AN ABSTRACT OF THE THESIS OF

Mario Hess for the degree of Master of Science in Bioresource Engineering presented on May 16, 1995. Title: Assessment of Variability and Monitoring Methods for Leaching Under Cover Crop Management.

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Abstract approved: ______________________

John S. Selker

The contamination of ground water resources represents a serious problem and a prominent threat to the health of our society. This study focuses on the leaching of inorganic anions as a function of agricultural practices under natural field conditions. In order to enhance the understanding of such leaching processes, this thesis evaluates the spatial variability of the leaching characteristics of a site, the factors controlling percolation, and the use of a cereal rye cover crop to reduce nitrate leaching.

Thirty-two Passive Capillary Wick Samplers (PCAPS) and 32 suction cups were installed at a depth of 120 cm under row crop produced in a Woodburn Variant loam (fine-loamy mixed mesic Aquultic Argixeroll). Significant correlation for the water flux was seen at the 2.0 m distance, beyond which values were uncorrelated. No spatial correlation was seen in hydrodynamic dispersion coefficients. Percolation was independent of field-saturated hydraulic conductivity, while the quantity of incident water was strongly correlated with percolation. The occurrence of preferential flow affected the leaching process as documented by solute breakthrough ahead of the main solute peak. Rates of nitrogen fertilizer application were proportional to observed nitrate leaching losses. The cover crop significantly reduced the amount of nitrate leaching at all N fertilizer application rates. At the recommended rate, nitrate-N concentrations were lowered on average from 22.2 to 9.9 mg/l; cumulative N mass losses were cut by 62% due to plant uptake by the cover crop. The study demonstrated the importance of conducting long-term field experiments under natural conditions to accurately assess leaching processes.

Assessment of Variability and Monitoring Methods for Leaching Under Cover Crop Management

by

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

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Mario Hess, Author

Dedication

For my mom; ich wünsche ihr von ganzem Herzen, dass die Chemotherapie erfolgreich ist, so dass sie noch viele glückliche und gesunde Jahre leben kann.

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First of all, I want to thank Dr. John S. Selker, my advisor, for his never-ending support and patience. The work with him on this project was an adventure, it was educational and loads of fun.

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Assessment of Variability and Monitoring Methods for Leaching Under Cover Crop Management

1. Introduction

Since the beginning of the industrial revolution about 200 years ago, the world's population has grown very rapidly. This development has caused increasing pressure on life's essential resources. Water is one of the most fundamental of these bioresources. Its intensified use for residential, municipal, commercial, recreational, and industrial purposes has led to diverse problems all over the world. To secure clean drinking water in sufficient quantities is one of our society's most important tasks.

Historically, drinking water was mainly extracted from surface waters (i.e., rivers and lakes). Because of population growth and surface water pollution, societies have become to rely more on ground water. In the former German Democratic Republic, for example, two thirds of the drinking water originates from ground water sources (Dyck and Peschke, 1989). In the United States in 1985, 53% of the nation's population and 97% of the rural population used ground water for drinking water. This resulted in a cumulative withdrawal of ground water during that year of 277.4 million m^3 per day (Moody, 1990).

Because of the importance of subsurface water resources, contamination of ground water represents a serious problem and a prominent threat to the health of our society. The degradation of ground water resources is especially grave because the removal of subsurface water contaminants is generally time-consuming, very expensive, and sometimes even impossible.

There are a variety of ground water contaminants, such as hydrocarbons, synthetic organic chemicals, inorganic cations, inorganic anions, pathogens, and radionuclides.

This study focuses on the leaching of inorganic anions due to agricultural practices. In order to enhance the understanding of the leaching of inorganic anions, this thesis addresses three areas. First, the spatial variability of the leaching characteristics of a site is analyzed. Second, we describe the factors that control percolation in the unsaturated zone at the site. Finally, we evaluate the use of a winter cover crop to reduce the leaching of nitrate to the ground water.

In the next chapter, I will describe the materials and methods used in my investigations. The subsequent three chapters relate to the three objectives outlined above. Each of these chapters includes an objective-specific introduction and literature review, combined with separate results and conclusions.

2. Materials and Methods

2.1 Site Characterization

2.1.1 Location

The study site is situated about 30 km south of Portland, Oregon, on the premises of the North Willamette Research and Extension Center (NWREC), owned by the College of Agriculture of Oregon State University. The NWREC is located at a latitude of 45° 17' N and a longitude of 122° 45' W at an elevation of 46 m above sea level. All results and conclusions we present are specific to this site. Climatological and pedological data for the site as well as the management practices are given in this chapter. This information should allow replication and comparison of our findings.

2.1.2 Climate

The climate is classified as dry-summer subtropical (Csb in the Koeppen classification system (Lutgens and Tarbuck, 1986)). Temperatures are generally mild throughout all seasons. In the winter, the climate at the site is dominated by maritime polar air. A local climate station is situated about 500 m north of the site. Measurements have been taken there every day since 1963 including air and soil temperature, precipitation, evaporation and wind speed and direction (Figure 1).

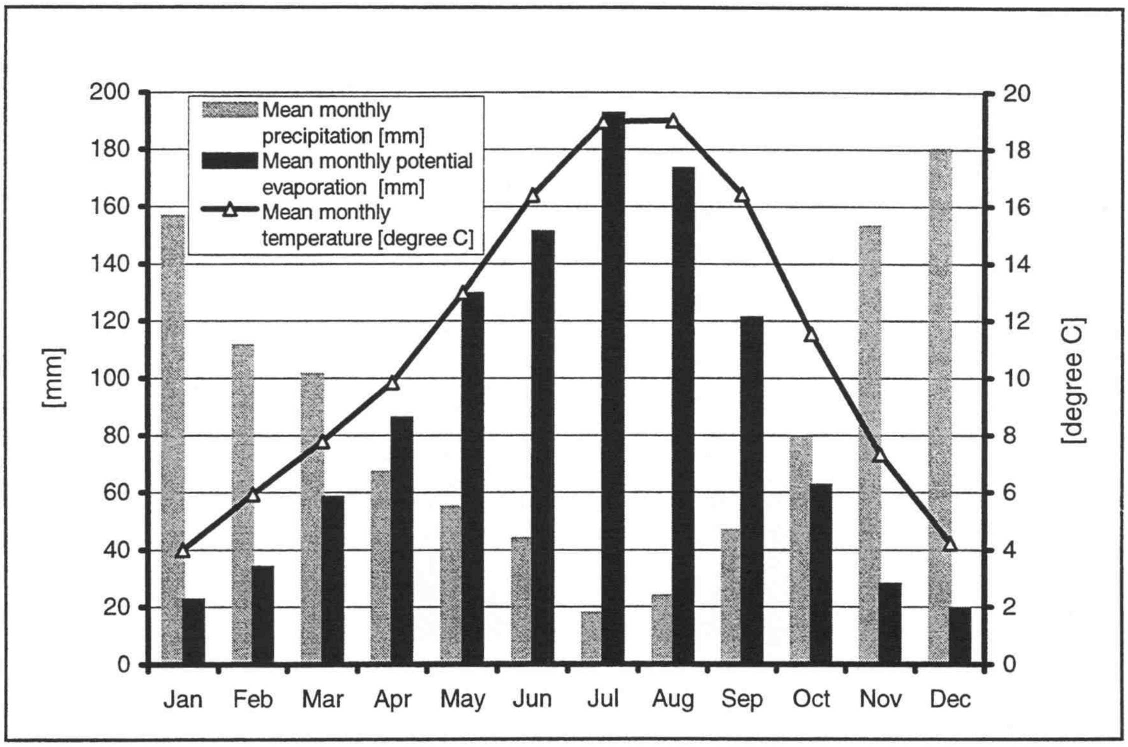

Figure 1. Summary of data from the local climate station at the NWREC 1963 - 1990 (courtesy of the Oregon Climate Service).

