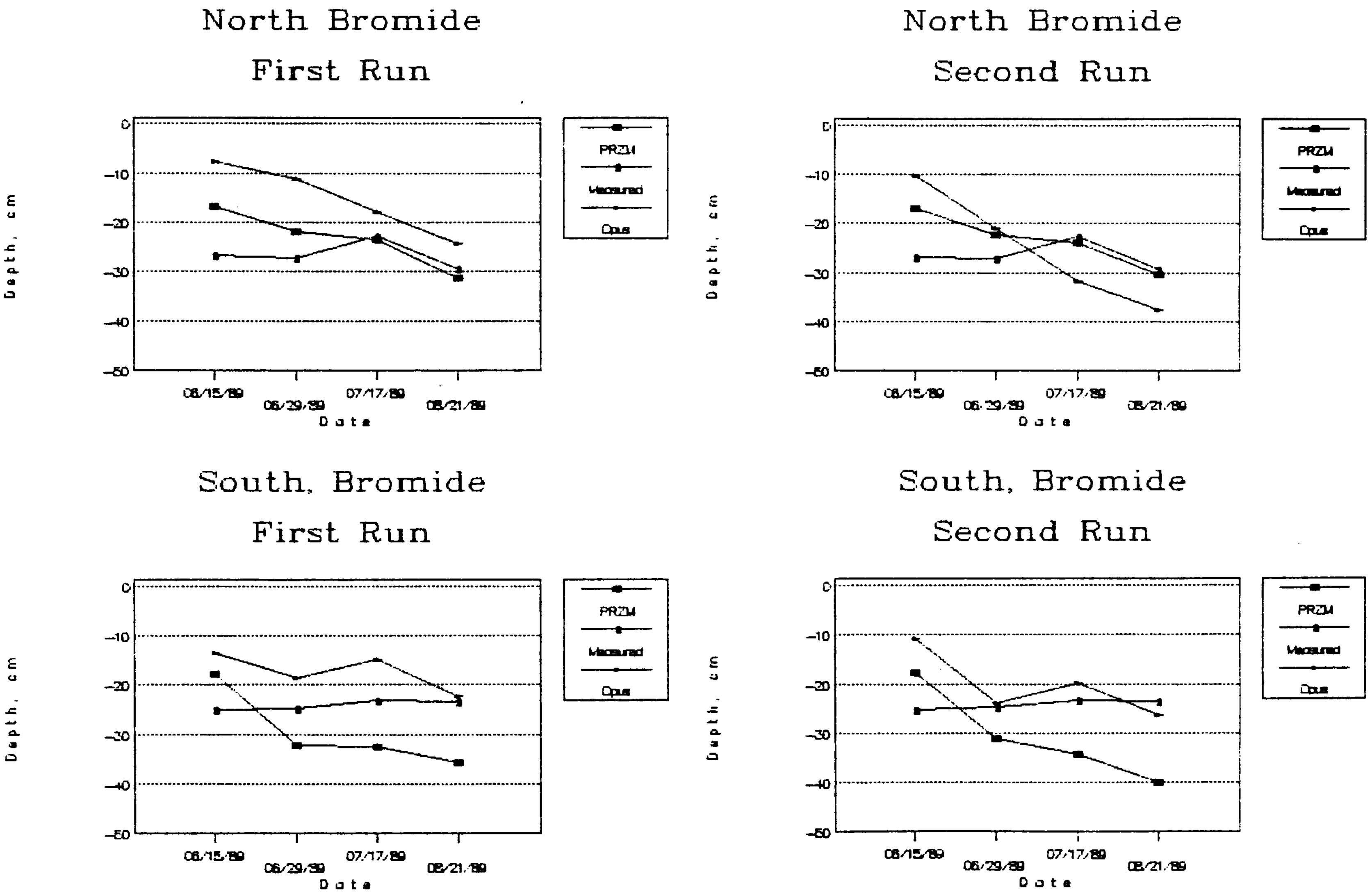


Figure A3: Calculated depth of the center of bromide mass as a function of time from Opus, PRZM and measured data for the first and second runs.

APPENDIX B

This section contains graphs which show the relationship between predictions from PRZM's initial run and measured data. The initial run is defined in the text. Moisture content, atrazine and bromide concentrations as a function of depth and time are graphed. Depicted in each graph are the upper and lower confidence intervals from measured data and PRZM output. The horizontal axis is soil depth in centimeters. The vertical axis is either volumetric water content or chemical concentration. All chemical concentrations have the units of milligrams of chemical per kilogram of dry soil.

Legend Definition

Maximum value from measured data.

Max

Minimum value from measured data.

Min

PRZM prediction from the previous day's calculations.

PRZM

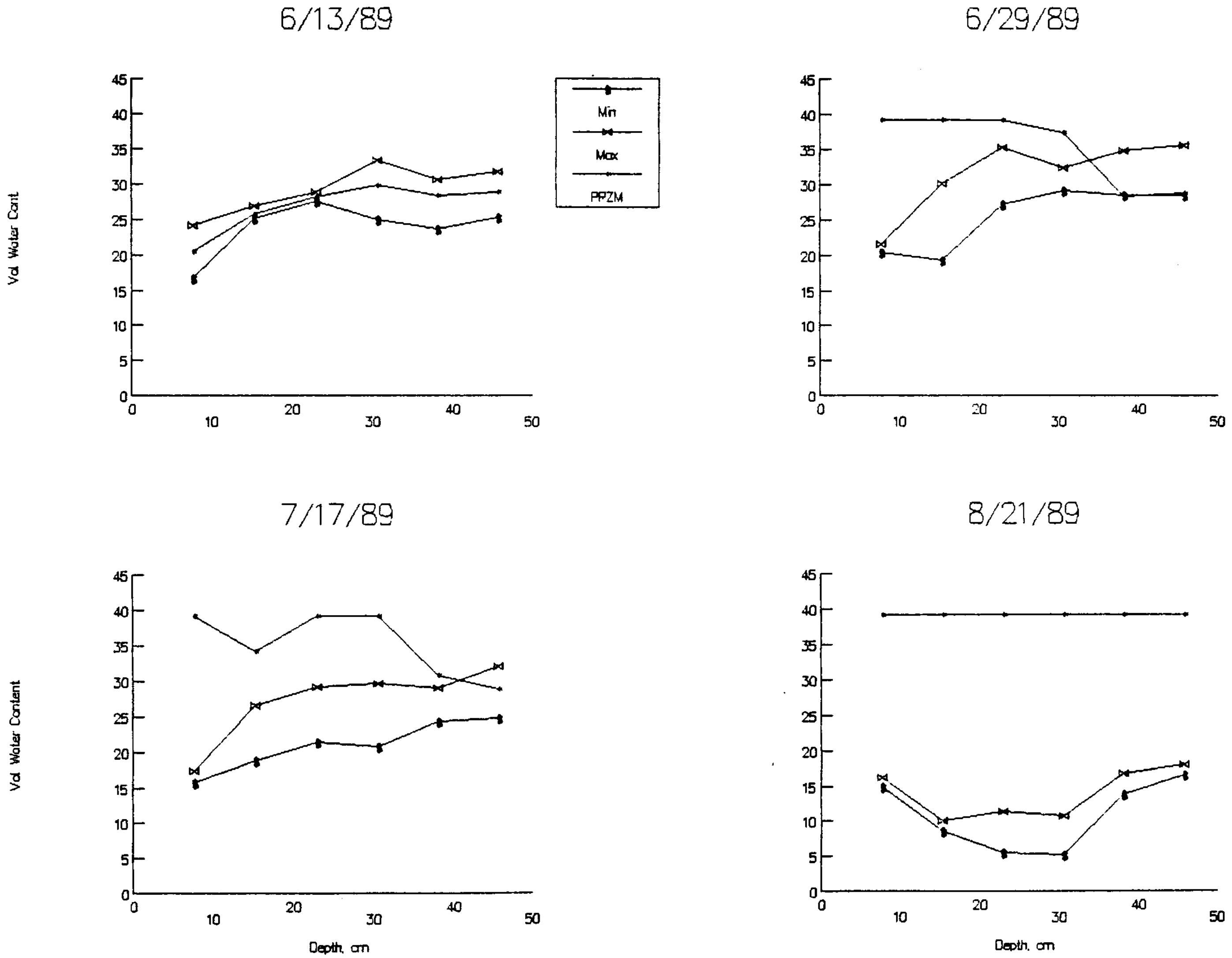


Figure B1: Volumetric water content on the north plot as a function of depth and time. Maximum and minimum measured values and the initial PRZM run predictions are displayed.

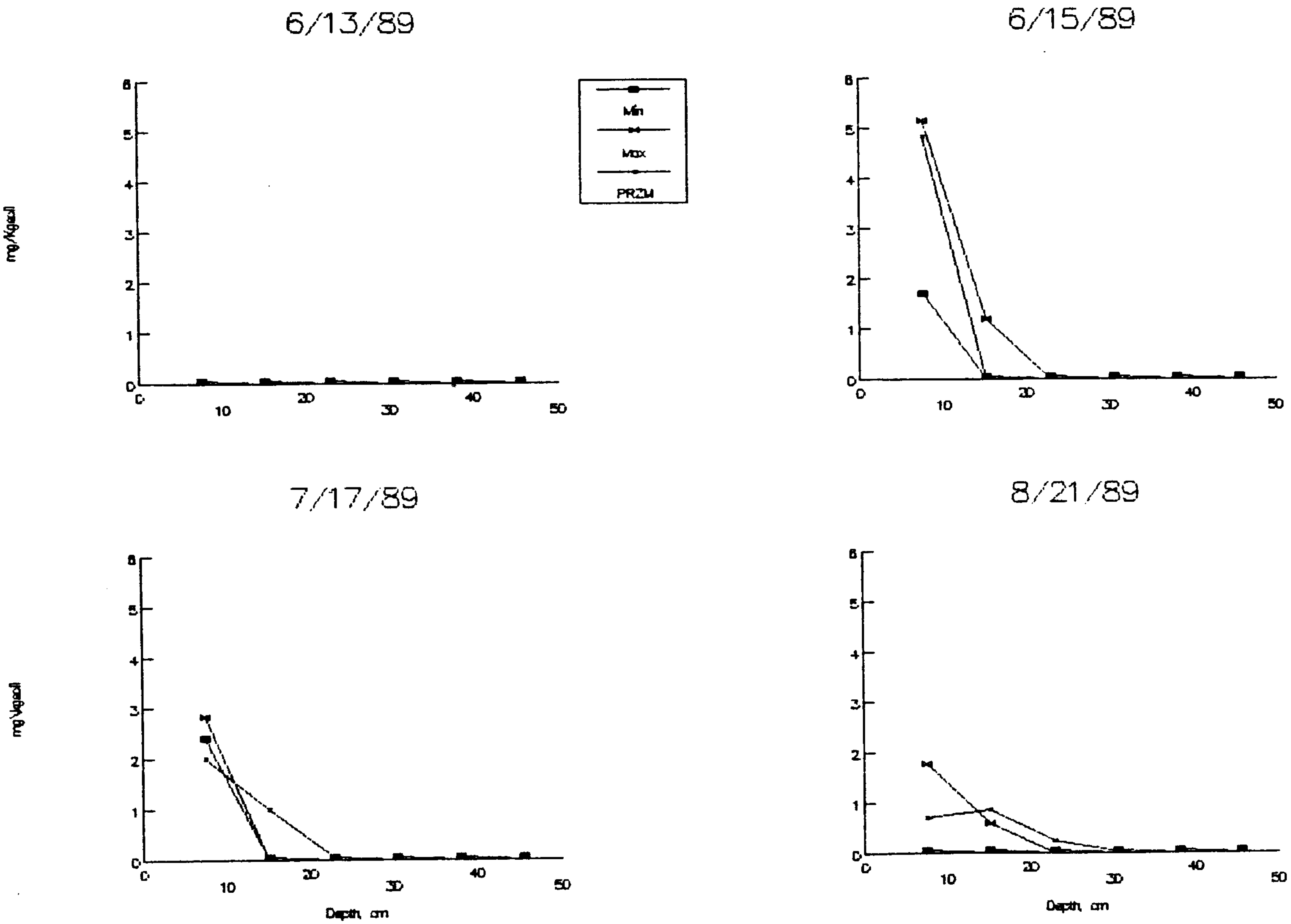


Figure B2: Atrazine concentrations on the north plot as a function of depth and time. Maximum and minimum measured values and the initial PRZM run predictions are displayed.

