

Effect of Hexazinone on Groundwater Quality in the Coastal Plain.
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ABSTRACT

Hexazinone (3-Cyclohexyl-6-(dimethyl-amino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione) was applied as the pelleted formulation Pronone 10G and the liquid Velpar L formulation to coastal plain study sites near Barnwell, South Carolina and Hughes Island Florida, respectively. These sandy sites were well drained and surface runoff was not observed at either site. Pronone application resulted in a shift towards a grass dominated understory. Pronone 10G application to the Barnwell, S C site resulted in no detectable groundwater residues up to 2 years post-application. Velpar L application to the Hughes Island site resulted in no persistent detectable residues in a down gradient stream or pond. One positive hexazinone residue pond sample was observed 15 days post-treatment after the first rain event. Significant hexazinone residues (10-35 ppb) were found in test wells located within the treatment area 1 year post-application. Hexazinone residues were not detected in up gradient, down gradient or control well samples throughout the study period.

Introduction

Control of competing vegetation is one of the most important steps in forest site preparation in the southeast Coastal Plain. While mechanical preparation is still used extensively, physical site degradation, accessibility problems on poorly drained soils, and high cost have resulted in a significant shift to chemical weed control in the past 5 years.

Hexazinone is registered for both site preparation and pine release in southern pine culture. The herbicide is absorbed by roots and readily translocated to active sites in the plant. Some of the absorbed material is metabolized by the plant. In soil, hexazinone is metabolized to some extent by microbes and several metabolites have been identified (1). Metabolism is more complete in clay than in sandy soil (2). Where there is sufficient microbial activity, the reduction of hexazinone to CO₂ is accomplished. The half life of hexazinone in soil may range from 1 month to 12 months. The movement of residues through the soil profile is known to be much faster in coarse than in fine textured soils (2). How deep the compounds move, and to what extent they contaminate groundwater are not known.

Hexazinone is relatively stable in water and shows little tendency to hydrolyze over periods of up to 2 months (3). It is slowly degraded in aqueous solution under light and the principal photodegradation products are the demethylated and hydroxylated metabolites found in soil and plant tissues.

Off site movement from upper Piedmont watersheds has been reported (4). Subsurface flow in the sandy loamy typic hapludult soils was recorded several months following treatment. Because potential movement through the deep sands of the central highlands of Florida and the coastal plain would be faster than that observed in the loamy soils of the mountains, it is necessary to determine the potential for groundwater contamination in this area.

The objective of these study was to monitor the movement of hexazinone to groundwater in typical forest management applications in the southeastern coastal plain. Hexazinone was applied as the pelleted formulation (Pronone) or Velpar L and groundwater concentrations of hexazinone were measured.

METHODS

Site Description

Hughes Island Study Site: This site is located on the Hughes Longleaf Island, Lake George Ranger District, Ocala National Forest, Marion County, Florida (Figure 1). The vegetation of the island is predominantly longleaf pine (Pinus palustris Mill.) with scattered sand pine (P. clausa (Chapm.) Vasey) and clusters of hardwoods. The 10 ha study site was occupied by Turkey oak (Quercus laevis Walt.) competition prior to use of hexazinone for weed control and pine establishment.

The soil on the site was mainly Astatula sand, a Typic Quartzipsamment found on level to gently sloping terrain (0 to 8% slope). This soil series is excessively drained, very rapidly permeable, and low in fertility and organic matter content. These deep sandy soils comprise over 36% of the Ocala National Forest. To the south of the study site the terrain slopes through a band of Eustis sand (Thermic Psammentic Paleudults) and into a pocket of Sellers sands (Hyperthermic Cumulic Humaquents) which surround a sinkhole lake. The Sellers soils are very poorly drained sandy soil with rapid permeability, high organic matter, and moderate fertility. A series of springs in the northern portion of the Sellers soil coalesce and flow southward about 50 m toward the Hughes Island sinkhole.