The mean annual temperature measured at the local climate station for the years 1963 - 1990 is 11.2°C. The mean annual precipitation for that period amounts to 1036 mm. The precipitation pattern divides the year into a wet winter period from November to April (mean cumulative precipitation = 770 mm) and a rather dry summer period from May to October (mean cumulative precipitation = 266 mm). Precipitation is measured every morning with a non-recording gage. Due to an average wind speed of 0.71 m s^{-1} , precipitation measurements for the 1993/94 season were adjusted by + 2% (Larson and Peck, 1974).

Potential evaporation is measured using an U.S. Class A pan. The pan-measured evaporation, E_{pan} [L] , was corrected by multiplying with a pan coefficient k_{pan} [ ]:

$$E_{rc} = k_{pan} E_{pan} \tag{1}$$

where E_{rc} [L] is the reference crop evaporation. The pan coefficient was determined on the basis of values for average wind speed, average monthly relative humidity, and for the conditions surrounding the climate station (Shuttleworth, 1993). The average value for k_{pan} during the observation period was 0.828.

2.1.3 Soil

The entire study is carried out on a 99 by 99 m large field which is slightly sloped towards the south (< 3%). Before installation of the samplers at 16 selected sites, extensive soil tests were conducted at depths of 13, 64 and 114 cm. We measured organic carbon content, pH, bulk density, particle size distribution, saturated conductivity and water retention. The number of tests considered necessary varied between measured soil properties and between chosen sites (Table 1, 2 and 3; from Brandi-Dohrn, 1993). The soil texture can be characterized as a loam/silt loam at the 13 cm depth, as a loam/clay loam at 64 cm, and as a loam at 114 cm using the USDA classification scheme. The soil is classified primarily as Woodburn Variant loam (fine-loamy mixed mesic Aquultic Argixeroll), with a strip of Willamette Variant loam, wet (fine-loamy mixed mesic Pachic Ultic Argixeroll) bisecting the plot in a north-south direction (Figure 2). Brandi-Dohrn (1993) gives a complete classification of all 16 soil profiles where samplers were installed.

Table 1. Organic carbon content, pH, and bulk density of Woodburn Variant loam and Willamette Variant loam, wet (from Brandi-Dohrn, 1993).

	Organic carbon		pH		Bulk density	
Depth	Mean	n*	Mean	n*	Mean	n*
cm	%				g cm^{-3}	
13	0.19 (13)[†]	16	6.2 (7)[†]	11	1.24 (4)[†]	4
64	0.19 (49)	14	5.7 (3)	11	1.35 (1)	4
114	0.08 (38)	9	5.8 (2)	12	1.29 (2)	4

[†] Number in parenthesis is coefficient of variation in units of percent.
* Number of tests conducted.

Table 2. Particle size distribution and saturated conductivity K_{sat} of Willamette Variant loam, wet (from Brandi-Dohrn, 1993).

	Particle Size Distribution				K_{sat}	
Depth	Clay	Silt	Sand	n*	Mean	n*
cm	%				cm day^{-1}	
13	16.8	50.0	33.2	1	500 (72)[†]	3
64	27.3	46.8	25.9	1	60 (115)	3
114	17.4	38.7	43.9	1	6 (83)	3

[†] Number in parenthesis is coefficient of variation in units of percent.
* Number of tests conducted.

Table 3. Water retention of Willamette Variant loam, wet (from Brandi-Dohrn, 1993).

		Moisture Content at				
Depth	n*	- 0.3 kPa	- 10 kPa	- 80 kPa	- 200 kPa	- 1500 kPa
cm		% by volume				
13	4	48	33	27	23	9
64	4	46	35	30	26	12
114	4	45	41	35	28	12

* Number of tests conducted.

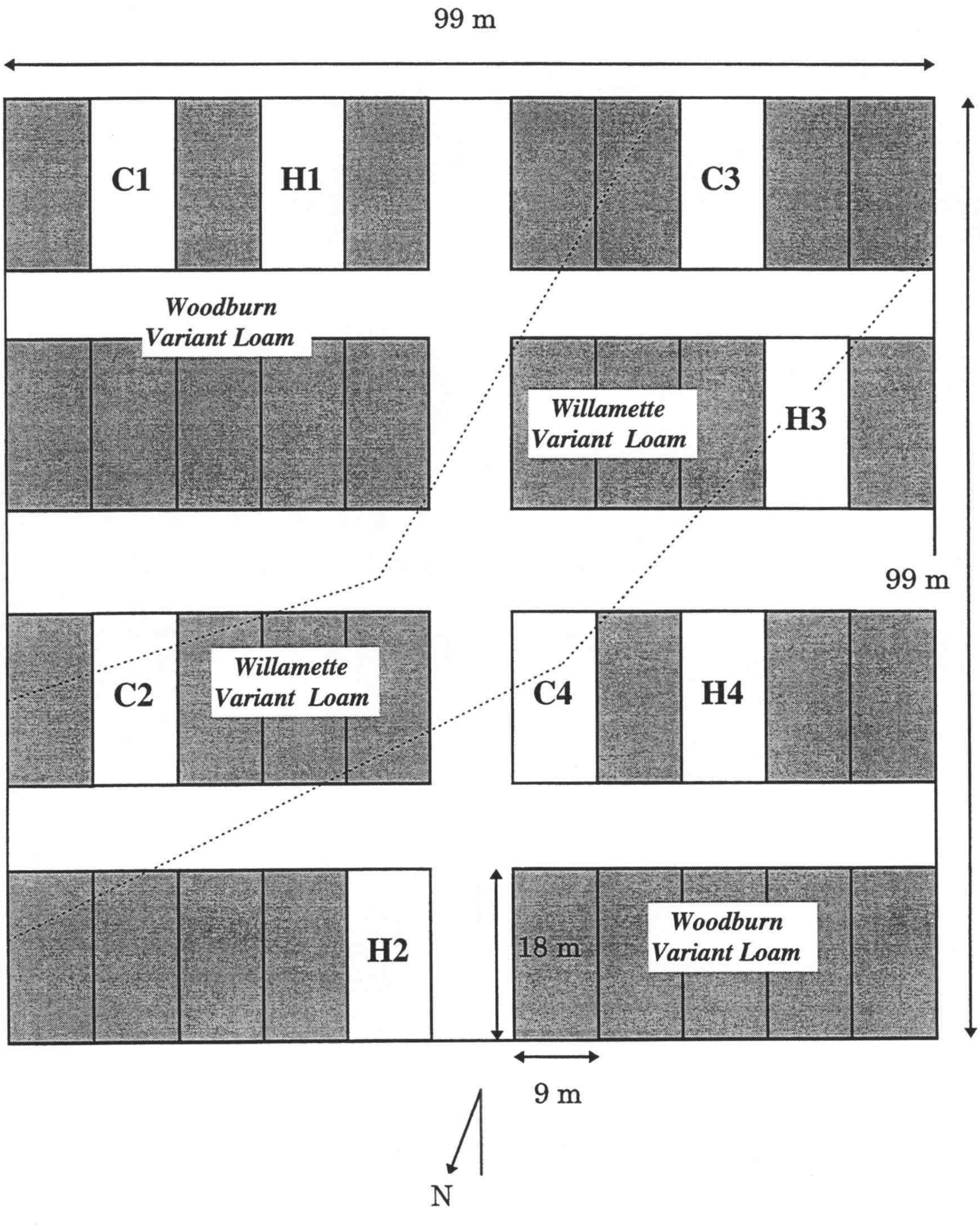

Figure 2. Layout of crop/cover crop rotation study at the NWREC with numbered plots indicating sample sites (C = conventional crop/fallow rotation, H = alternative crop/cover crop rotation; dotted line represents approximate division line between Woodburn Variant loam and Willamette Variant loam; drawn to scale).