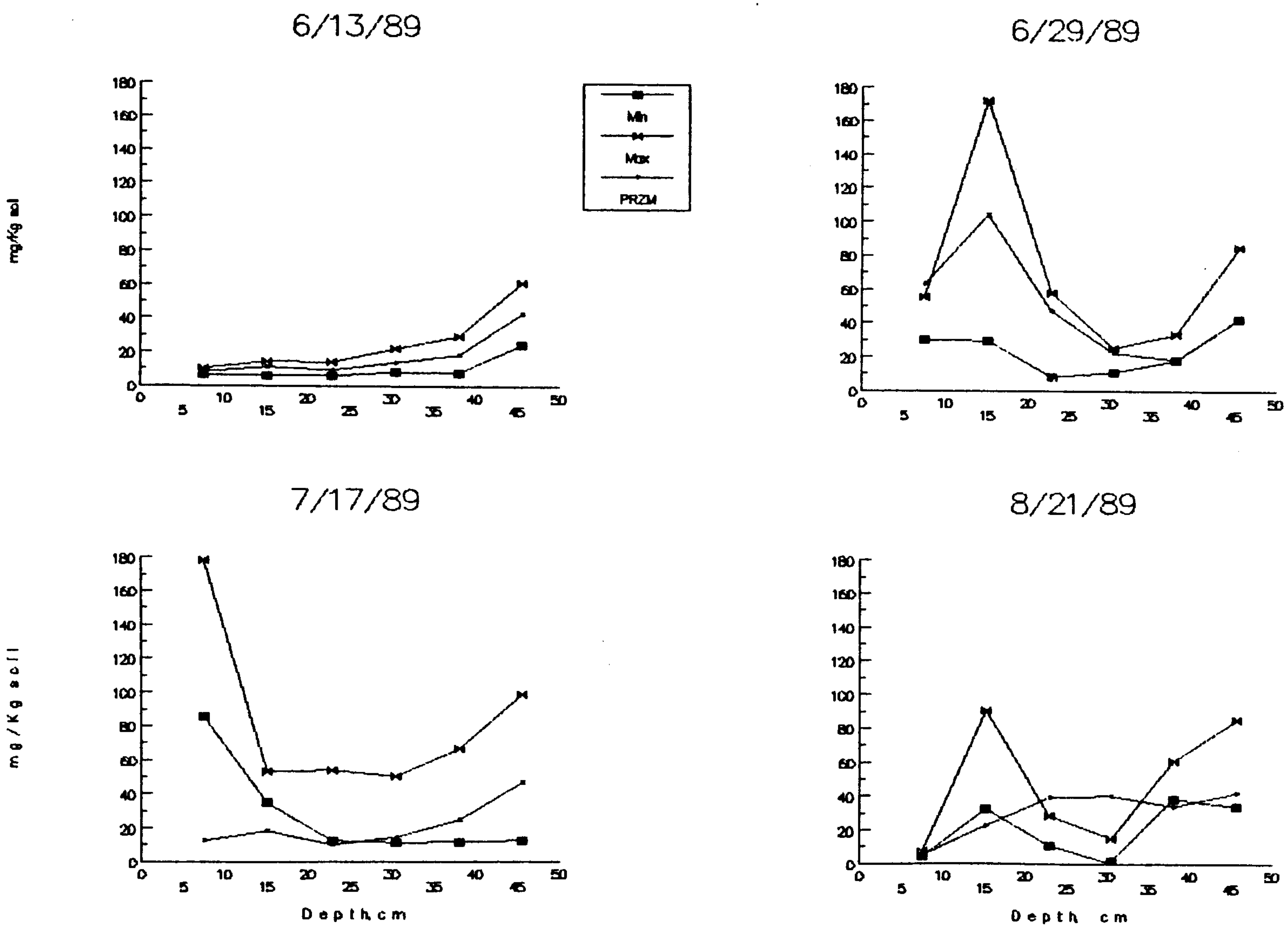


Figure B3: Bromide concentrations on the north plot as a function of depth and time. Maximum and minimum measured values and the initial PRZM run predictions are displayed.

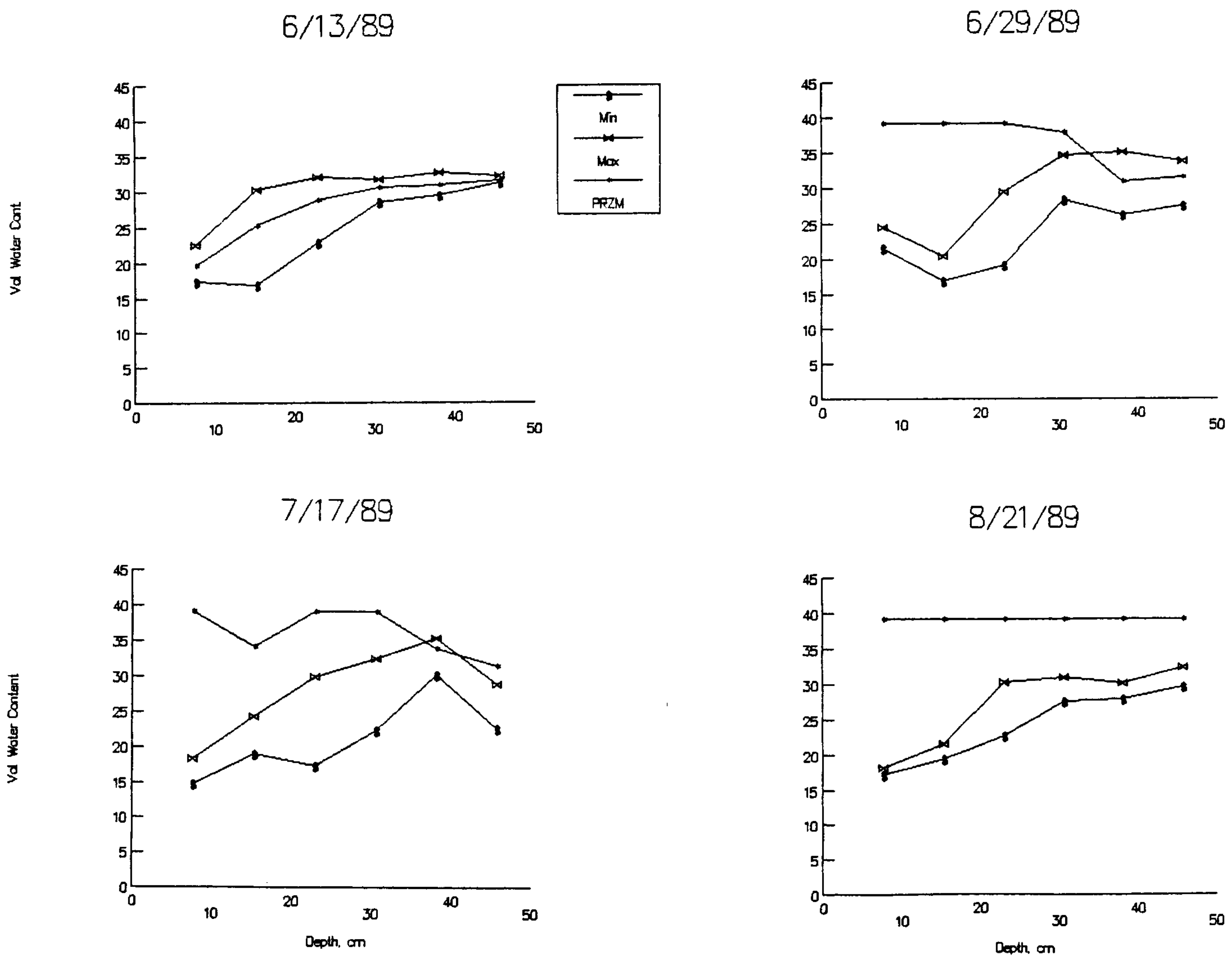


Figure B4: Volumetric water content on the south plot as a function of depth and time. Maximum and minimum measured values and the initial PRZM run predictions are displayed.

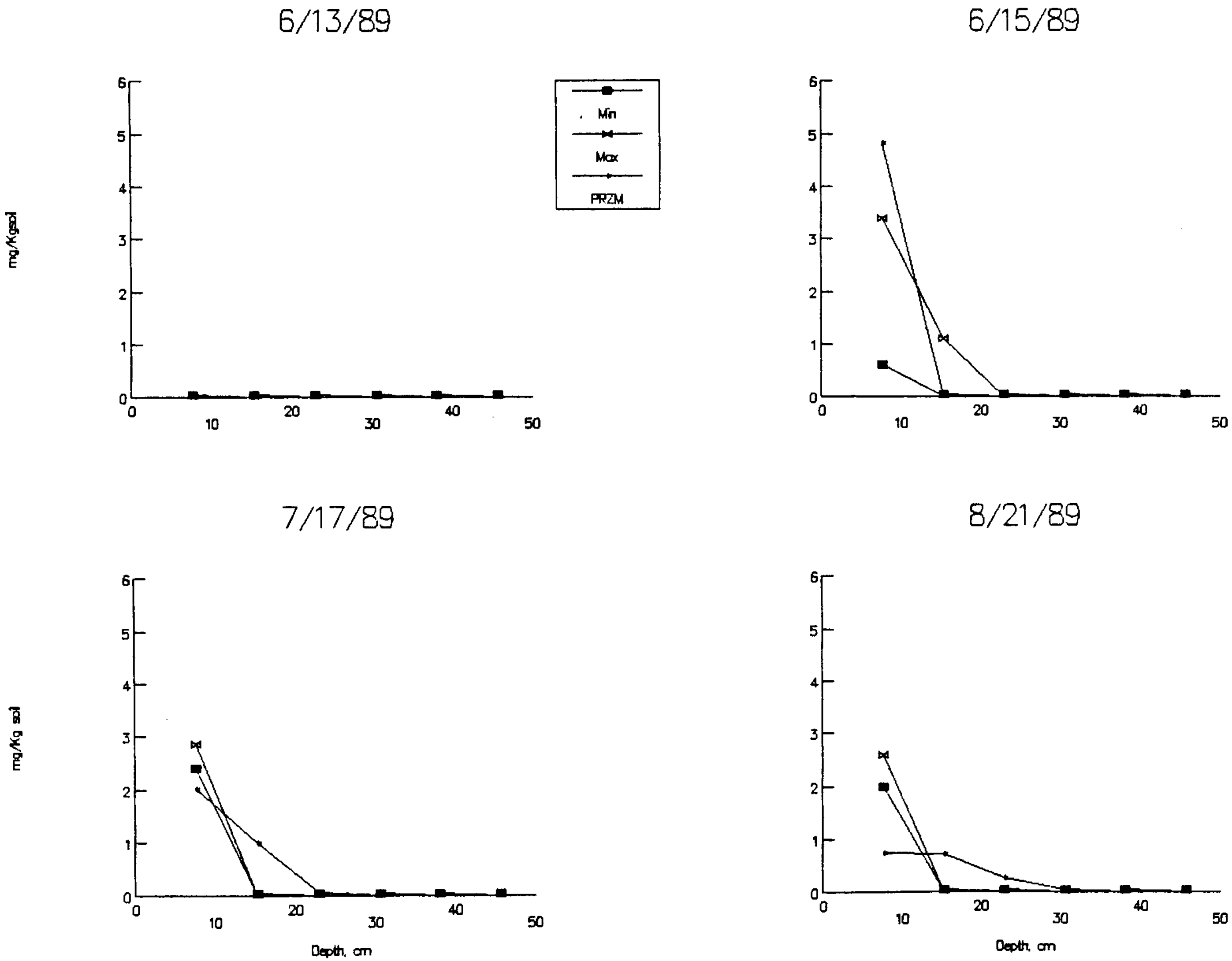
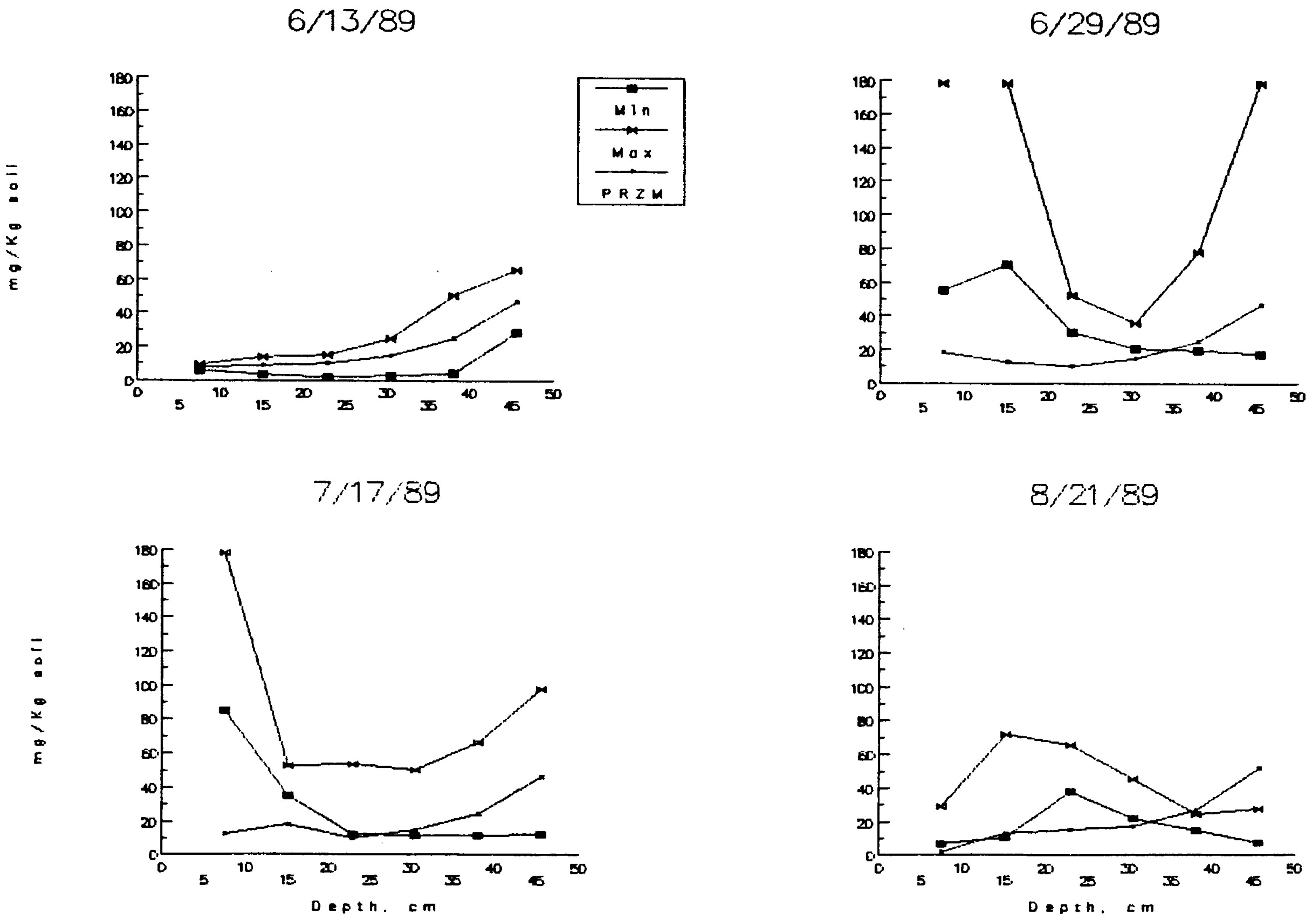


Figure B5: Atrazine concentrations on the south plot as a function of depth and time. Maximum and minimum measured values and the initial PRZM run predictions are displayed.