Barnwell South Carolina Site (Figure 1): The Upper Coastal Plain Pronone groundwater monitoring study site was located on Federal Paper Board's Jefferies Track (Barnwell, SC). The gently sloping study site (2-6% slopes) contains soils of the Dothan loamy-sand series on the broad ridges with Fuquay sandy soils on the lower slopes. The creek bottoms contain Johnston mucky sandy

loam soils. These soils are typical of the highly productive pine forest of the upper coastal plain of Georgia and South Carolina.

The Dothan soil series consists of deep, well-drained soils. In a representative profile, the surface layer is grayish-brown loamy sand about 17 cm thick. The subsurface layer is light yellowish-brown sand about 10 cm thick. The upper part of the subsoil to a depth of 83 cm, is yellowish-brown sandy-loam, and yellowish-brown sandy clay loam that contains plinthite. Water permeability is moderate in the upper part of the subsoil and moderately slow in the lower part. Runoff potential and the available water capacity are moderate. The lower slope consists of the Euquay soil series of deep, well-drained soils with low runoff potential. In a representative profile, the surface is grayish-brown sand about 25 cm thick. The subsurface layer is light yellowish-brown sand 30 cm thick. The upper part of the subsoil is yellowish-brown sandy loam 30 cm thick. The lower part, extending to a depth of 200 cm, is yellowish-brown and strong-brown sandy clay loam that contains plinthite. Permeability is rapid in the surface and subsurface layers, moderately rapid in the upper part of the subsoil, and slow in the lower part of the subsoil. Available water capacity is low.

Watershed Instrumentation

Hughes Island, Florida Site: Seventeen wells were installed on the site to depths of approximately 7.5 m. The bottom 1.6 m foot portion of each well was screened. Samples were collected monthly. Because of the drought, it was not possible to purge the wells at each sampling period as originally planned. Wells 5, 11, 17, and 27 were located in the untreated check area. Wells 16, 18, 20, and 22 were in the up gradient treated area. Wells 6, 7, 8, 10, and 14 were located down gradient in the test plot area, and wells 1, 2, 3, and 4 were down gradient. Based on groundwater elevations, the general hydrologic flow appears to be from north to south with a slight west to east gradient.

There were two springs on the site. These two springs gave rise to a stream which drained from just below the treated area into a sinkhole pond approximately 45 meters below the treated area. Samples collected from the springs were labeled S1 and S2 to indicate the upper and lower springs, respectively. Grab samples were collected weekly from the sinkhole lake located below the treated area. Water samples for hexazinone analysis were frozen in polypropylene bottles and shipped to USFS Laboratory in Auburn, AL for analysis. All samples were maintained frozen until analyzed.

Barnwell, South Carolina Site: Three monitoring wells were installed on the Barnwell, South Carolina site during June-July 1997. Two well sites (#1 and #6) were located up gradient and one down gradient (pond-well) of the Pronone treatment. Wells were lined with 5 cm PVC pipe and the wells were screened to intercept the upper 1.5 meters of the saturated zone. Well water

samples were collected by bailer, after recording the water surface elevation and evacuating three well volumes. Well water samples were collected monthly for two years. Samples were placed on ice and delivered to the University of Georgia laboratory where analysis was initiated within 24-48 hours.

A perennial stream located down gradient of the Pronone treatment area was instrumented with V-notch weirs and Parshall flumes. Stream water samples were collected above and below the treatment area.

At the beginning of the study, depth to groundwater in the deep well was 14 meters (up gradient well) below the surface along the ridge, and was 1.7 meters near the stream channel. Comparison of depth to groundwater between the deep wells and shallow wells indicated the wells were screened in separate aquifers that were hydraulically connected.

As the study progressed and the drought worsened, there was a steady increase in depth to groundwater in both the shallow and deep aquifers. The trend over time of depth to groundwater in both aquifers is the same and both aquifers appeared to have similar responses to the drought and the increase in rainfall, near the end of the study period.

In general, depth to groundwater on the ridge (Well 11 and planted pin? control (Well 6) declined approximately 3m until the spring of 1989 when water levels began to rise. Total recovery by August 1989 was about 0.9m, leaving a deficit of about 2.1m over the two year period. Increase depth to groundwater along the stream channel ranged from 1.7 to 1.4 meters and recovery ranged from 1.5 to 0.7m. The water table in all wells appeared to decline and recover at the same rates.