In-situ measurements of field-saturated conductivity were conducted at all 16 sample sites between April 30 and May 7, 1994 using the well permeameter (a.k.a. Guelph permeameter) method (Reynolds and Elrick, 1987; Reynolds et al., 1985; Reynolds et al., 1992). The infiltration tests were located on the nitrogen (hereafter abbreviated with N) fertilizer application division line about 2 m away from the former trench at a depth of 100 cm (Figure 3). An auger with an outside diameter of 8.6 cm was used to drill a 1 m deep cylindrical hole with its bottom well above the water table. Within this hole, a constant ponding depth was established and maintained using an in-hole Mariotte apparatus (Figure 4). At each site, the three-dimensional infiltration process reached steady state within ten minutes after the start of the experiment. The steady recharge from such a cylindrical well into uniform, unsaturated media can be described by (Reynolds et al., 1992):

$$K_{fsat} = \frac{CQ}{2\pi H^2 + C\pi a^2 + \frac{2\pi H}{\alpha *}} \qquad (2)$$

K_{fsat} = field-saturated conductivity [LT^{-1}],
C = dimensionless shape factor [ ],
Q = steady-state flow rate [$L^3 T^{-1}$],
H = constant ponding depth [L],
a = well radius [L],
α^* = site-estimated weighting factor [L^{-1}].

The dimensionless shape factor C is based on the ratio of H/a and can be determined using Reynolds and Elrick (1987, p.292). The site-estimated weighting factor α^* categorizes the porous media and can be taken as 12 m^{-1} for the soil at this study site (Reynolds et al., 1992).

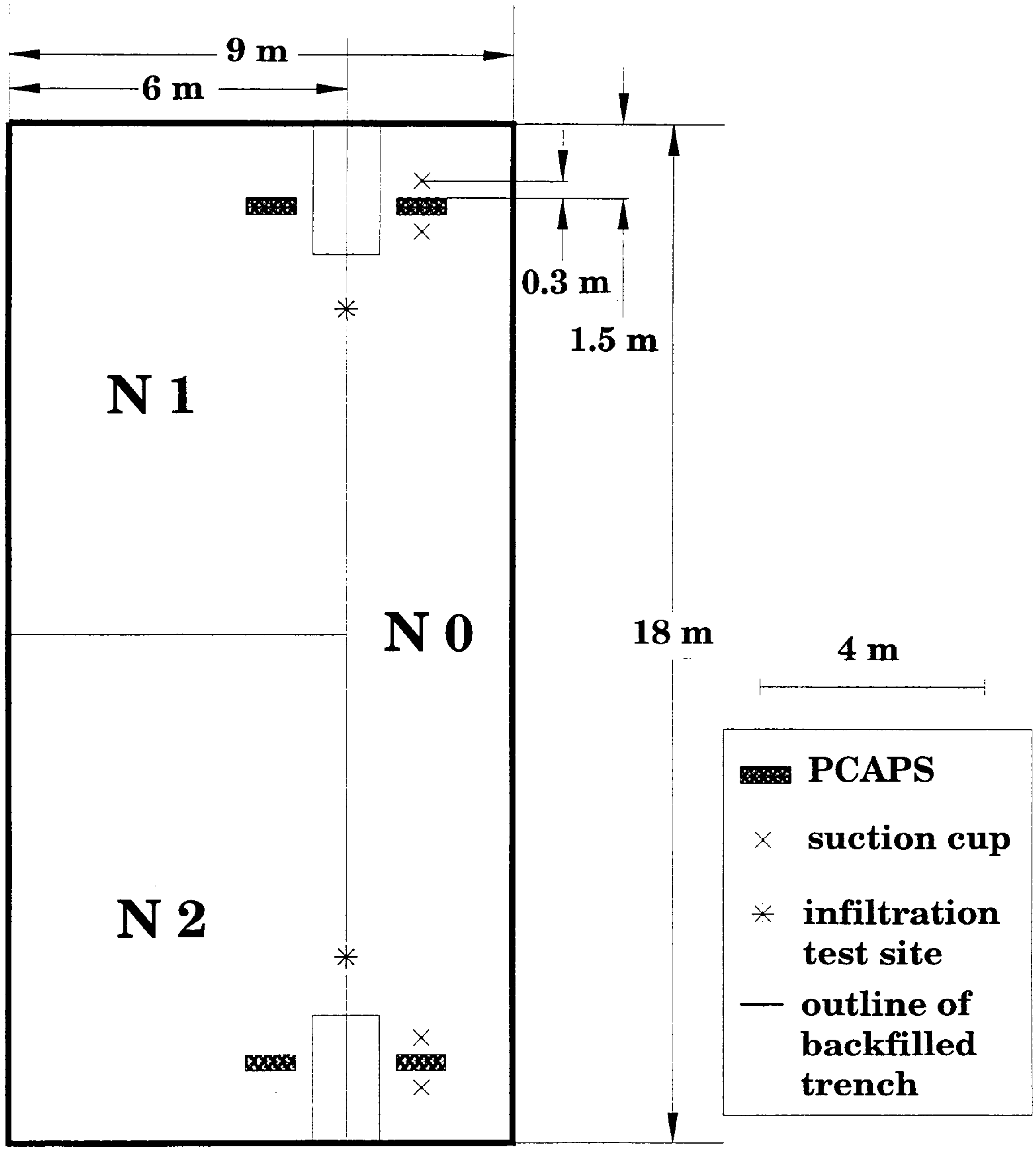

Figure 3. Layout of plot and placement of samplers (from Brandi-Dohrn, 1993).