6/13/89

6/29/89

7/17/89

8/21/89

Figure B6: Bromide concentrations on the south plot as a function of depth and time. Maximum and minimum measured values and the initial PRZM run predictions are displayed.

APPENDIX C

This section contains graphs which show the relationship between predictions from Opus's initial run and measured data. The initial run is defined in the text. Moisture content, atrazine and bromide concentrations as a function of depth and time are graphed. Depicted in each graph are the upper and lower confidence intervals from measured data and Opus output. The horizontal axis is soil depth in centimeters. The vertical axis is either volumetric water content or chemical concentration. All chemical concentrations have the units of milligrams of chemical per kilogram of dry soil.

Legend Definition

Minimum value from measured data.

Min

Maximum value from measured data.

Max

Opus prediction from the previous day's calculations.

Opus

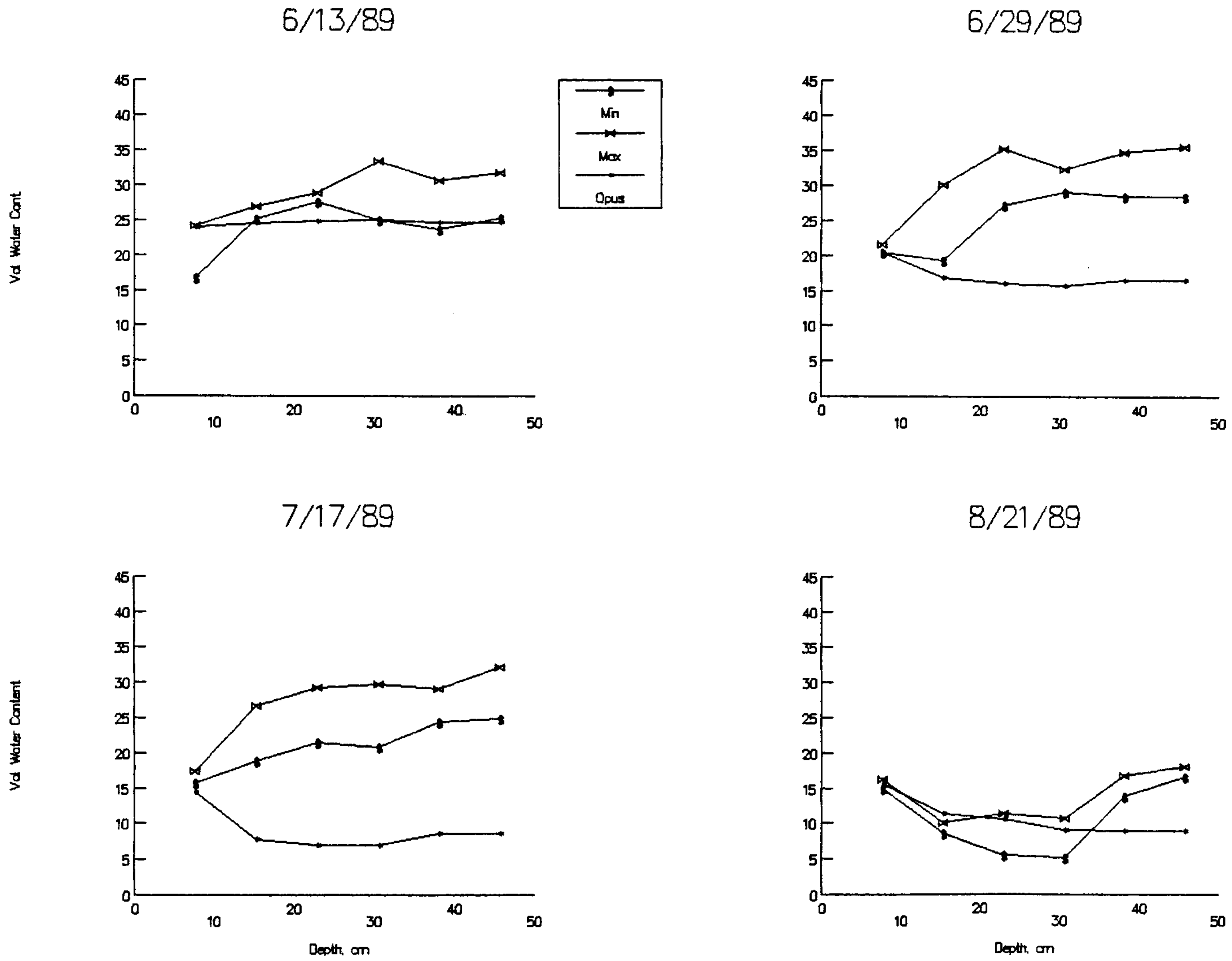


Figure C1: Volumetric water content on the north plot as a function of depth and time. Maximum and minimum measured values and the initial Opus run predictions are displayed.

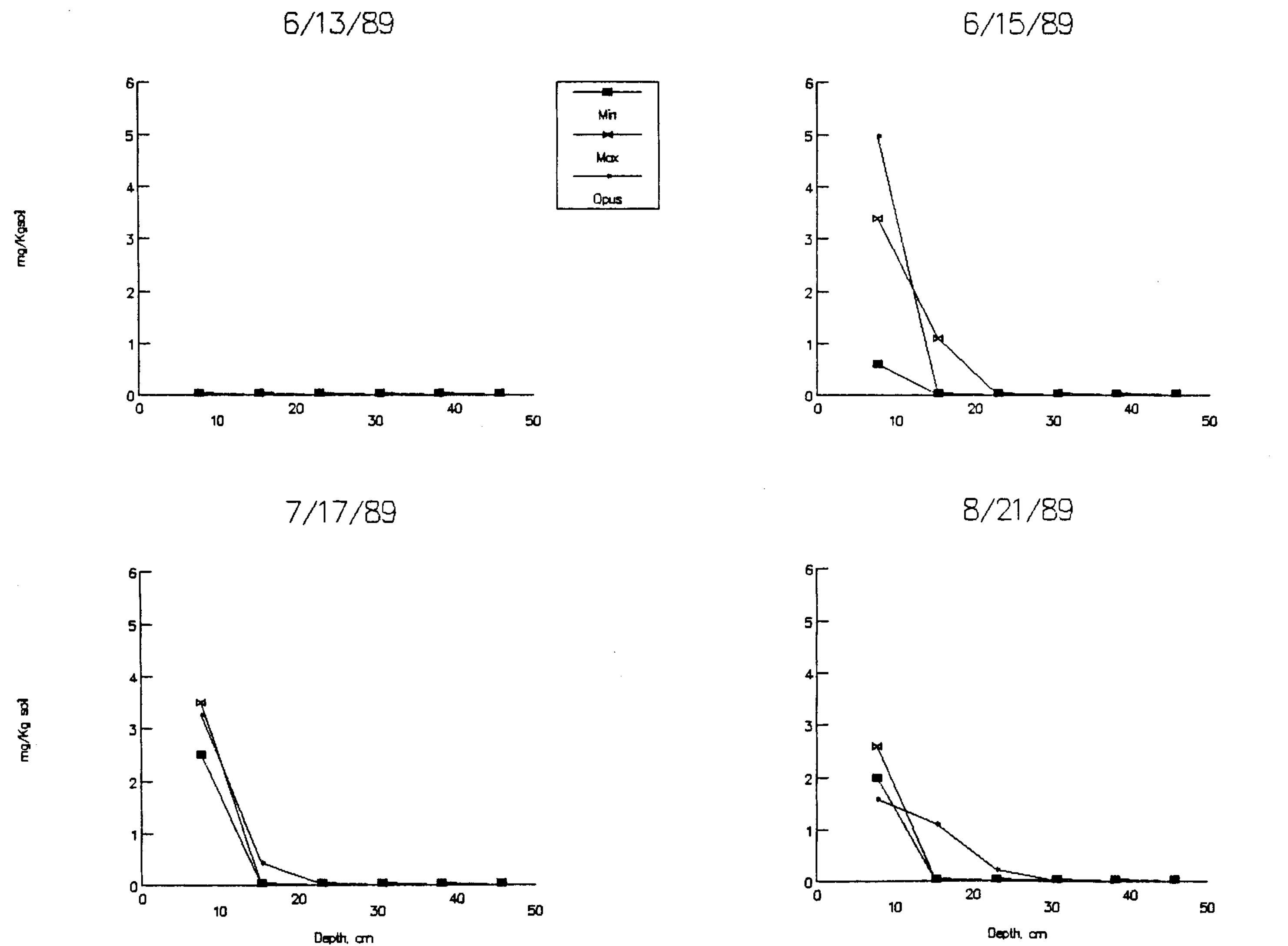


Figure C2: Atrazine concentrations on the north plot as a function of depth and time. Maximum and minimum measured values and the initial Opus run predictions are displayed.

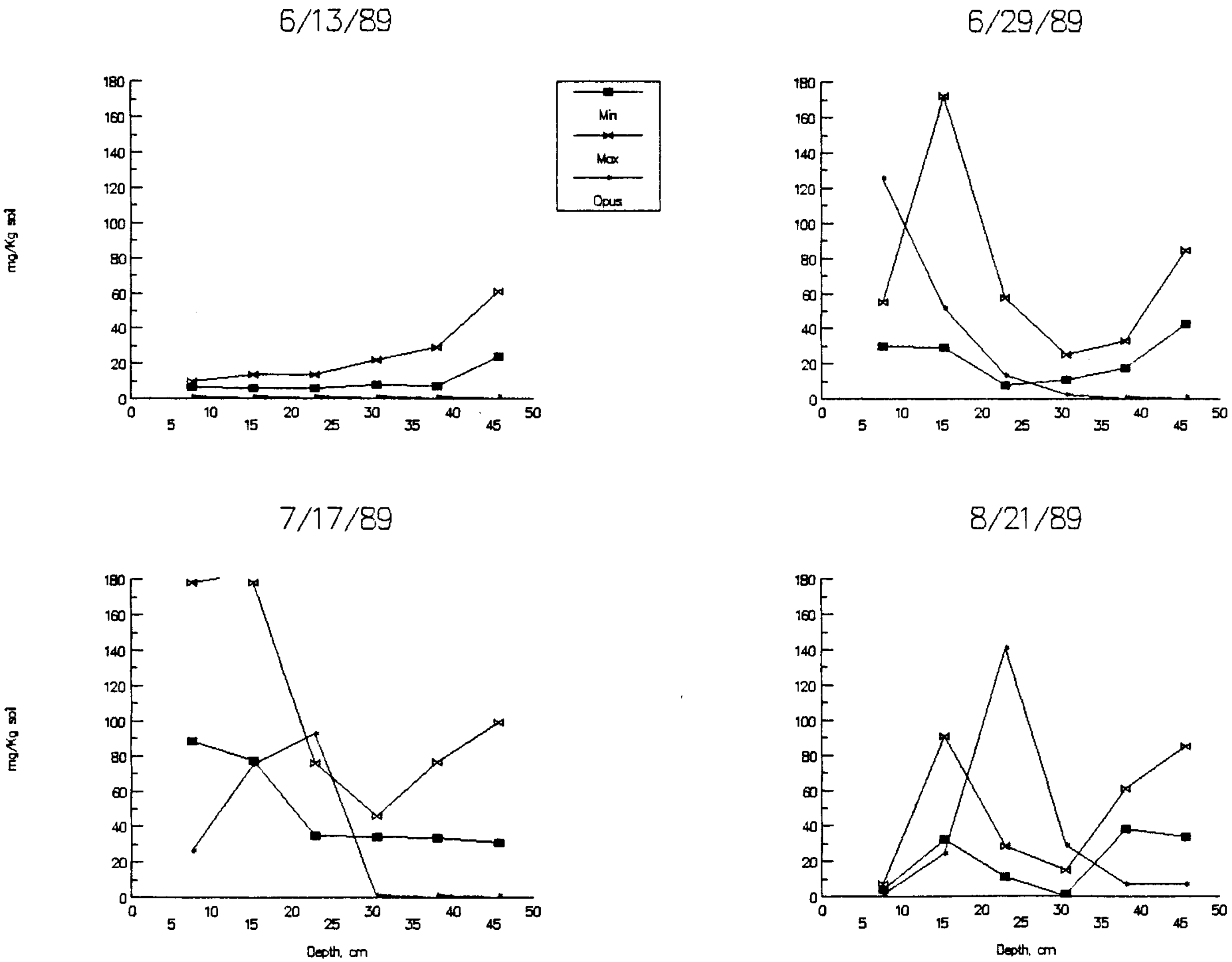


Figure C3: Bromide concentrations on the north plot as a function of depth and time. Maximum and minimum measured values and the initial Opus run predictions are displayed.