Based on the groundwater elevations, the general hydrologic gradient at the ridge and in the center of the site appears to be from the west to the east diagonally across the study site at about a 30-degree angle to the stream channel. Near the stream channel, the flow is likely parallel to the channel. There were insufficient wells to construct a piezometric surface map for the study site.

Herbicide Application

The Hughes Island Florida study site was treated with 1.7 kg ai/ha hexazinone as Velpar L. Application was by ground-based tractor mounted sprayer on 25-26 April 1985. Velpar L was mixed with water and Polycontrol to provide approximately 370 L/ha carrier.

The Barnwell County, South Carolina site was treated with Pronone 10G at a rate of 2.8 kg ai./acre with an Omni spreader in June 1987. The treated area was burned during October 1987 and pine seedlings were planted in February 1988.

Residue Analysis

Hexazinone water samples from the South Carolina study were extracted with ethyl acetate (NaCl was added to facilitate extraction). Hexazinone residue levels were analyzed using a Tracor Model 565 Gas Chromatograph equipped with Tracor NP Detector (Nitrogen-Phosphorous Specific) and dual 30 meter large bore (0.53mm) capillary columns. The two columns consisted of Supelco SP-5 and SPB-35. The oven was temperature programmed from 150 to 275 C at 10C/min.

The extracts were initially screened on the SPB-5 Capillary Column. Positive residues were confirmed by analysis utilizing the SPB-35 column. All residue levels were quantified by comparison of sample peak heights with known analytical standards. 4 reagent blank and spiked samples were included with each set of analyses. Average recoveries ranged from 88.5 to 108.0%.

Analysis of samples from the Hughes Island Florida Study Site for hexazinone content was conducted at the George W. Andrews Forestry Sciences Laboratory, Auburn, Alabama. The method is a reversed-phase liquid chromatographic method (column: C-18; mobile phase - water: acetonitrile/27:73; Flow rate = 1.5 ml/min; UV detection at 200 nm).

Hexazinone was extracted and concentrated from water using solid phase extraction techniques with C-18 columns. Average hexazinone recovery was 94.6%. A reagent blank and fortified samples were included with each set of analyses.

RESULTS AND DISCUSSION

Efficacy

Barnwell Site: Grasses, primarily Cynodon dactylon, Panicum spp., and Andropogon sp., were the predominant vegetative type on the Pronone treated Barnwell site. Mean percent cover by grasses (28.6%) exceeded percent cover on an adjacent mechanically treated site (11.1%). Total biomass of grasses was 737 kg/ha in the hexazinone treated site and 222 kg/ha on the mechanically treated site.

Legumes were more abundant on the hexazinone site (8.2% cover; 120 kg/ha) than on an adjacent mechanically prepared area (2.0% cover; 11 kg/ha). Total forb production was higher on the roller-chopped site (27.0% cover; 992 kg/ha) than on hexazinone treatment (17.7% cover; 287 kg/ha). Dominant forbs on the Pronone treated sites included Lespedeza spp., Cassia fasciculata, Diodia teres, Tragia urens, and Croton granulosus. Predominant species on the roller-chopped area were Eriogonum spp., Ipomoea sp., Lechea villosa, and Diodia teres. Woody vegetation (vines, shrubs, trees) likewise were most abundant on the mechanically treated area (14.5% cover; 360 kg/ha) vs. the Pronone treatment (4.0% cover; 245 kg/ha).

Wildlife habitat values of site preparation methods vary with the habitat requirements of the particular wildlife species. Forb and woody vegetation production on the roller-chopped area provided abundant forage for white-tailed deer (Odocoileus virginianus). Although total production of forbs and woody vegetation was less on the chemical area, several preferred forb species were as abundant or more abundant. The hexazinone treated area produced the greatest amount of legumes favored by bobwhite quail (Colinus virginianus). The heavy grass cover on the chemically prepared sites likely favored many rodent species and provided summer foraging sites for wild turkey (Meleagris gallapavo). The preservation of snags on these areas provided habitat for several cavity nesting or hawk foraging birds as well as raptors.