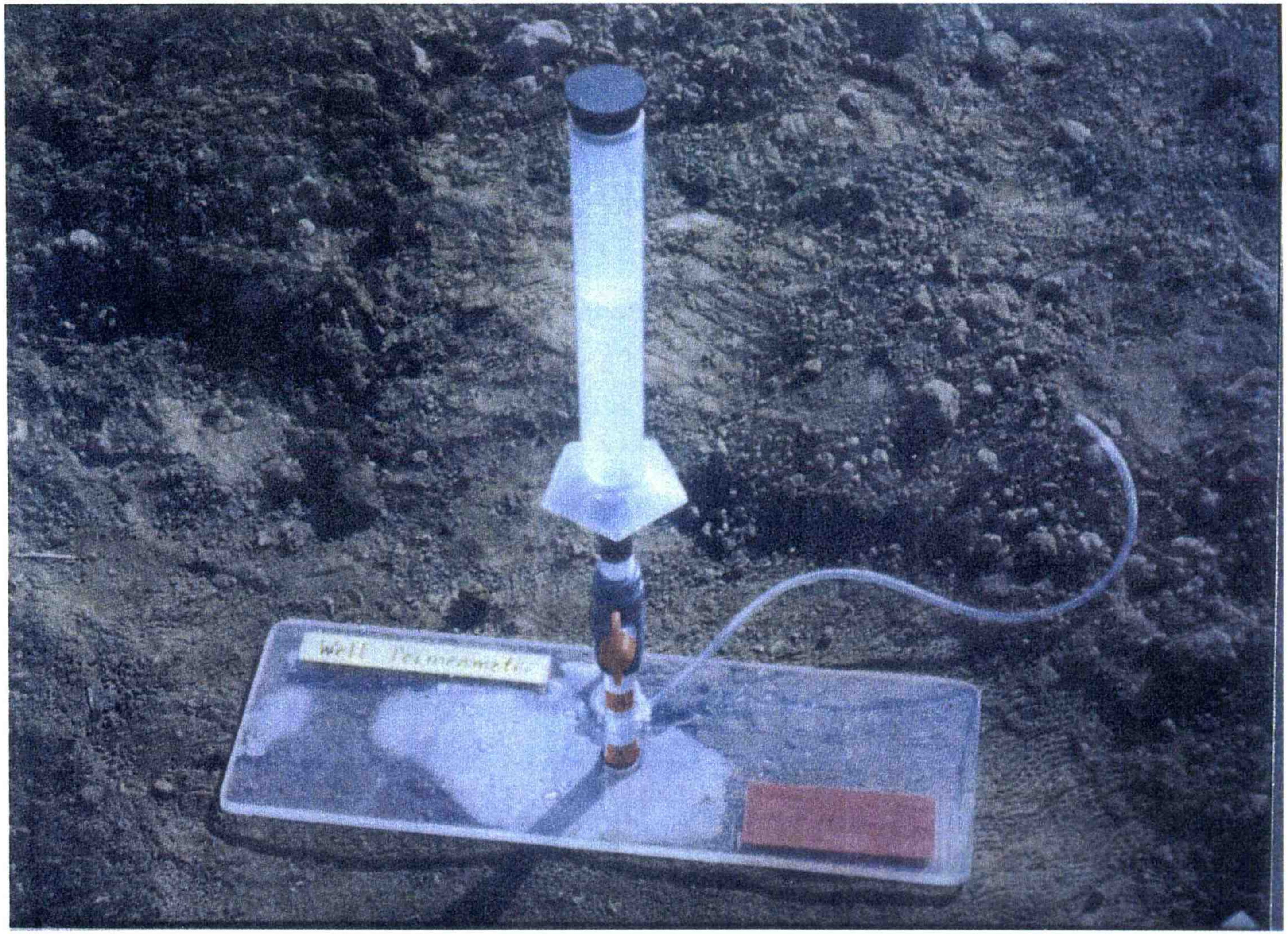

Figure 4. Well permeameter.

2.1.4 Management

The 0.98 ha field was in a wheat/fallow rotation from 1982 until 1989. In 1989, a crop/cover crop rotation study was established dividing the field into 40 equal-sized plots with various rotation categories and different treatments (Figure 2). In the summer of 1992, 32 passive capillary wick samplers (a.k.a. PCAPS) were installed along with 32 suction cup samplers. Four conventionally managed C-plots (crop/fallow rotation) and four alternatively-managed H-plots (crop/cover crop rotation) were chosen as sites for the 64 samplers. The crop/cover crop rotation study was designed as a complete block split plot, with cropping system as main plot (i.e., C-plot or H-plot) and N fertilizer application rate (N0, N1, N2) as the subplot (Figure 3).

The cropping system history for C- and H-plots is summarized in Table 4. Table 5 displays seeding and harvest times for the 1993/94 season of the experiment. In 1993, broccoli was the spring crop on all C-plots and H-plots. The only fertilizer used was urea. Three different N fertilizer application rates, referred to as N0, Nl, and N2, were utilized in the appropriate subplots within each plot as portrayed in Figure 3. The rates and timing of fertilization with urea for the broccoli are shown in Table 6. Additionally, 1.46 kg ha^{-1} active ingredient of Lorsban insecticide and 0.84 kg ha^{-1} active ingredient of Treflan herbicide were applied on all plots during soil preparation. During the growing season, 1.12 kg ha^{-1} diazinon was applied for cabbage maggot control. The cereal rye cover crop, seeded in the fall of 1993, did not receive any fertilizers or pesticides.

Table 4. History of conventionally-managed C-plots and of alternatively-managed H-plots.

Plot	1989	1990		1991	
	Fall	Spring	Fall	Spring	Fall
C	fallow	sweet corn	fallow	broccoli	winter wheat
H	cereal rye	sweet corn	cereal rye	broccoli	cereal rye

Plot	1992		1993		1994
	Spring	Fall	Spring	Fall	Spring
C	winter wheat	fallow	broccoli	fallow	sweet corn
H	sweet corn	cereal rye	broccoli	cereal rye	sweet corn

Table 5. Seeding and harvest times for C- and H-plots for the 1993/94 season.

Crop	Seeding	Harvest
broccoli (C, H)	June 9, 1993	August 30, 1993 ①
cereal rye (H)	September 30, 1993	April 13, 1994 ②

① First harvest (only heads of broccoli) on August 19, 1993.

② Mowed on April 13, 1994 and worked under over the next two weeks.

Table 6. Rates and time of urea application for conventionally- and alternatively-managed plots in the summer of 1993.

		1. Application		2. Application		Total
Crop	N category	Rate	Date	Rate	Date	Rate
		kg N ha^{-1}		kg N ha^{-1}		kg N ha^{-1}
Broccoli	N0	0		0		0
Broccoli	N1	70	June 16	70	July 21	140
Broccoli	N2	140	June 16	140	July 21	280

2.2 Tracers

To mimic the water and solute movement, three tracers were applied in a single application on November 4, 1992: Bromide as a conservative tracer to model the soil water flux, Brilliant Blue FCF (also known as FD&C Blue No.1) as a non-conservative dye tracer to model the movement of compounds which sorb to soil organic matter and clay particles, and Rhodamine WT (also known as Acid Red 388) as a back-up tracer for Brilliant Blue FCF. Bromide was chosen because its ions do not adsorb to negatively charged soil minerals and because it has a low natural background concentration. Bromide represents an ideal tracer moving approximately at the same velocity as the soil water does. Bromide is favorable because it has a low acute and chronic toxicity to mammals and aquatic organisms (Flury and Papritz, 1993). The anionic dye tracers Brilliant Blue FCF and Rhodamine WT were selected due to their moderate mobility and their low toxicity (Everts and Kanwar, 1994; Flury and Flühler, 1994; Flury and Flühler, 1995; Smart and Laidlaw, 1977).

All three tracers were mixed in 11.34 l of tap water at concentrations of 29.6 g l^{-1} (Bromide); 67.9 g l^{-1} (Brilliant Blue FCF); and 27.0 mg l^{-1} (Rhodamine WT). They were then applied to the soil surface above adjacent pairs of PCAPS on a 3 by 7.5 m area using a 3-m wide pesticide bicycle sprayer. The application of tracer solution totalled a depth of 0.5 mm. The four days following the application (November 5 - 8, 1992) had 0, 0, 3.5, and 4.5 mm of precipitation, respectively. Assuming a 2.0 cm mixing zone and estimating field capacity to be 0.344, initial tracer concentrations C_0 were calculated as mass of tracer over the volume of water at field capacity within the 2.0 cm mixing zone. This technique resulted in C_0 values of 2168 mg l^{-1} for bromide, 4973 mg l^{-1} for Brilliant Blue FCF, and 1.98 mg l^{-1} for Rhodamine WT.