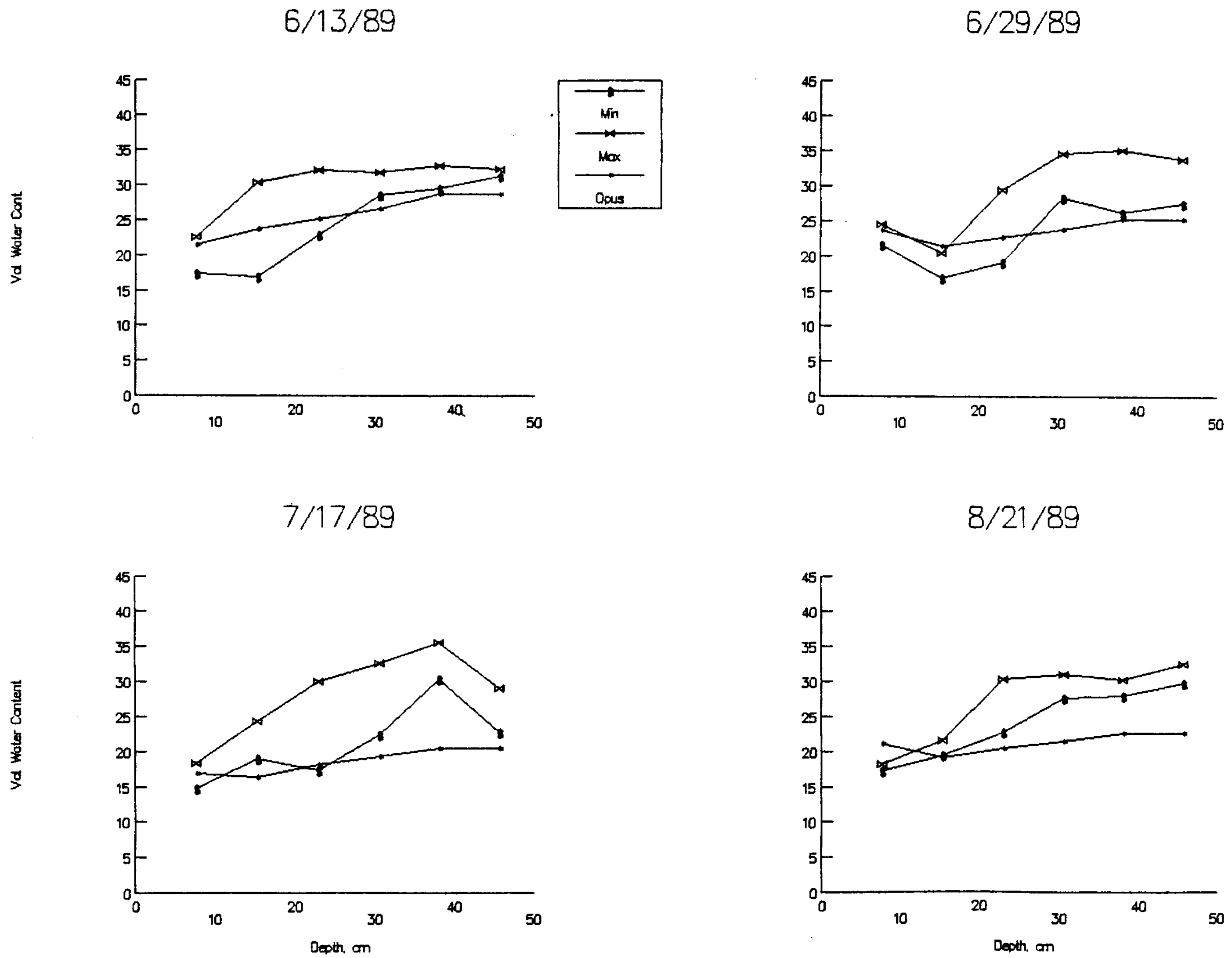


Figure C4: Volumetric water content on the south plot as a function of depth and time. Maximum and minimum measured values and the initial Opus run predictions are displayed.

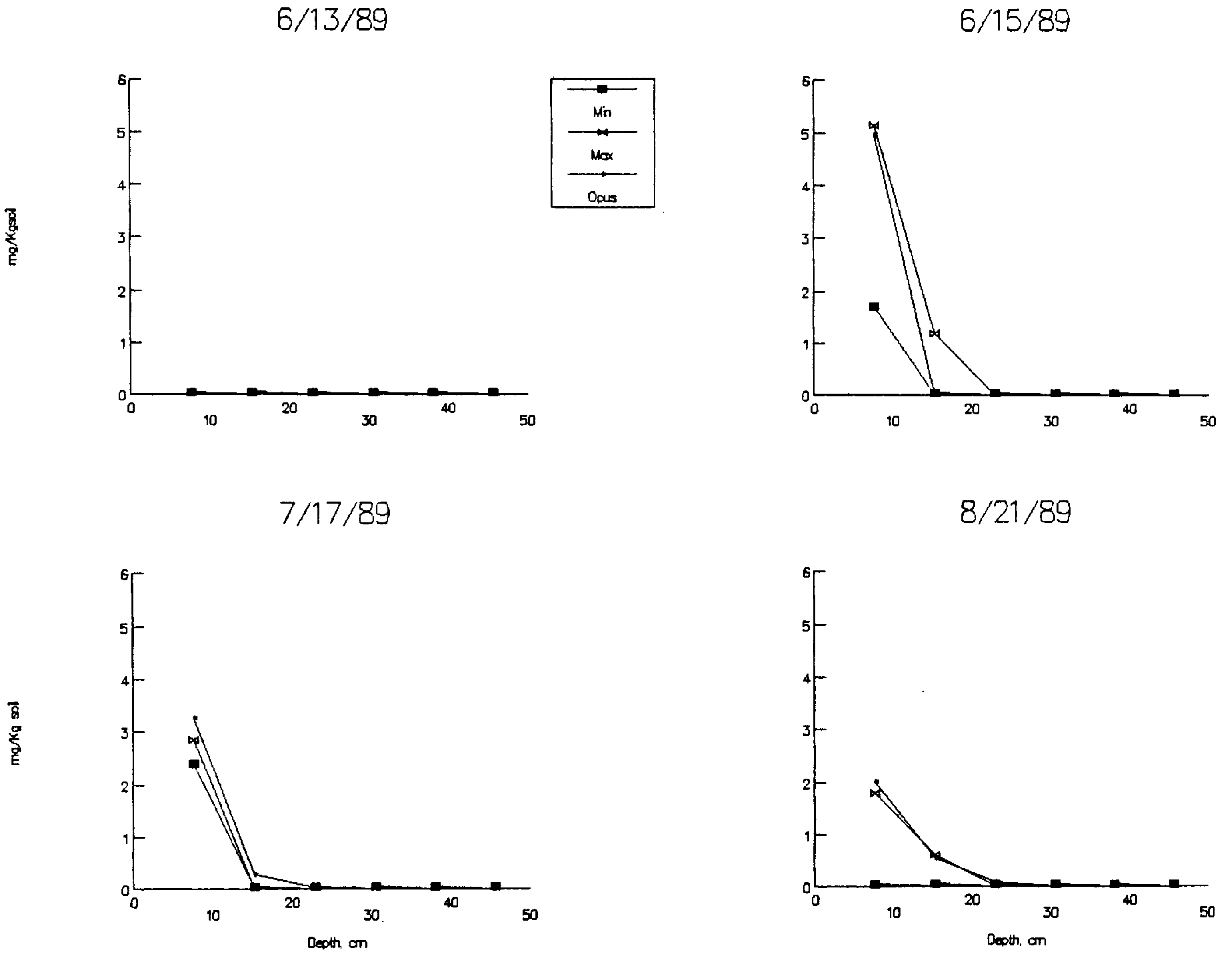


Figure C5: Atrazine concentrations on the south plot as a function of depth and time. Maximum and minimum measured values and the initial Opus run predictions are displayed.

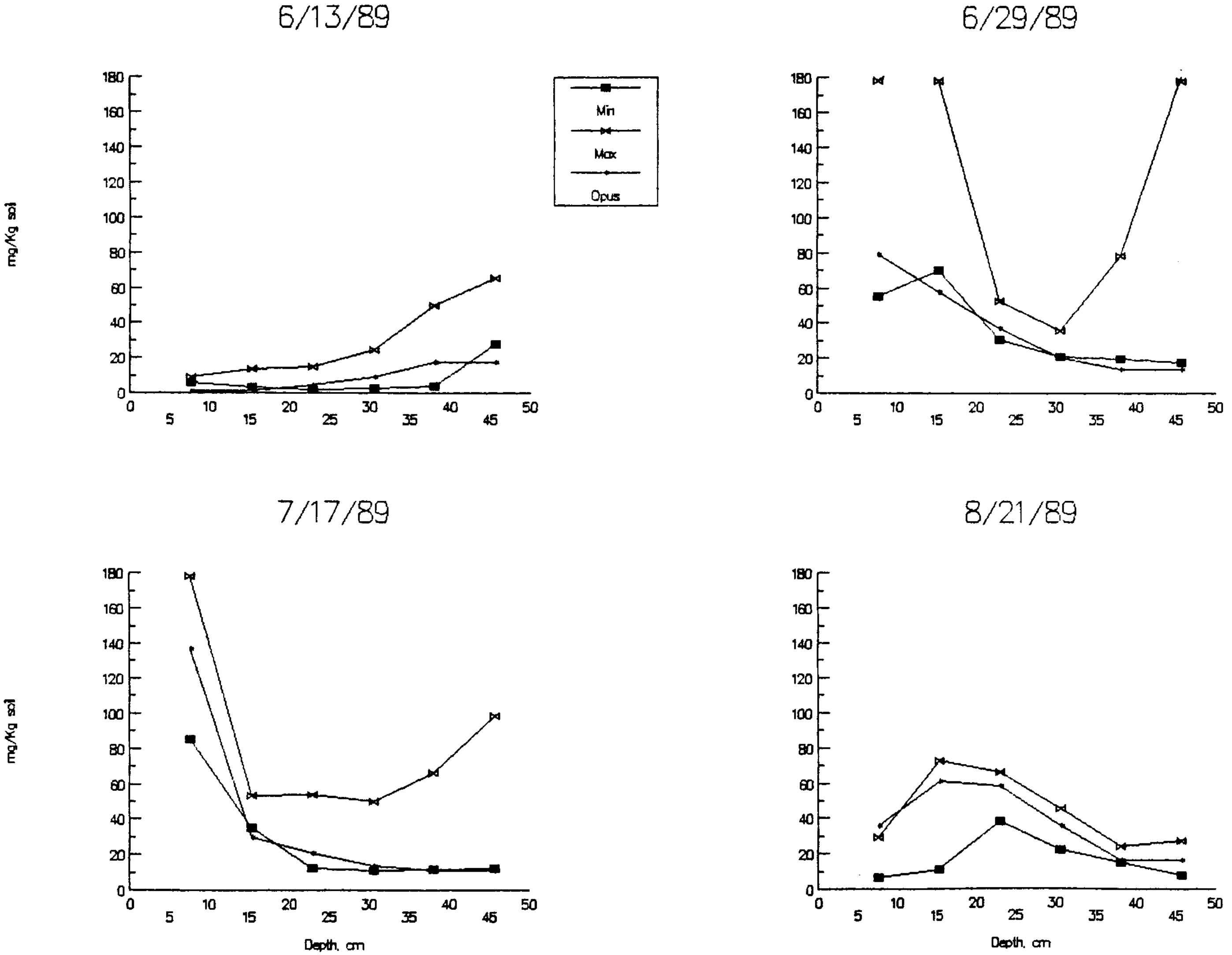


Figure C6: Bromide concentrations on the south plot as a function of depth and time. Maximum and minimum measured values and the initial Opus run predictions are displayed.

APPENDIX D

This section contains graphs which show the relationship between predictions from PRZM's second run and measured data. The initial run is defined in the text. Moisture content, atrazine and bromide concentrations as a function of depth and time are graphed. Depicted in each graph are the upper and lower confidence intervals from measured data and PRZM output. The horizontal axis is soil depth in centimeters. The vertical axis is either volumetric water content or chemical concentration. All chemical concentrations have the units of milligrams of chemical per kilogram of dry soil.

Legend Definition

Minimum value from measured data.

Min

Maximum value from measured data.

Max

PRZM prediction from the previous day's calculations.

PRZM

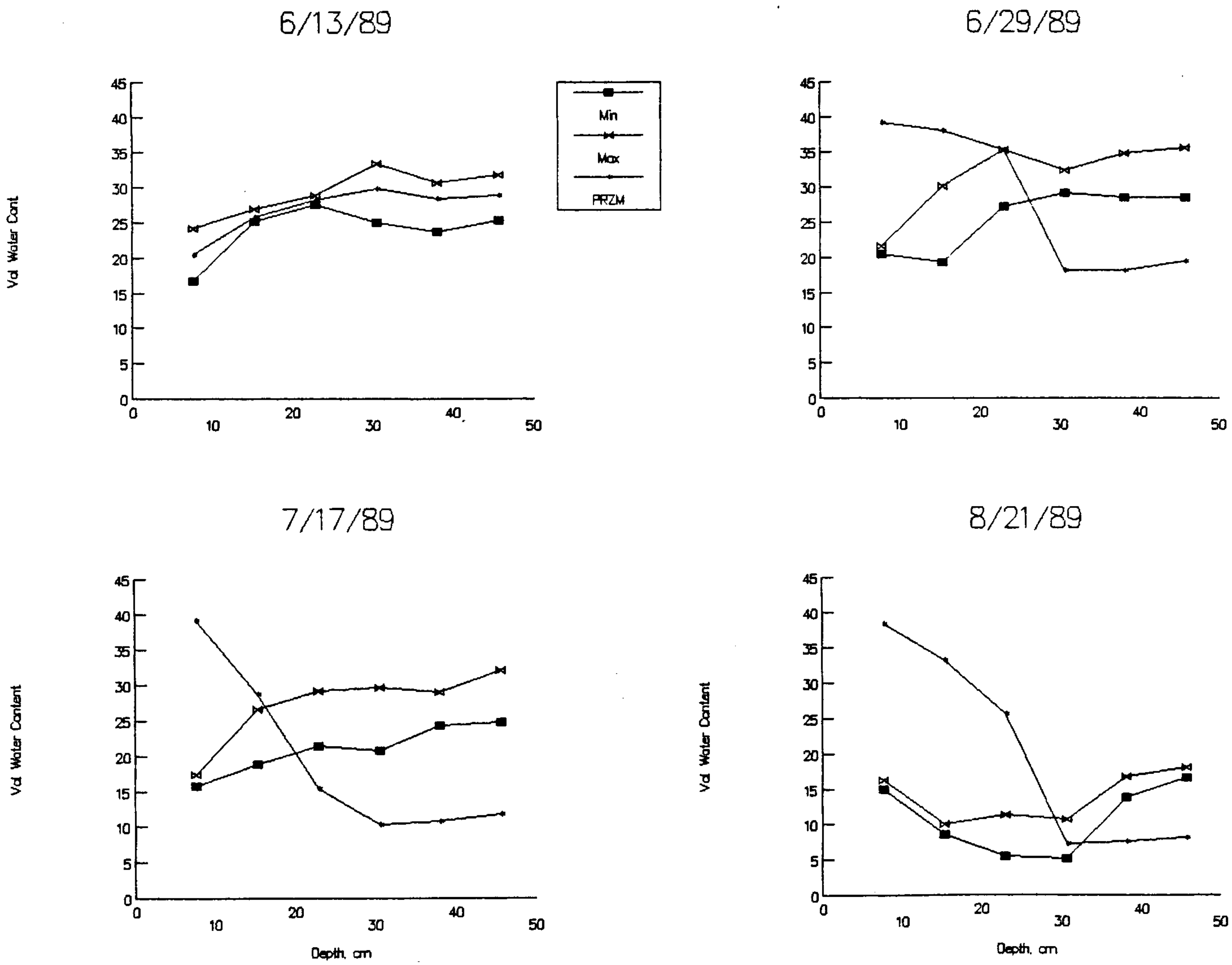


Figure D1: Volumetric water content on the north plot as a function of depth and time. Maximum and minimum measured values and the second PRZM run predictions are displayed.