Hughes Island Site: Hexazinone was effective in controlling turkey oak as most stems and ground clusters were killed. There was some mortality among the scattered sand pine. Longleaf pine seedlings burst out of the grass stage within the first year after the control of the turkey oak. Grasses, primarily wiregrass (Aristida strict.71) and chunky bluestem (Andropogon capillipes), were not affected by hexazinone.

Rainfall

The total rainfall on the Barnwell, SC site for 1987, 1988 and the first half of 1989 was 105.7 cm, 92.2 cm and 60.7 cm, respectively (Figure 2). The 1987 annual rainfall was 7.6 cm below normal and most of the rainfall occurred prior to the herbicide application. The 1988 rainfall was 20.3 cm below normal and the spring of 1989 rainfall was 4.6 cm above normal. Likewise the rainfall for the Hughes Island site was low.

Hughes Island Site: Rainfall For this part of central Florida averages 1350 mm, with 52% occurring from June through September. Rainfall for the summer months of 1984 was only 55% of normal. During 1985, rainfall was 81% of normal, with all the deficit occurring in the first 5 months. Rainfall from June through December was near normal, but did not eliminate the deficit for the previous 12 months. Rainfall in 1986 was near normal.

Residues in Runoff

Velpar L was applied to the Hughes Island study site on April 25, 1995 and the first rain event occurred 14 days later. No surface runoff was observed. Water grab samples collected monthly from the spring down gradient of the treatment area were found to contain no detectable hexazinone residues for up to 18 months after application (Figure 3). A trace (1? ppb) of hexazinone was detected in one sinkhole pond sample collected after the first rain event. No further detectable residue levels were detected throughout the 18-month study period.

Pronone 10G was applied to the Barnwell, South Carolina, site in June 1937. No runoff was observed and analyses of pond

grab samples collected 1-2 months after application resulted in no detectable hexazinone residues. Due to drought conditions, the pond went dry 6 months into the study.

Residues in Groundwater

Hushes Island Site: Water samples collected from monitoring wells installed to depths or up to 7.5m were monitored periodically for 1 year. Detectable residues (17-35 ppb) were observed in samples collected from plot wells (Table I). Approximately 1 year after application, no hexazinone residues were detected in the up gradient or control well samples. The only detectable residues found in down gradient wells occurred residues found in down gradient wells occurred after the first rainfall event. This may represent sample cross contamination in the field, since the time required for water applied to the surface of the test area to move to a depth 20-25 feet offsite is considerably greater than 1 to 2 days.

Barnwell Site: No detectable hexazinone residues were observed in the control well or in the test area well located in the up gradient portion of the plot (Table I). One detectable hexazinone residue (3.6 ppb) was observed in the down gradient well 126 days after application. All other hexazinone groundwater samples were non-detectable.

The lower level of groundwater contamination observed at the Barnwell, South Carolina site can be attributed to: (1) greater depth to ground water; (2) reduction in hexazinone levels by burning the Barnwell site 7-4 months after application; and (3) timing of rain events.

SUMMARY AND CONCLUSIONS

Hexazinone application for vegetation control on test plots in the coastal plain did not adversely impact down gradient surface water quality. Hexazinone residue levels (3 ppb) were detected in only one sinkhole pond water grab sample from Hughes Island, collected after the first rain event. At the Hughes Island study site, all other spring or sinkhole pond water samples contained no detectable hexazinone residues.

In sandy soils with low organic matter, hexazinone may be expected to reach shallow groundwater if heavy rainfall events occur. In the current study, hexazinone residues were detected in the Hughes Island Florida monitoring wells one year after application. Only a trace of hexazinone was found in a Barnwell, South Carolina shallow, down gradient monitoring well 4 months after application. No other detectable hexazinone residues were observed at the Barnwell, South Carolina study site. None of the hexazinone residues measured in groundwater exceeded the suggested water quality standard for hexazinone.