2.3 Characterization of Samplers

2.3.1 Passive capillary wick samplers

In the summer of 1992, 32 passive capillary wick samplers (a.k.a. PCAPS) were constructed. Custom molded 15 kg epoxy-coated fiberglass boxes (32 cm wide, 85.5 cm long, and 62 cm deep) with a 10 by 20 cm access window on the side and a stainless steel panel (31 cm wide, 84.5 cm long, and 1 mm thick) on the top were used as outer frames of the samplers. Each frame holds three wicks and three 3.78 l collection glass vessels inside encompassing three separate sampling units (Figures 5 and 6). We used braided 2.93 cm thick medium density Amatex fiberglass wicks (#10-863 KR-08, Amatex Co., Norristown, PA). The top 22 cm of each wick were unraveled into single filaments. The wicks were then combusted at 400°C to clean them (Knutson et al., 1993), before being spread out radially on top of the panel.

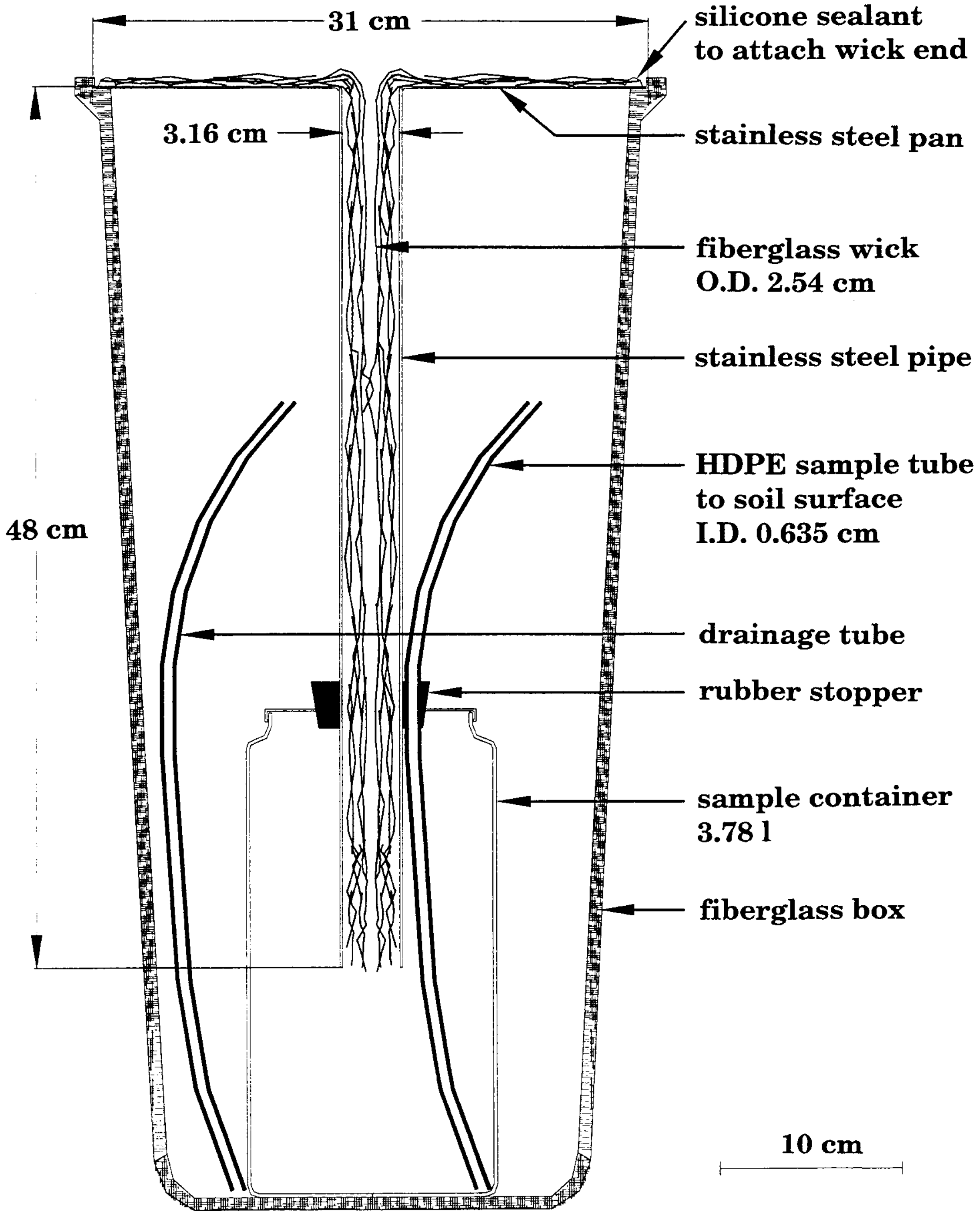

Figure 5. Crossectional view of PCAPS (from Brandi-Dohrn, 1993).