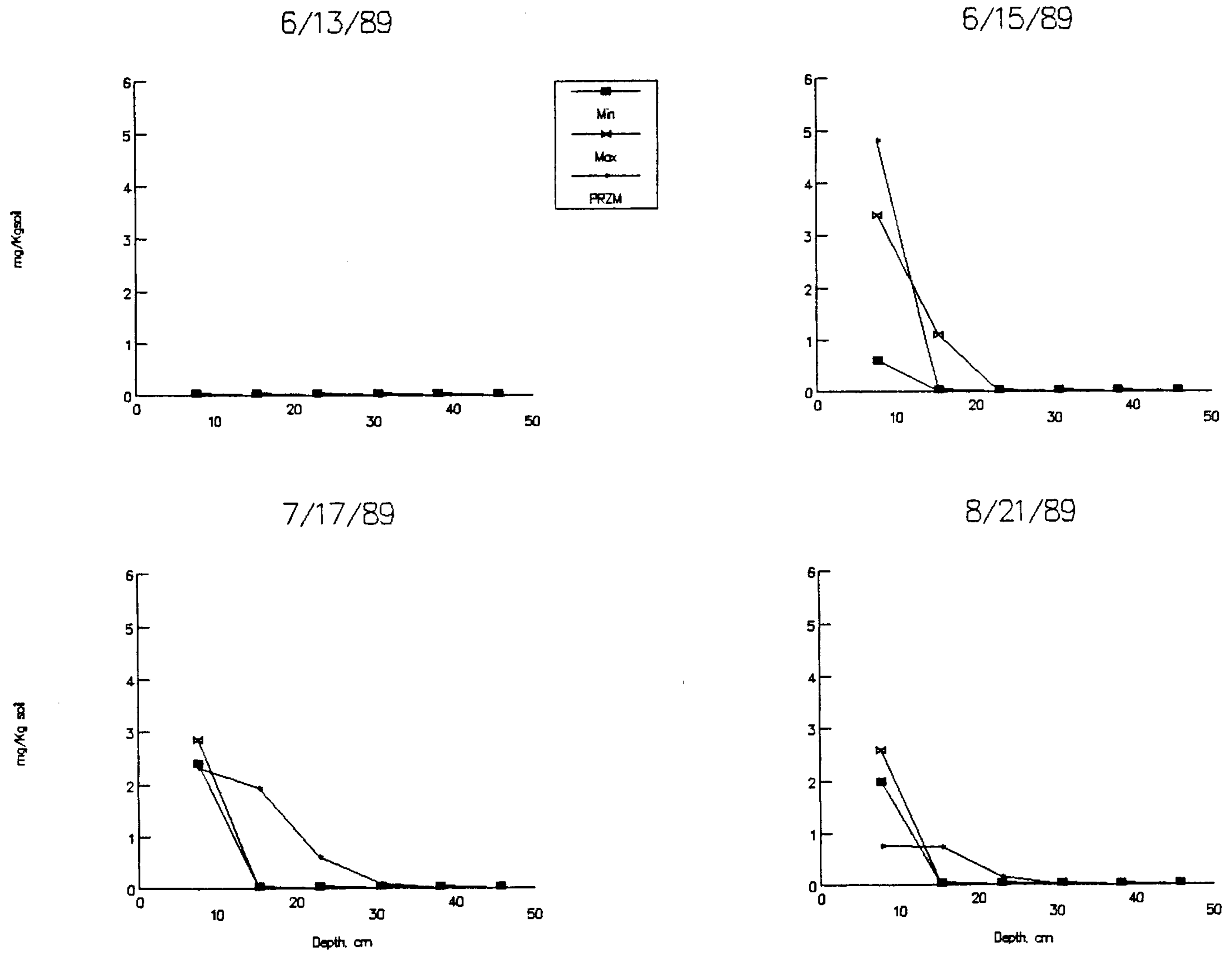


Figure D2: Atrazine concentrations on the north plot as a function of depth and time. Maximum and minimum measured values and the second PRZM run predictions are displayed.

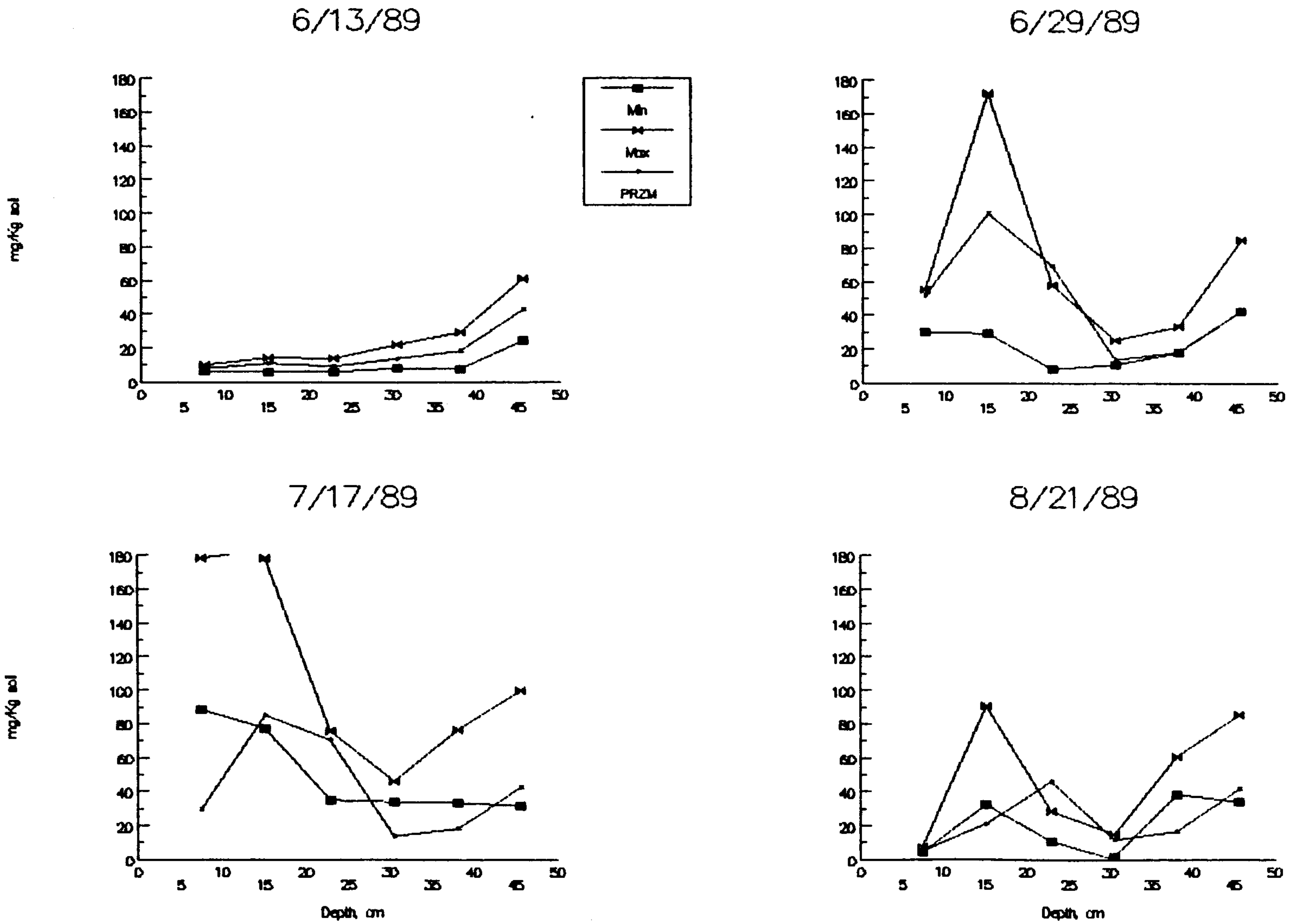


Figure D3: Bromide concentrations on the north plot as a function of depth and time. Maximum and minimum measured values and the second PRZM run predictions are displayed.

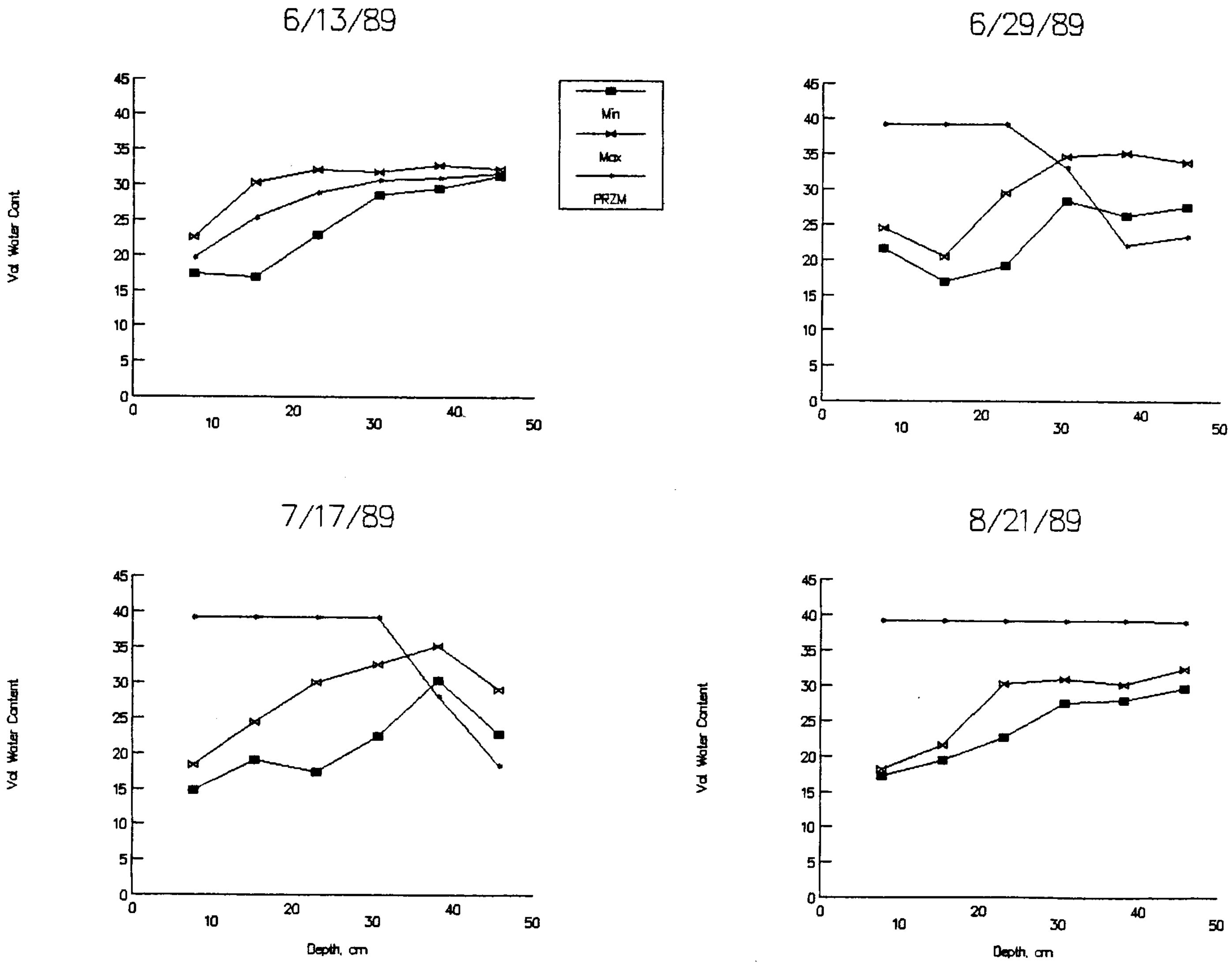


Figure D4: Volumetric water content on the south plot as a function of depth and time. Maximum and minimum measured values and the second PRZM run predictions are displayed.