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TABLE I: Hexazinone residue levels (ppb) in groundwater samples collected from the Hughes Island Florida and the Barnwell, SC Study Sites.

Sampling Date	Study Date	Control	Plot	Down Gradient
=====				
Hughes Island Florida				
16 May 1985	21	No Sample	No Sample	3.0 ppb
06 Jun 1985	42	No Sample	No Sample	< 1.0
20 Aug 1985	117	No Sample	No Sample	< 1.0
25 Feb 1986	307	No Sample	No Sample	< 1.0
19 Mar 1986	328	No Sample	No Sample	< 1.0
17 Jun 1986	418	No Sample	No Sample	< 1.0
18 Jun 1986	419	No Sample	(18.9, 20.1 ppb)	< 1.0
19 Jun 1986	420	No Sample	(17.2, 35.3 ppb)	< 1.0
29 Jul 1986	460	No Sample	No Sample	< 1.0
Barnwell, South Carolina				
10 ,404 1987	35	< 1.0 w p b	< 1.0 ppb	< 1.0
14 Sep 1987	70	< 1.0	< 1.0	< 1.0
05 Oct 1987	91	< 1.0	< 1.0	< 1.61
09 Nov 1987	126	< 1.0	< 1.0	3.62
30 Nov 1987	147	< 1.0	< 1.0	< 1.0
07 Dec 1987	154	< 1.0	< 1.0	< 1.0
04 Jan 1988	182	< 1.0	< 1.0	< 1.0
01 Feb 1988	210	< 1.0	< 1.71	< 1.0
07 Mar 1988	245	< 1.0	< 1.0	< 1.0
04 Apr 1988	273	< 1.0	< 1.0	< 1.0
25 Apr 1988	294	< 1.0	< 1.0	< 1.0
02 May 1988	301	< 1.0	< 1.0	< 1.0
06 Jun 1988	336	< 1.0	< 1.11	< 1.3
01 Jul 1988	361	No Sample	No Sample	< 1.0
01 Aug 1988	392	< 1.0	< 1.0	< 1.0
07 Sep 1988	429	< 1.0	< 1.11	< 1.9
03 Oct 1988	469	No Sample	No Sample	< 1.0
09 Nov 1988	492	< 1.0	< 1.0	< 1.0
14 Dec 1988	527	< 1.0	< 1.0	< 1.0
01 Jan 1989	557	< 1.0	< 1.8	< 1.11
17 Feb 1989	592	< 1.0	< 1.0	< 1.0
24 Mar 1989	627	< 1.0	< 1.0	< 1.0
13 Apr 1989	649	< 1.0	< 1.0	< 1.0
15 May 1989	679	< 1.0	< 1.0	< 1.0
05 Jun 1989	700	< 1.0	< 1.0	< 1.0
13 Jul 1989	738	< 1.0	< 1.0	< 1.0
11 Oct 1989	828	< 1.0	No Sample	< 1.0
=====				

FIGURE 1. MAP OF BARNWELL, SOUTH CAROLINA (TOP) AND HUGHES ISLAND, FLORIOA (BOTTOM) HEXAZINONE STUDY SITES. SHADED AREA ON BARNWELL STUDY SITE WAS TREATED WITH PRONONE 10G.