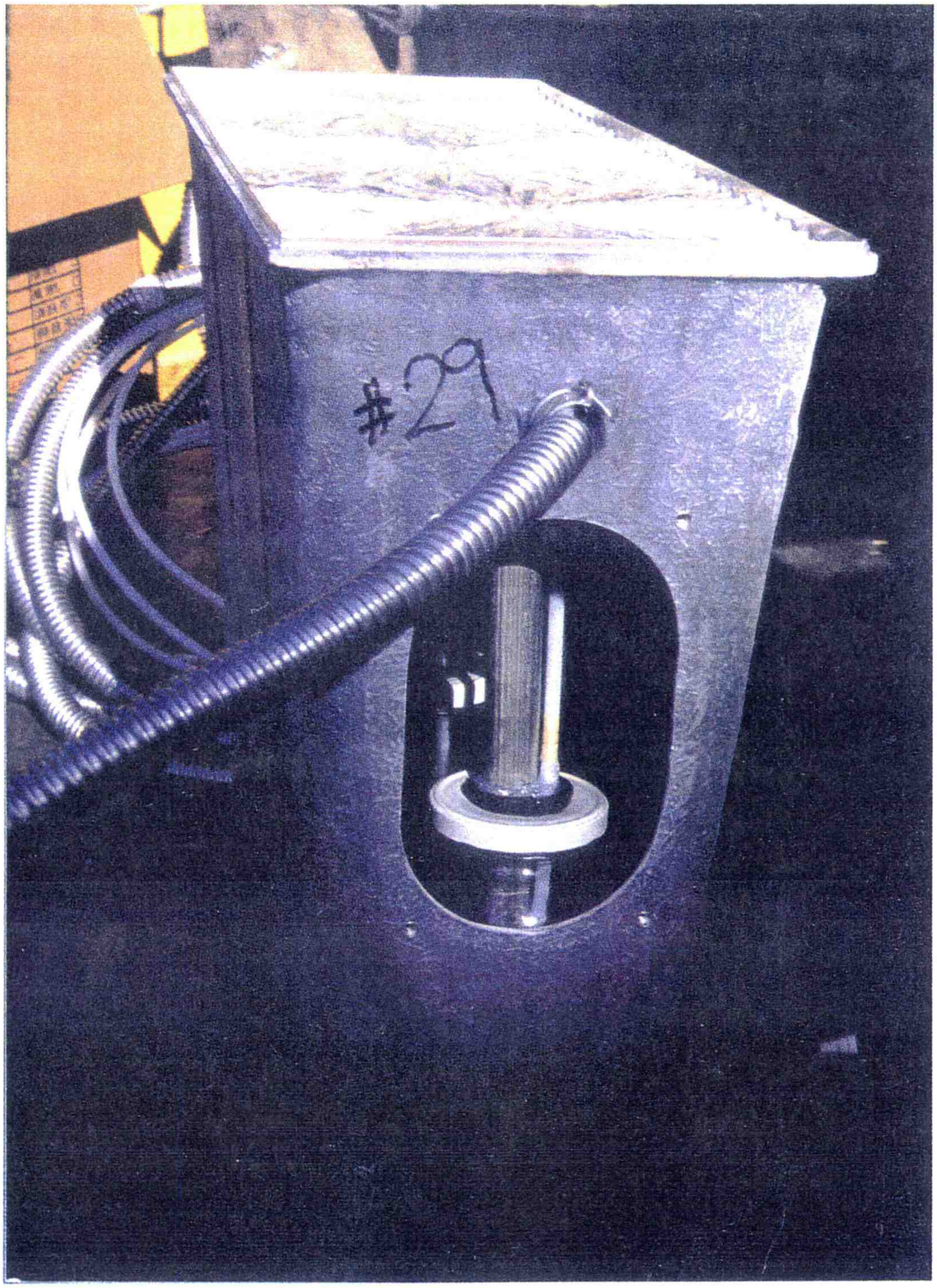

Figure 6. Passive Capillary Wick Sampler (PCAPS).

The ends of all filaments were glued to the panel using a single drop of silicone. The lower 48 cm of each wick were directed through a hole in the middle of the three 31 by 28 cm subsections of the top steel panel and down a 31.6-mm I.D. alloy 304 stainless steel pipe which had been pushed through the top panel. The steel pipe encasing the wick together with the High Density Polyethylene (HDPE) sample unit access tube were inserted into the actual collection vessel. The vessel was then sealed using a black rubber stopper and silicone (Figure 5). The three HDPE sample unit access tubes and a HDPE drainage tube (built in, in case water enters the outer fiberglass box) were guided through the lateral access window of the outer frame. Finally, the top steel panel as well as the lateral access window were sealed using silicone sealant.

In the field, a back hoe was used to dig trenches on the north and the south side of each of the eight chosen plots (Figure 2). The trenches were 2.3 m long, 1.2 m wide, and 2.7 m deep. They were situated exactly along the division line between N0 and N1/N2 treatments (Figure 3). As final sites for the PCAPS, 1.2 m long lateral tunnels were excavated from the side of the trench to position the samplers 0.9 m away from the N fertilizer application rate division line at a depth of 1.2 m. The tunnel roofs were leveled, smoothed, and finally scraped carefully with a serrated scythe to avoid smearing pores with clay. The top panels of the PCAPS were filled with 2 layers of sieved, native soil. Upon final installation, two wooden wedges (10 cm wide, 10 cm deep, 100 cm long) were used to bring each PCAPS into very firm contact with the tunnel roofs (Figure 7). The four HDPE tubes, coming out of the lateral access window of the PCAPS, were encased in a 2.54 cm aluminum flex hose and run to a concrete irrigation box at the soil surface. The originally installed plastic irrigation boxes were mostly crushed by heavy machinery running over them. From September 19 to 21, 1994 they were replaced by concrete irrigation boxes.

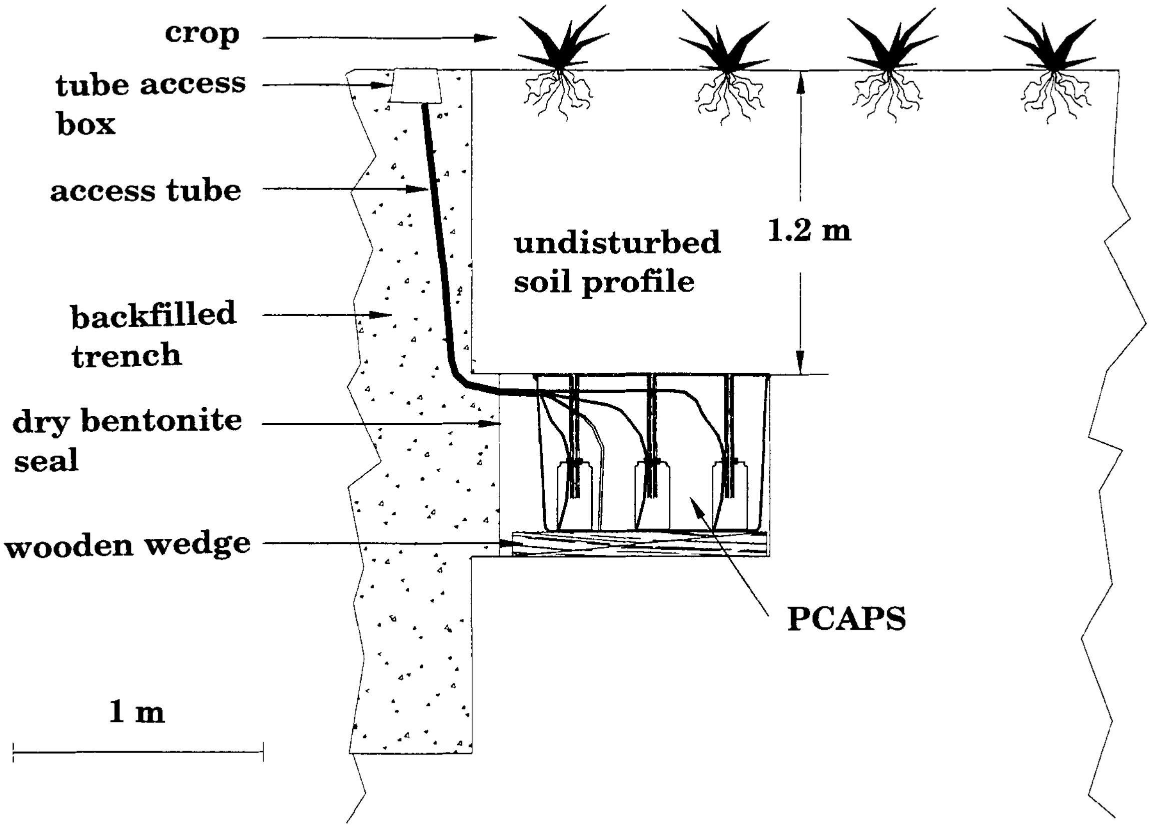

Figure 7. Crossectional view of installed PCAPS in the field (from Brandi-Dohrn, 1993).

Finally, a 4.0 cm thick dry bentonite seal was used to separate the PCAPS from the trenches. The trenches were refilled in two lifts. A back hoe mounted hydraulic compactor was used after each lift compacting the soil in the trenches to the original bulk density. Further details upon construction and installation of the PCAPS are given by Brandi-Dohrn (1993).