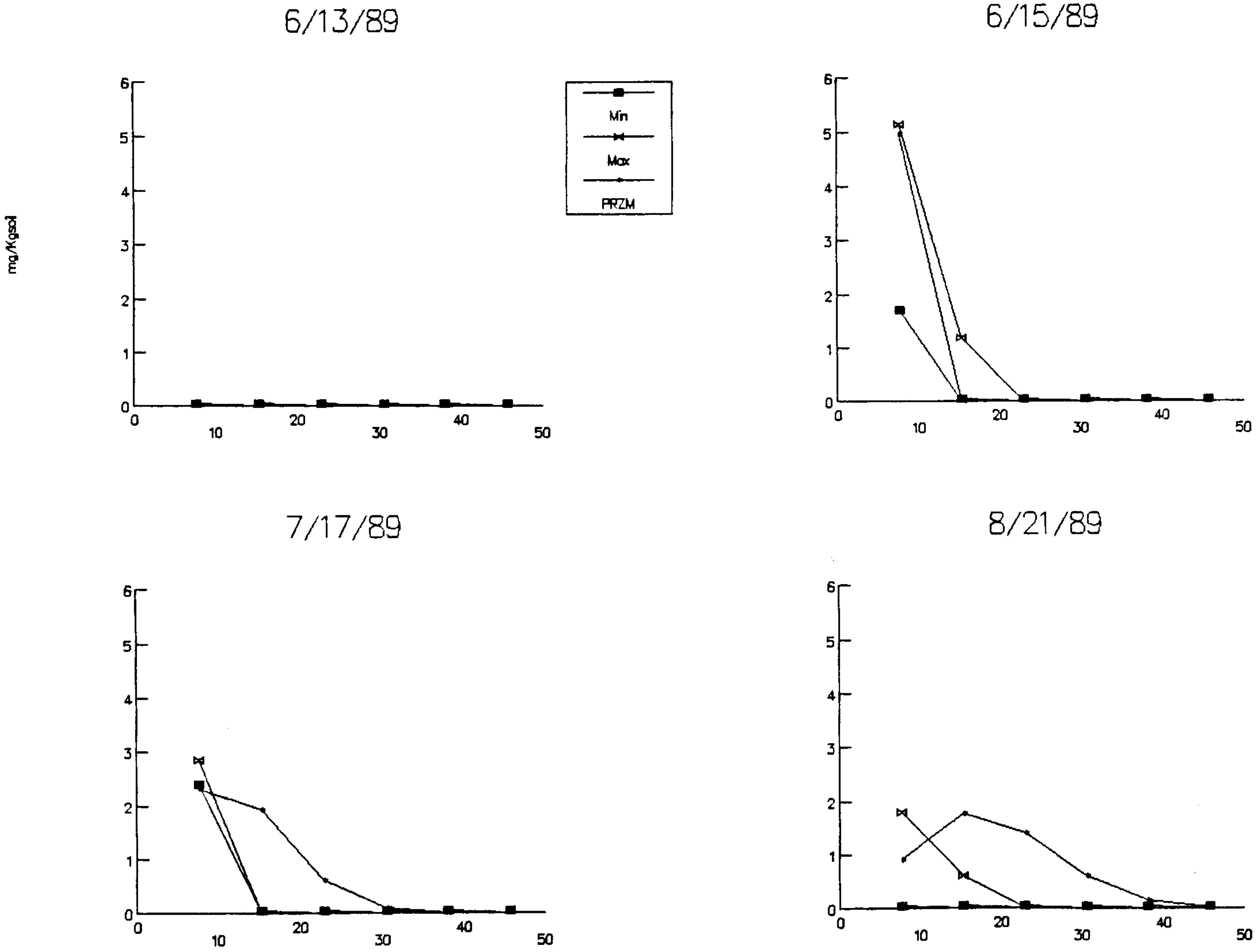


Figure D5: Atrazine concentrations on the south plot as a function of depth and time. Maximum and minimum measured values and the second PRZM run predictions are displayed.

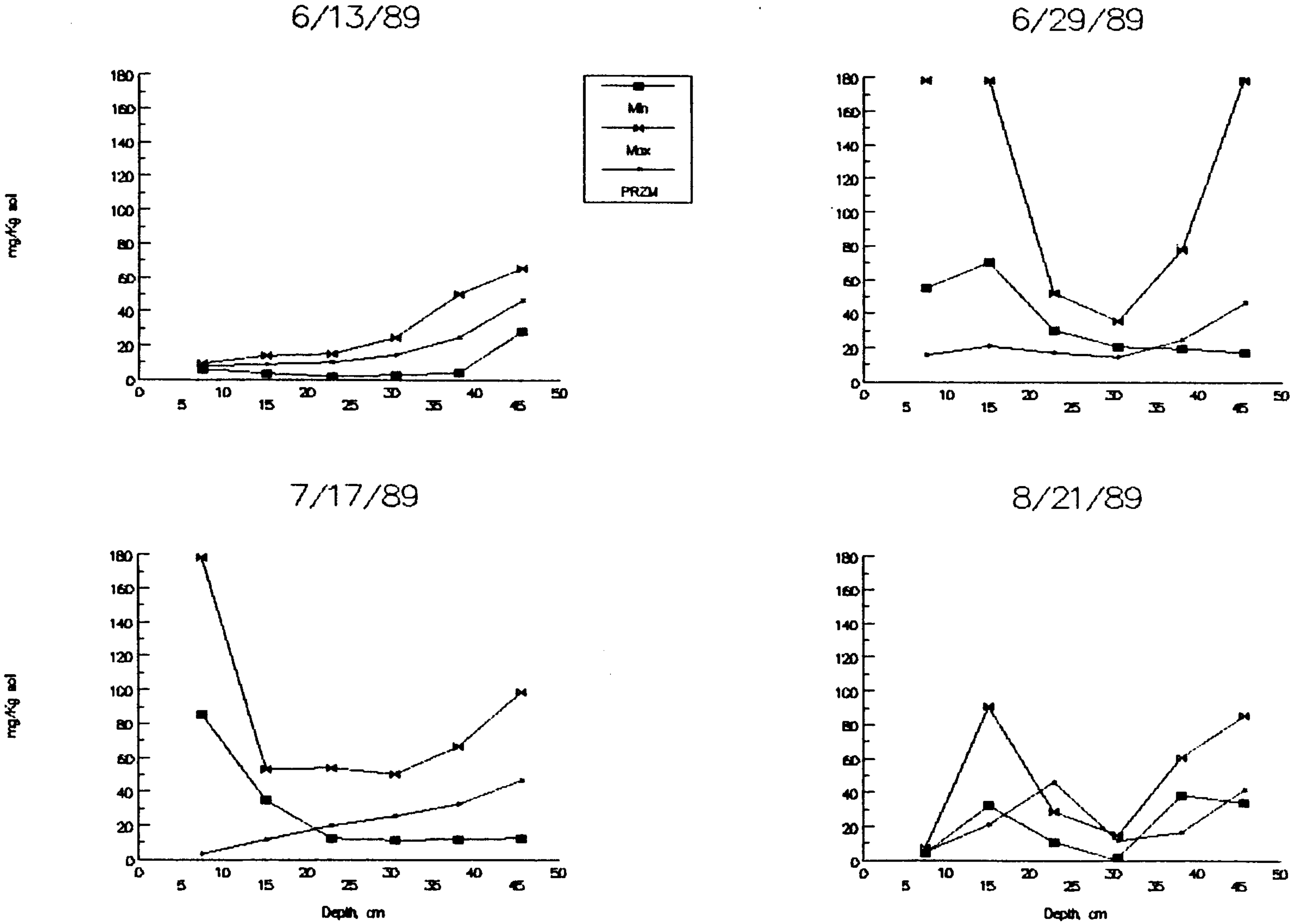


Figure D6: Bromide concentrations on the south plot as a function of depth and time. Maximum and minimum measured values and the second PRZM run predictions are displayed.

APPENDIX E

This section contains graphs which show the relationship between predictions from Opus's second run and measured data. The initial run is defined in the text. Moisture content, atrazine and bromide concentrations as a function of depth and time are graphed. Depicted in each graph are the upper and lower confidence intervals from measured data and Opus output. The horizontal axis is soil depth in centimeters. The vertical axis is either volumetric water content or chemical concentration. All chemical concentrations have the units of milligrams of chemical per kilogram of dry soil.

Legend Definition

Minimum value from measured data.

Min

Maximum value from measured data.

Max

Opus prediction from the previous day's calculations.

Opus

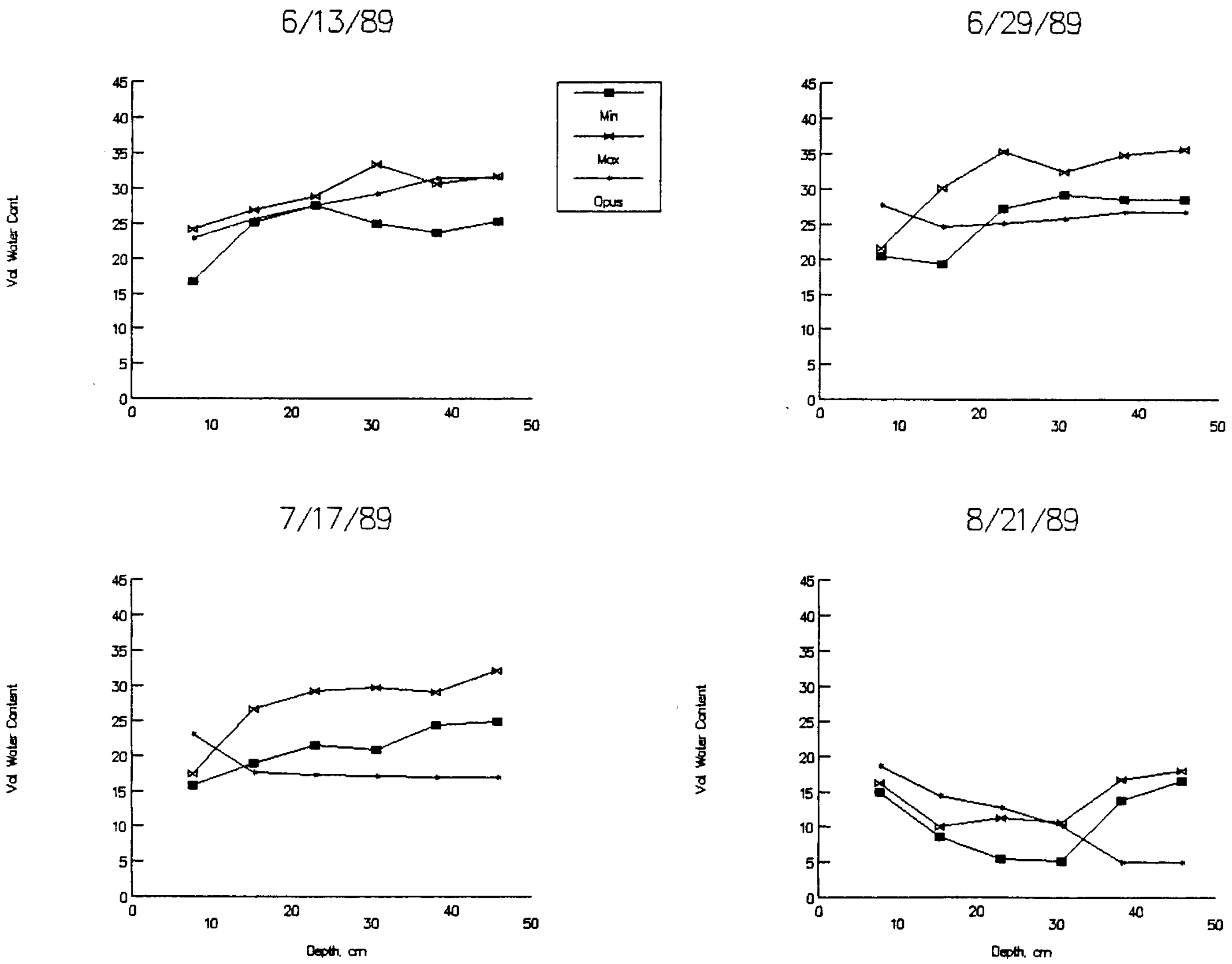


Figure E1: Volumetric water content on the north plot as a function of depth and time. Maximum and minimum measured values and the second Opus run predictions are displayed.

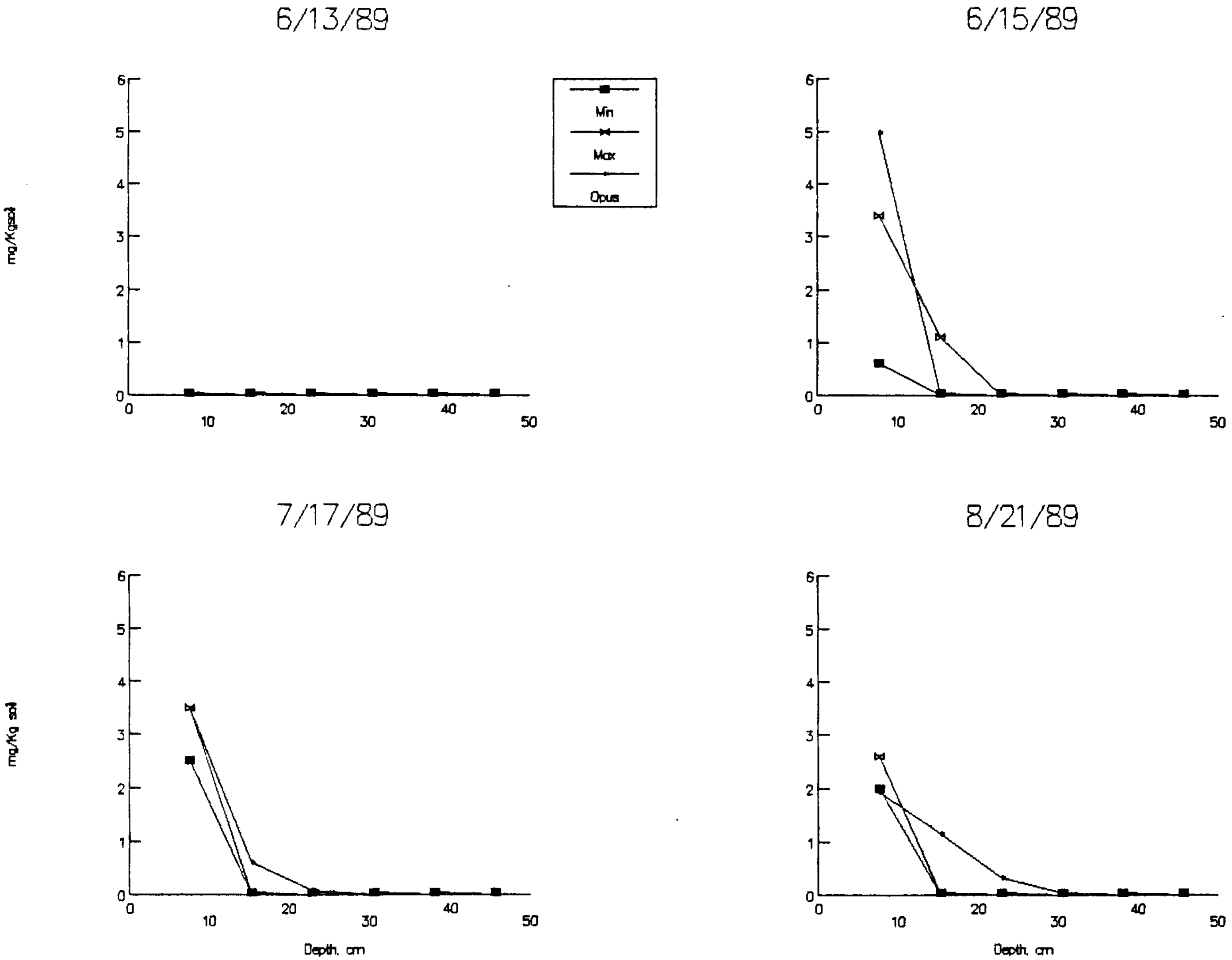


Figure E2: Atrazine concentrations on the north plot as a function of depth and time. Maximum and minimum measured values and the second Opus run predictions are displayed.