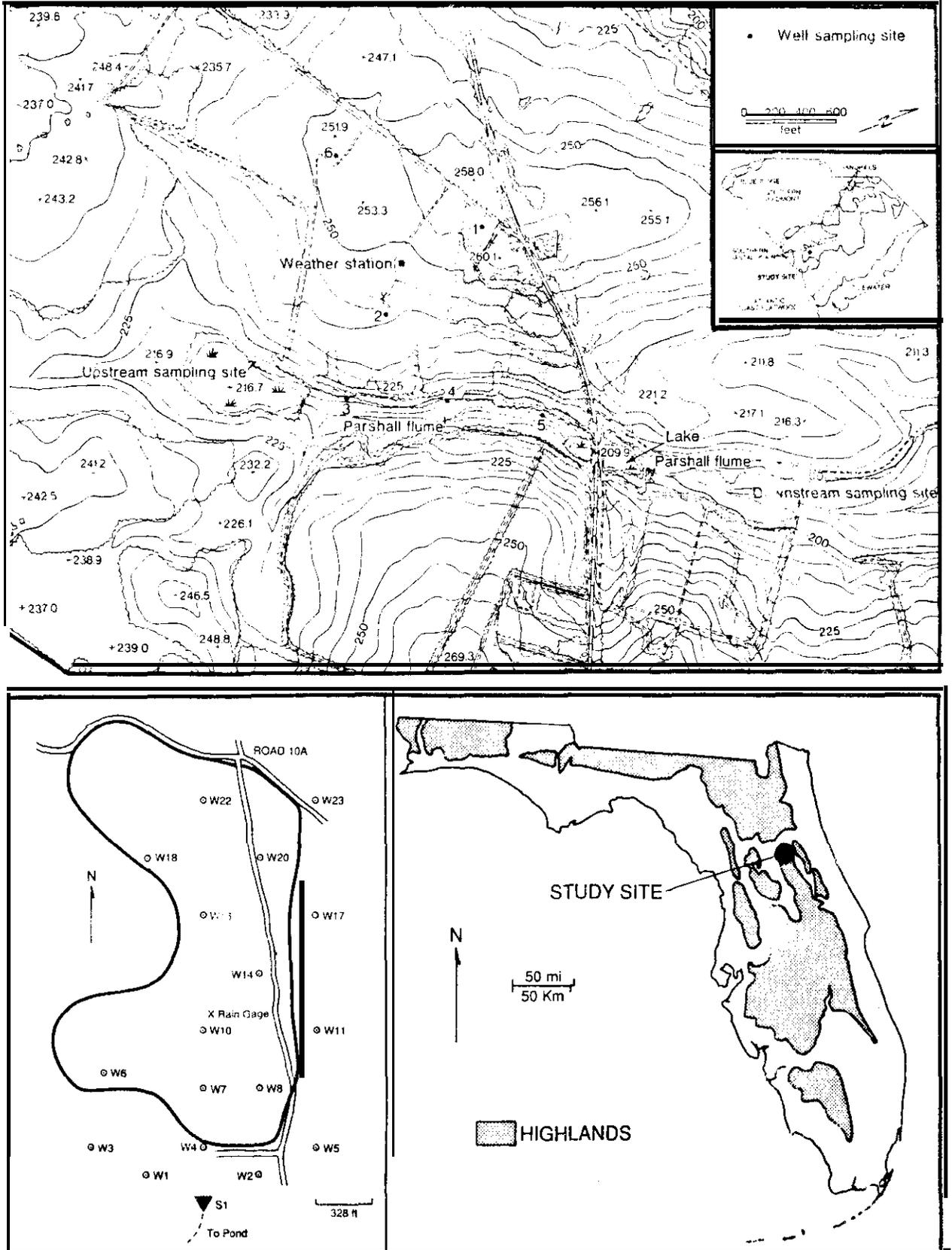


FIGURE 2. RAINFALL DISTRIBUTION FOR HUGHES ISLAND AND BARNWELL SC. STUDY SITES. DAY ZERO FOR HUGHES ISLAND IS JANUARY 1, 1985 AND JANUARY 1, 1987 FOR BARNWELL SC.