2.3.2 Suction cup samplers

Thirty-two suction cup samplers were constructed using highflow porous ceramic cups (# 653X01.B1M3, Soilmoisture Equipment, Santa Barbara, CA). These ceramic cups were 6.0 cm long, had an outside diameter of 5.0 cm and an air entry pressure of 1000 hPa. PVC pipes (15 cm long, 4.4 cm I.D.) were glued to the porous cups using epoxy. Each cup sampler has a volume of approximately 250 ml. Two HDPE tubes (one for sampling, the other to apply a vacuum) led into the sampling unit which was sealed on top by a black rubber stopper.

Two suction cup samplers were installed per trench. They were all located on the N0 side of the plots at the same depth as the PCAPS, one 30 cm to the north of the N0-PCAPS, the other correspondingly 30 cm to the south of that PCAPS (Figure 3). A hand auger was used to drill 5.0 cm wide holes into the trench walls at an angle of 45°. The ceramic cups were dipped into a silica flour slurry before they were placed in the holes containing 50 ml of the same slurry. The two HDPE tubes were encased in an aluminum flex hose leading to the irrigation box at the soil surface. A double sequence of native soil/bentonite was used to seal off the suction cup sampling unit from the trench following standard installation protocol (ASTM, 1992). On each sample date, a vacuum of approximately 54 kPa was applied to the suction cup samplers.

2.4 Samples

2.4.1 Collection of samples

Samples from the PCAPS and the suction cup samplers were collected regularly, depending on the amount of precipitation. For the 1993/94 season, the crucial period of leaching lasted roughly five months from December 1993 until April 1994. During this time, fourteen sample sets were taken. A total of 47 sampling events were conducted over the two years of the study (November '92 - November '94). To collect samples, a vacuum was applied to the sample access tubes for PCAPS and suction cup samplers. A vacuum was needed to overcome the elevation head between the sampling units at a depth of 1.2 m and the graduated cylinders serving as collection and measuring units. For each sampler, the volume sampled was recorded and a subsample was taken and stored in a 60 ml amber HDPE bottle. During the first year of the experiment, Brandi-Dohrn (1993) found that nitrate-N concentration measurements did not vary significantly between the three sampling subunits within one PCAPS. Therefore, only one subsample was taken per PCAPS during the second year of the experiment (1993/94), combining the content of the three subunits in a bucket to receive flow-weighted anion concentrations. After returning from the field, the samples were stored below 5°C overnight and processed the following day.

2.4.2 Analysis of samples

Bromide, nitrate, and phosphate concentrations for all samples were determined using a Dionex 2000I ion chromatograph (IC) with a Dionex AS4A-SC separator column and an AG4A-SC guard column. All samples were diluted 1:1, put into numbered vials, and then frozen at -12.7°C until the ion chromatograph processing run. Preceding the preparations for the IC run, back-up samples were taken from each subsample. They were also numbered and put into frozen storage at -21°C.

After warming to room temperature, samples were analyzed for Brilliant Blue FCF using a spectrophotometer (Milton Roy Spectronic 20, Rochester, NY) and for Rhodamine WT using a fluorometer (Turner Filter Fluorometer Model 111, Mountain View, CA). The Brilliant Blue FCF dye tracer concentration of the samples was determined using a calibration curve at a wave length of 630 nm :

$$C_B = 6.7445\ A \tag{3}$$

where C_B denotes the concentration of Brilliant Blue FCF [mg L^{-1}] and A represents the absorbance reading [%].

Because of the presence of Brilliant Blue FCF, fluorescence readings for Rhodamine WT had to be corrected using the following empirical relationship (from Brandi-Dohrn, 1993):

$$C_R = k_1\, F \exp\,(k_2\, C_B{}^{k_3}) \tag{4}$$

where C_R denotes the concentration of Rhodamine WT [mg L^{-1}], F represents the relative fluorescence reading [ ], and C_B the concentration of Brilliant Blue FCF [mg L^{-1}]. The coefficients k_1, k_2, and k_3 had to be determined by non-linear regression. Rhodamine WT readings were generally very low so that we had to use the most sensitive fluorometer aperture setting (x30). In the presence of less than 10.0 mg L^{-1} of Brilliant Blue FCF and at the above fluorometer setting (x30), the coefficients were determined to be $k_1 = 0.0054$, $k_2 = 0.019$, and $k_3 = 1.87$ (Brandi-Dohrn, 1993).

Following the two dye tracer analyses, all HDPE sample bottles were washed in a dish washer. They were then rinsed three times with distilled water and placed on a metal tray to air dry before being reused in the field. Tests confirmed that HDPE sample bottles did not adsorb any detectable amounts of dye.

3. Spatial Variability of the Leaching Characteristics of a Field Soil

3.1 Introduction and Literature Review

As a part of the global hydrologic cycle, water infiltrates into soil, transporting soluble substances such as nitrates, phosphates, and pesticides. The water continues to percolate through the vadose zone inexorably to the underlying ground water, carrying solutes with it. Its pathway is restricted by the soil's structure and texture as well as boundary conditions such as climate, vegetation, and irrigation. The downward movement of solutes through the vadose zone is called leaching; understanding this process is critical to protecting the quality of ground water resources. The goal of this chapter is to examine the spatial variability of the leaching process as it relates to the transport of hazardous solutes in a field setting.

To comprehend the leaching of solutes, knowledge of water retention and water movement in the vadose zone is necessary. The amount of water in the soil, generally stated as soil water content, affects several important processes including changes in soil temperature, gas exchange with the atmosphere, and diffusion of nutrients to plant roots. The upper limit for the soil water content is defined by the porosity of the soil. If all the pores are filled with water, the soil is fully saturated. By definition, the soil water content within the vadose zone is below saturation, and moisture held in the soil is at a negative pressure. This pressure (a.k.a. matric potential) can hold the water against the force of gravity. Soil water content can be modeled as a power function of matric potential (van Genuchten, 1980). As long as the water content is above field capacity, water can move due to gradients in the total mechanical potential, which is the sum of the gravitational and matric potentials. At water contents below field capacity, the water is considered to be essentially immobile.

In mathematical terms, water flow through the unsaturated zone can be described using Buckingham-Darcy's law (Equation 5) combined with the conservation of mass equation (Equation 6):

$$q = -k(\theta)\ \nabla H \qquad (5)$$

$$\frac{\partial \theta}{\partial t} + \nabla \cdot q = 0 \qquad (6)$$

q = water flux [LT^{-1}],
$k(\theta)$ = conductivity as a function of water content [LT^{-1}],
∇H = gradient of head [ ],
t = time [T].
θ = water content [ ]

The resulting Richards' equation (Richards, 1931) shows that changes in water content over time depend on the gradients of the present conductivity and head as well as the changes in conductivity over depth z:

$$\frac{\partial \theta}{\partial t} = \nabla \cdot (k \nabla H) \, . \qquad (7)$$

Since natural soils generally have macroscopic structure, field-scale water movement cannot be characterized appropriately using the Buckingham-Darcy equation alone. For a more accurate description, an additional component of water transport, encompassing preferential flow, must also be considered.

Preferential flow includes all processes which give rise to infiltrating water by-passing the bulk soil (Luxmoore and Ferrand, 1993). Examples are fingered flow, resulting from unstable wetting fronts (Hill and Parlange, 1972; Selker, 1991; Dekker and Ritsema, 1995), and macropore flow, where water flows along macroscopic channels through soils (Beven and Germann, 1982). Water and solute transport through connected mesopores (pores smaller than one millimeter) is another example of preferential flow (Bronswijk et al., 1995).