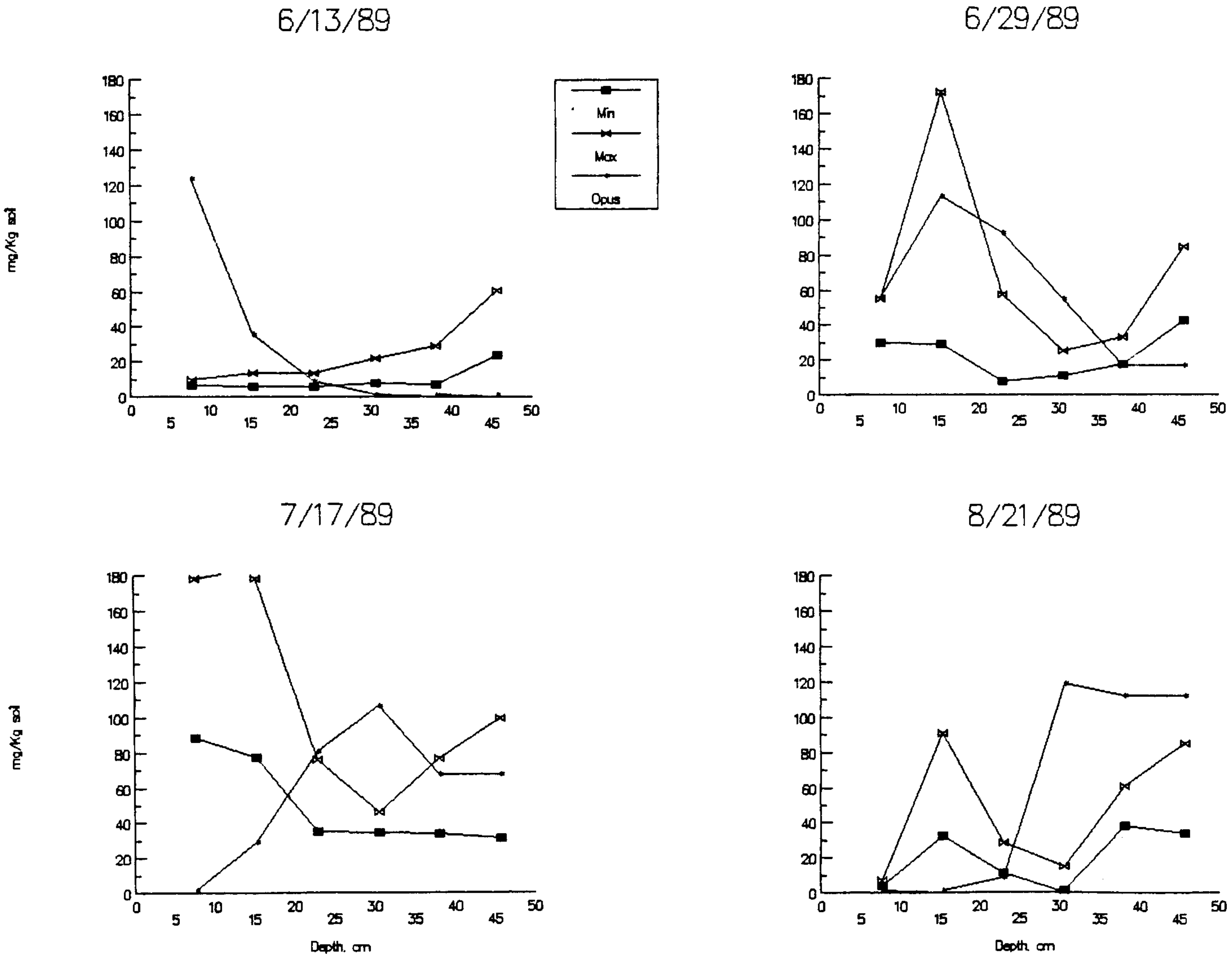


Figure E3: Bromide concentrations on the north plot as a function of depth and time. Maximum and minimum measured values and the second Opus run predictions are displayed.

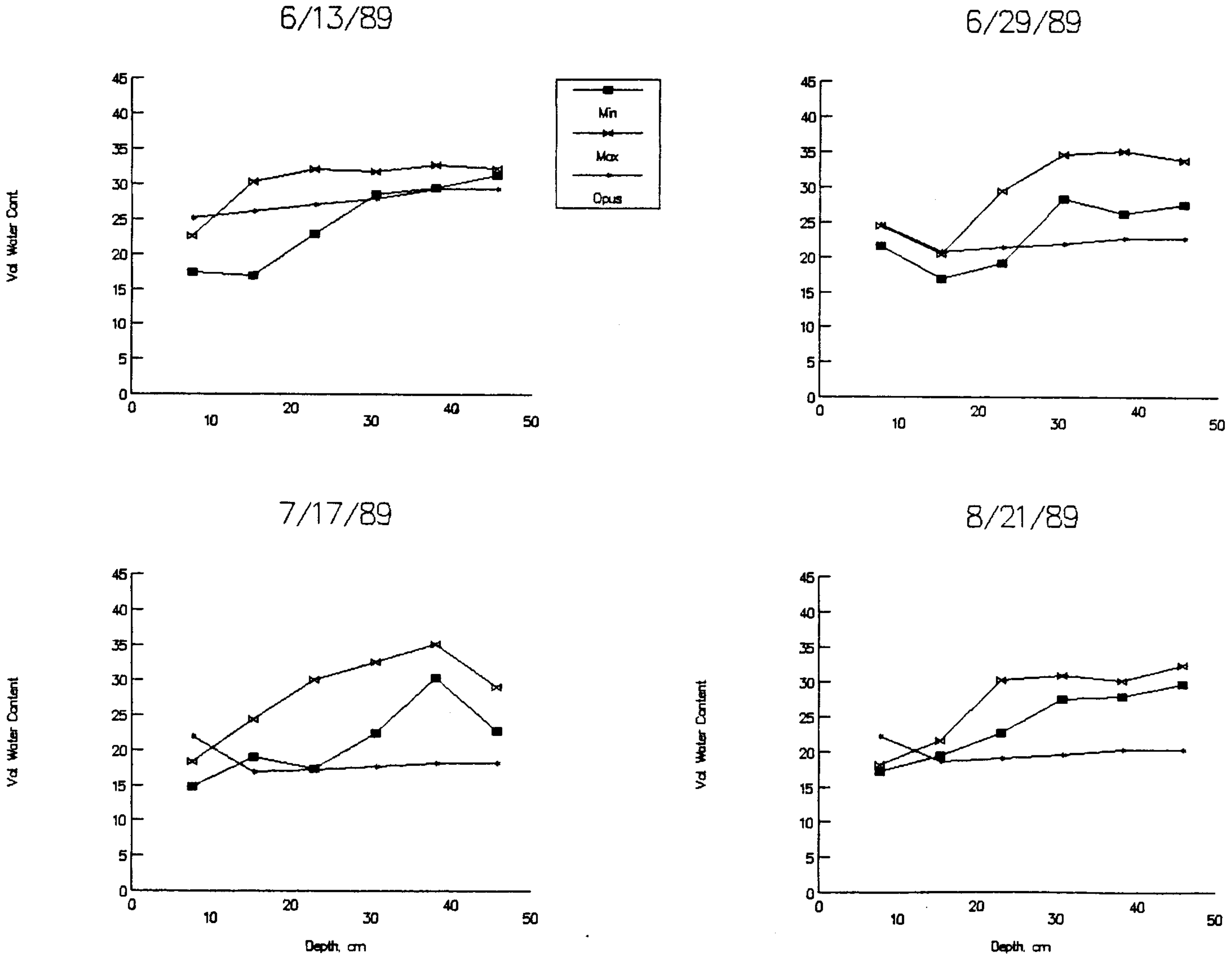
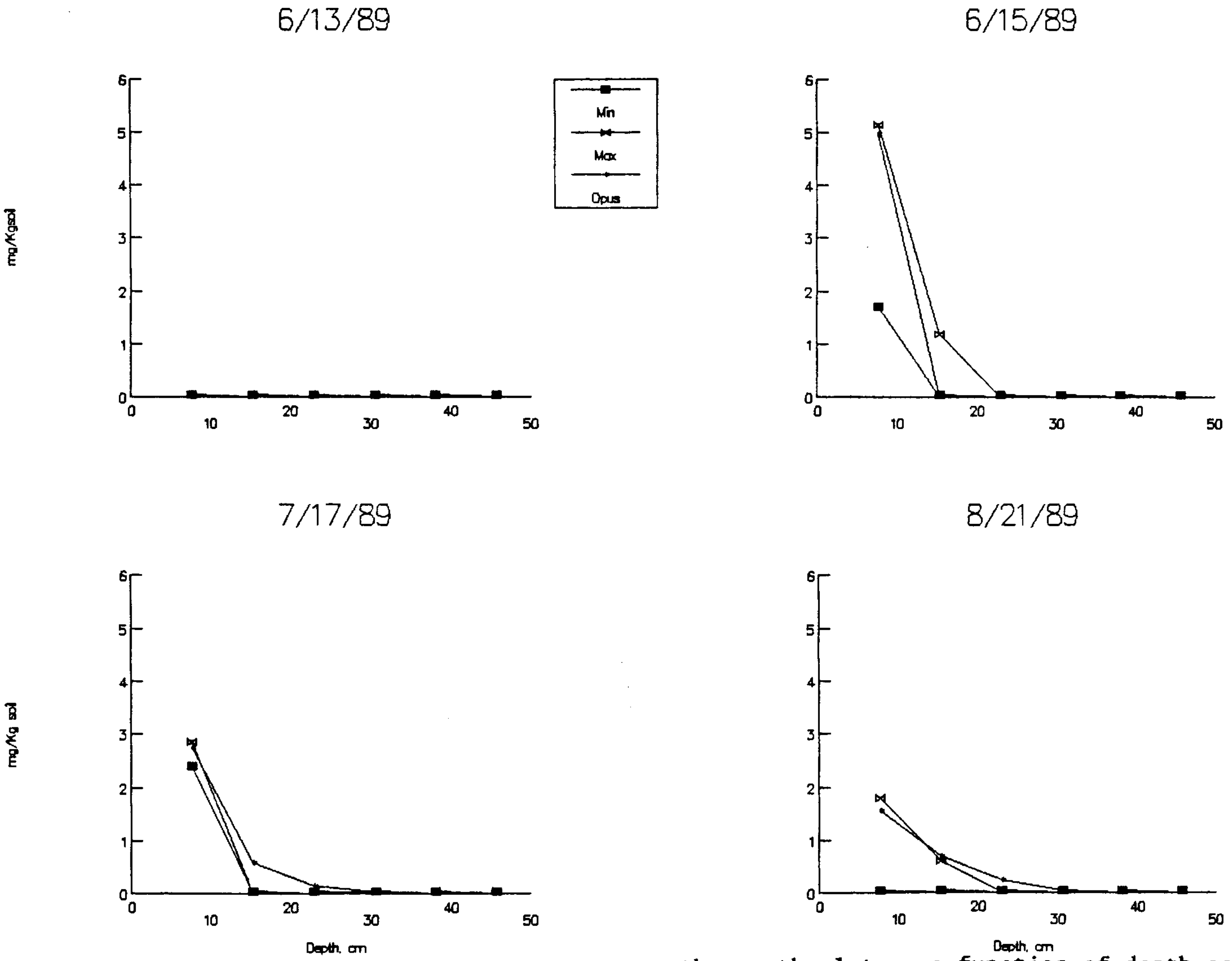


Figure E4: Volumetric water content on the south plot as a function of depth and time. Maximum and minimum measured values and the second Opus run predictions are displayed.



6/13/89

6/15/89

7/17/89

8/21/89

Figure E5: Atrazine concentrations on the south plot as a function of depth and time. Maximum and minimum measured values and the second Opus run predictions are displayed.