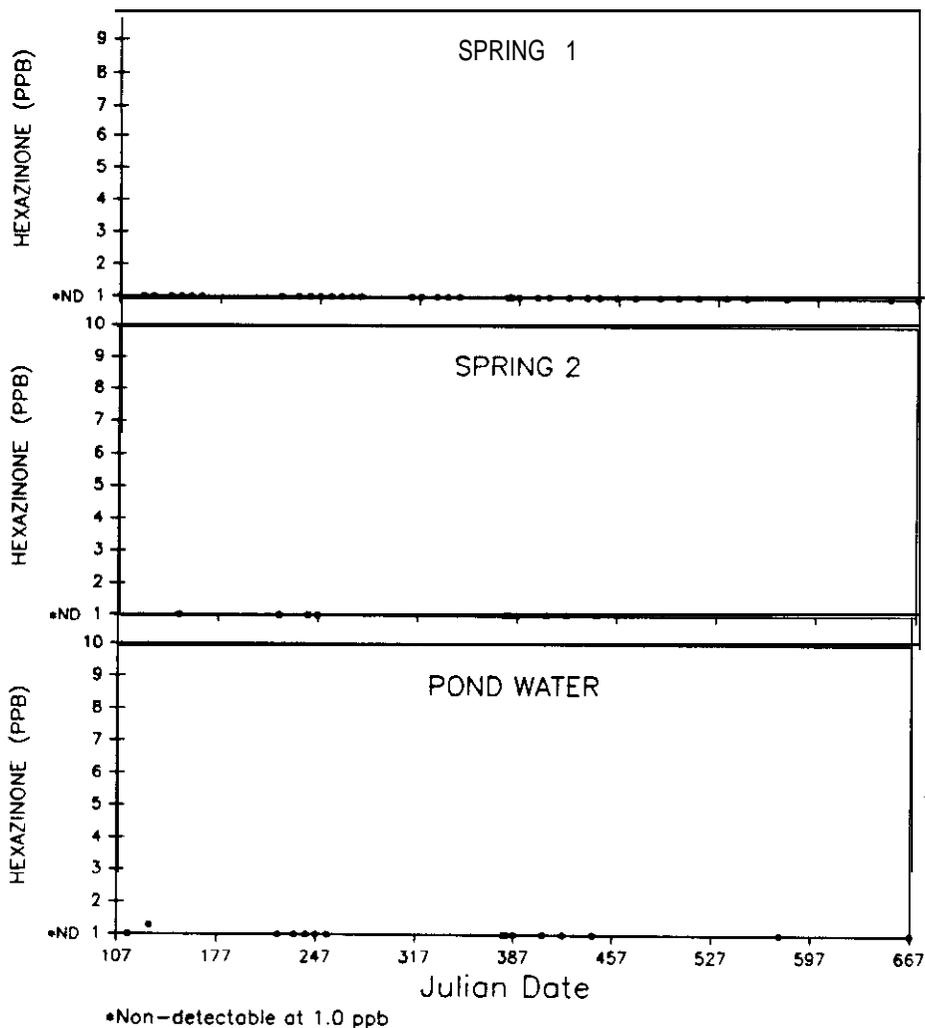
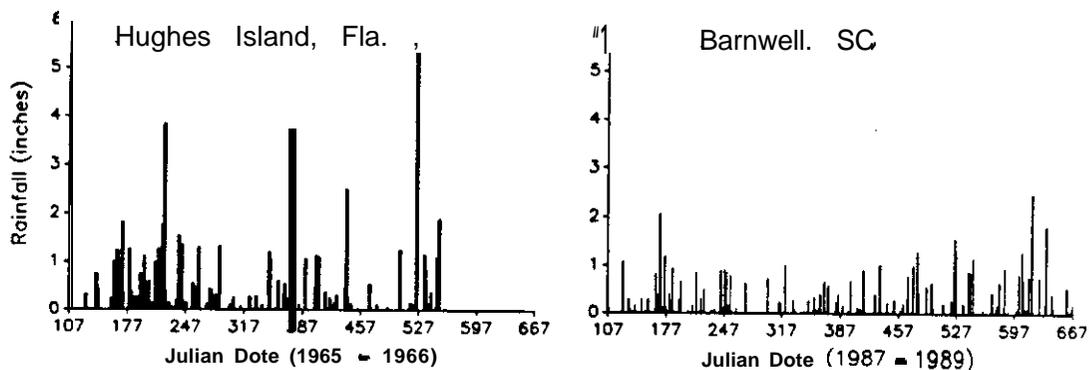


FIGURE 3. HEXAZINONE RESIDUE LEVELS IN SPRING AND SINKHOLE WATER SAMPLES FROM HUGHES ISLAND, FLORIDA STUDY SITE.