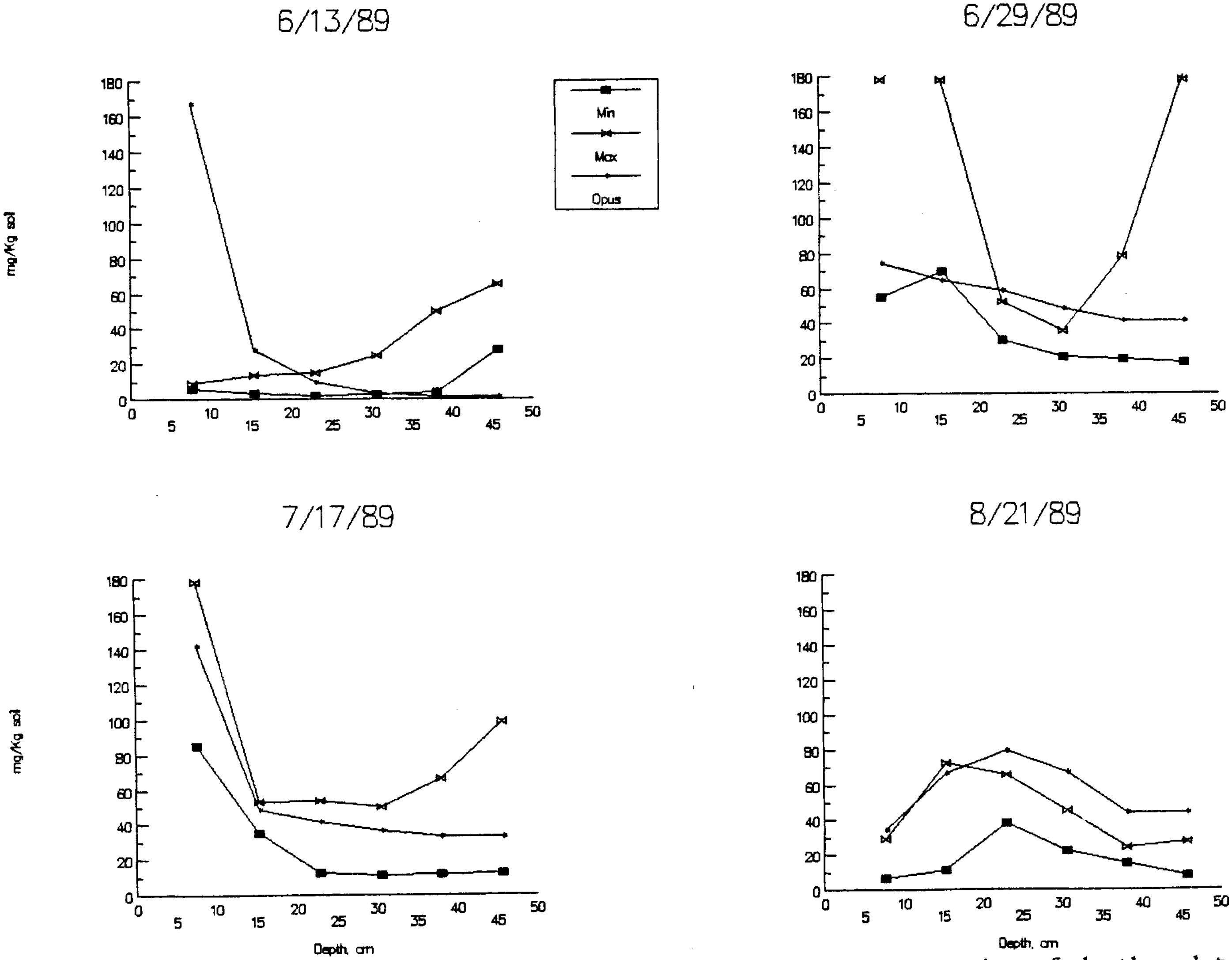


Figure E6: Bromide concentrations on the south plot as a function of depth and time. Maximum and minimum measured values and the second Opus run predictions are displayed.

APPENDIX F

This section shows results of Opus when a slight "calibration" of some parameters was performed. A calibration is usually performed by changing the input parameters until a good fit is obtained. In this section, input values are chosen that are expected to provide a good fit. So, this is not a true calibration. For this run, p_{cb} and μ were changed to values that were to improve the output. Since the soil had been tilled to a depth of 11 cm (4.5 in) and it is believed that the main mass of the corn roots are in this zone, values of p_{cb} and μ for a more course soil were assumed. The rest of the soil profile was assumed to be a finer soil. Thus for the top 15 cm (7.9in), p_{cb} was set equal to -589 mm (23.1 in) and μ was set equal to 0.25. For the rest of the soil profile, p_{cb} was assigned a value of -780 mm (30.7 in) and μ was set equal to 0.182. These values correspond to a soil type of a sandy clay loam for the top layers and a sandy clay for the lower layers. The values of p_{cb} and μ for the gravel layer remain unchanged from the previous runs. Also, a half life of atrazine was chosen from the Opus User's Manual to see the effects of this degradation parameter.

As can be seen from figure F1, Opus is able to predict soil moisture distributions up to July 17th. The predictions on July 17th and August 21st are close to the measured range. For the predictions to fall exactly into the measured ranges, slight adjustments need to be made to p_{cb} and μ for the separate layers. The lowest layers need to be have smaller μ's while the upper need higher values of μ. Literally hundreds of hours may be spent on calibration before the profiles would match exactly.

Figure F2 shows how changing the half life effects the models output. The shape of the atrazine profile predicted by Opus is relatively the same as it was in the first two runs, only this time more atrazine is present in the profile. Opus predicts that 1.4g (0.05oz) of atrazine are removed from the soil profile. This value is too low. It is difficult to say if this new half life value is correct or not. Measured data does not allow us to distinguish between pesticide degradation and plant uptake. For a calibration to find the correct half life, a measured value of pesticide degradation needs to be known.

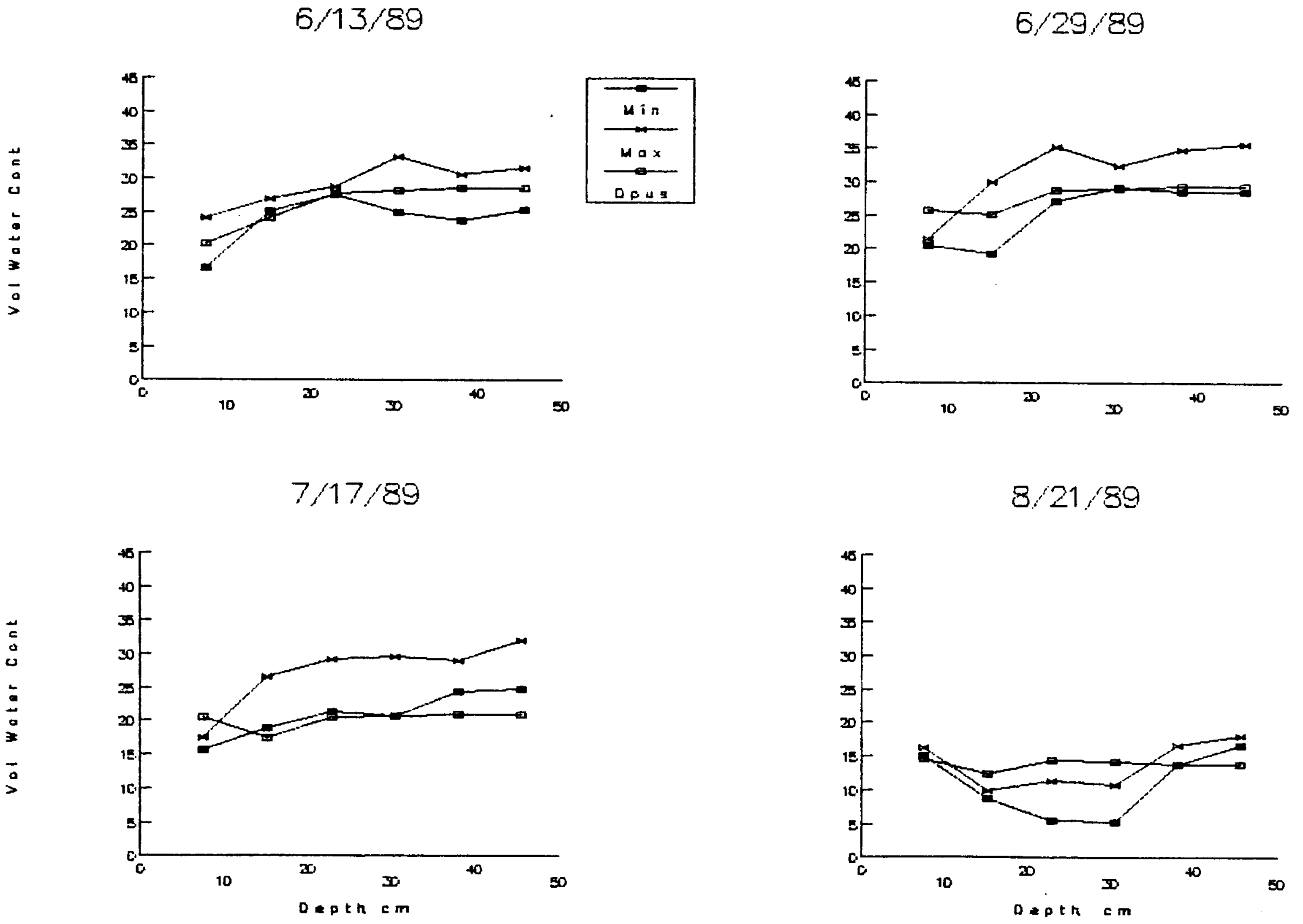


Figure F1: Volumetric water content on the north plot as a function of depth and time. Maximum and minimum measured values and the calibration Opus run predictions are displayed.

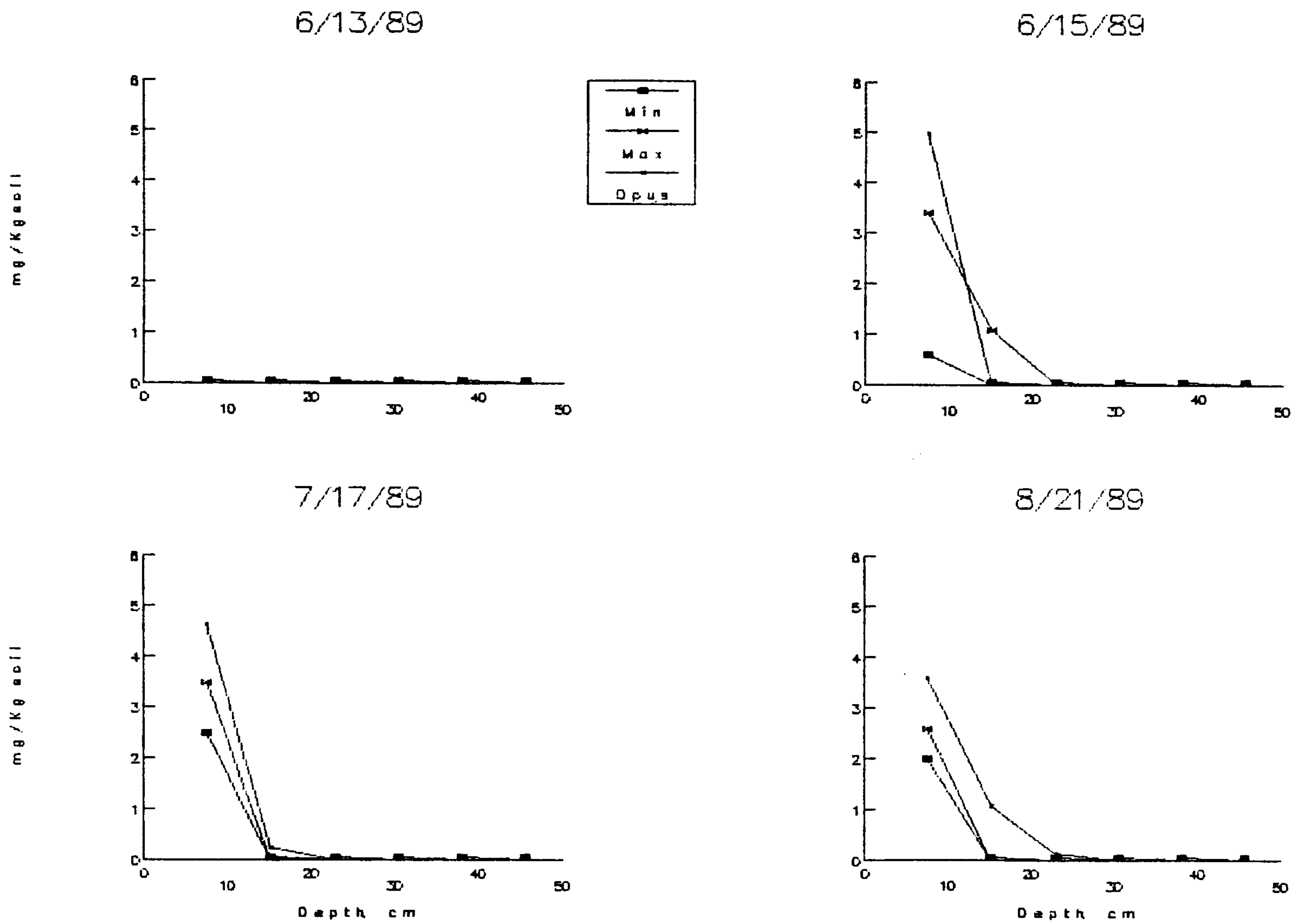


Figure F2: Atrazine concentrations on the north plot as a function of depth and time. Maximum and minimum measured values and the calibration Opus run predictions are displayed.

APPENDIX G

A similar study was performed during the summer of 1988 with a few exceptions. Soil sampling for soil moisture and chemical concentrations was carried out with a 1.9cm (0.75in) diameter probe. Runoff was induced during chosen rainfall events. Corn was grown on both plots.

As mentioned in the text, the variability in soil sampling was very large. The smaller diameter probe was the main cause. Bromide analysis for the soil samples were performed by another laboratory. It took three to four months to receive results. The methods used for analysis were not precise enough to correctly relate bromide concentrations to soil mass. Therefore, the data was unusable. The methods for soil atrazine analysis were still being developed. Thus, atrazine data were not available for use.

High volumes of runoff were induced twice during the season. Water samples were collected periodically during each event for chemical analysis. The samples were destroyed during storage resulting in no data from runoff events. Opus was used to simulate the 1988 study. Hydrologic parameters input in the model were from literature. Opus was able to match the weekly measured soil moisture contents. It was interesting to note that when simulating the 1989 summer using the same hydrologic parameters for the 1988 year, Opus predictions did not match measured values.