Macropores may be formed by the activity of the soil fauna (e.g., moles, mice, and earthworms), the decay of root channels, the shrinking of clay soils or by inter-aggregate voids (Beven and Germann, 1982). Luxmoore (1981) defines macropores as soil pores with matric potentials greater than -0.3 kPa and corresponding diameters greater than one millimeter. Most soils exhibit some sort of macroporosity. Macroporosity affects the movement of water in such a way that water fluxes may vary several orders of magnitude over distances of only a few centimeters (Beven and Germann, 1982).

With preferential flow, percolating water bypasses the sorbing soil matrix and may tremendously alter water and solute fluxes. Under natural conditions in the field, the phenomenon of preferential flow may be critical to the amount of percolation and the leaching of harmful solutes. Flury et al. (1994) concluded that various soil types in Switzerland exhibit preferential flow and are potentially susceptible to pesticide leaching. Preferential movement of dye tracers and pesticides through a loamy soil in Willsboro, New York was observed by Steenhuis et al. (1990). Ghodrati and Jury (1990) found that dye movement through a loamy sand soil in Etiwanda, California followed preferential flow paths, including vertical fingers of dye down to twice the depth of the mean dye displacement.

Water percolating through the vadose zone contains not only H_2O, but also dissolved chemicals and gases. The sorbing and filtering capacity of the soil matrix, once believed to ensure clean ground water, is limited as demonstrated by the pollution of ground water with leaching of fertilizers and pesticides from agricultural lands (Nielsen et al., 1986). The movement of various kinds of solutes within percolating water is controlled by the processes of convection, mechanical dispersion and molecular diffusion.

Convection describes the simple mass flow of solutes along with the infiltrating/percolating water. The one-dimensional convection transport equation is:

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} \qquad (8)$$

C = solute concentration [ML^{-3}],
t = time [T],
v_x = pore water velocity in direction x [LT^{-1}],
x = length [L].

Molecular diffusion (or for short, diffusion) describes the self-induced mixing of molecules due to atomic scale Brownian motion. The rate of diffusion is highly temperature dependent. Fick's first law for one-dimensional steady-state diffusion describes the quantitative movement of solutes from areas of high concentration to areas of low concentration in pure liquid solution:

$$J_S = -D_{diff} \frac{\partial C}{\partial x} \tag{9}$$

J_S = diffusive mass flux of solute per unit area per unit time [$ML^{-2}T^{-1}$],
D_{diff} = diffusion coefficient [L^2T^{-1}],
C = solute concentration [ML^{-3}],
x = length [L].

The spreading of solute-containing water due to the locally variable flow characteristics of the soil pore system is called mechanical dispersion (Scheidegger, 1961). This phenomenon can be attributed to friction within pores (i.e., water moves faster in the center of a pore), path length (path tortuosity forces water to travel different paths), and pore size (water moves faster in large pores). There is mechanical dispersion in the direction of bulk flow, called longitudinal dispersion, as well as normal to this direction, known as transverse dispersion.

The combination of mechanical dispersion and molecular diffusion is referred to as hydrodynamic dispersion, D. Assembling the effects of convection and hydrodynamic dispersion, one can derive the convection-dispersion equation, which has been used in a large variety of laboratory and field solute movement experiments. We used the convection-dispersion equation to model the one-dimensional transport of the applied bromide tracer:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial x}, \tag{10}$$

where R denotes a dimensionless retardation factor. This equation states that the rate of change for the concentration of a solute over time is the sum of the effects of hydrodynamic dispersion and convection (Equation 8).

Numerous field experiments have been conducted to assess the temporal and spatial variability of leaching characteristics of soils. Nielsen et al. (1973) used tensiometers at various depths to monitor water storage and subsequently calculate hydraulic conductivity at 20 sites within a 150 ha field. They concluded that field measured hydraulic conductivities varied greatly over space, especially with increasing matric potential. In a ground-breaking article on spatial variability of field leaching characteristics, Biggar and Nielsen (1976) observed chloride and nitrate breakthrough curves at 20 initially ponded locations within a 150 ha field using suction cup samplers. They found that observed values of pore water velocity and the hydrodynamic dispersion coefficient were both log-normally distributed in respect to area and depth. In another study, chloride and tritium were added to irrigation water applied on an 8 by 8 m plot at the Plant Research Center at New Mexico State University (van de Pol et al., 1977). Suction cup samplers at various depths were used to determine the solute breakthrough. The findings were very similar to the results of Biggar and Nielsen (1976).

Russo and Bresler (1981) found in a field setting (30 sites on a 0.8 ha plot) that values for water content were normally distributed throughout the field. However, values for hydraulic conductivity were found to be log-normally distributed, as long as soil water potentials were greater than -9.806 kPa (-100 cm H_2O). Sisson and Wierenga (1981) used different size ring infiltrometers and observed that steady-state infiltration rates were log-normally distributed. Jury et al. (1986) leached chloride and napropamide (an herbicide) through a loamy sand soil. Leachate concentrations, determined from soil cores, showed that the water flow varied substantially within the 1.44 ha field. The deep penetration of some of the napropamide indicated the occurrence of preferential flow. Smettem (1987) found that soil macroporosity affected the spatial variability of field infiltration parameters. Butters et al. (1989) leached bromide through a non-structured loamy sand soil profile. They observed that there was significant lateral and considerable vertical variability of the solute movement. In an herbicide leaching experiment under natural rainfall conditions, Hall et al. (1989) discovered that annual leaching losses to the ground water were strongly related to that year's present precipitation pattern.

A ponded infiltration study by Suggs and Hopmans (1991) suggested that subsurface heterogeneities such as soil layering are likely to cause varying infiltration rates. Roth et al. (1991) and Sassner et al. (1994) both used chloride to demonstrate that soil exhibits large variabilities in flow and transport properties. As with Jury et al. (1986), the occurrence of preferential flow of chloride was also observed by Roth et al. (1991).

However, spatial variability is not limited to the soil's physical properties. Chemical and biochemical properties of soils also influence spatial variability patterns. Bonmati et al. (1991) showed that urease and phosphatase activities (measured in 24 soil cores) varied widely throughout a 15 by 40 m meadow (coefficients of variation of 88% and 36%, respectively). Total N content and organic carbon content displayed smaller but still considerable variations.

These field studies indicate that the spatial variability of physical, chemical and biochemical properties of soils represent an important determinant to water and solute movement through the vadose zone. Since our study site is located in a high pesticide and N fertilizer leaching risk zone (Kellogg et al., 1994), an assessment of the spatial variability of the leaching characteristics is critical in order to estimate ground water recharge quality. The primary importance of our long-term experiment is that it is conducted in the field under natural rainfall conditions.

The first part of the variability analysis will consist of several comparisons of water flux data. In the second part, we will assess variability by fitting observed tracer breakthrough curves to the convection-dispersion equation using CXTFIT, a one-dimensional solute transport model developed by Parker and van Genuchten (1984).

3.2 Results

3.2.1 Variability of water flux

Suction cup samplers do not provide data on the amount of percolating water (van der Ploeg and Beese, 1977). Since the exact volume of soil from which suction cup samplers extract water remains unknown, attempts to estimate soil solution fluxes using suction cups can be very complicated (Litaor, 1988). Tseng et al. (1995) found that the operation of suction cup samplers dramatically influenced the flow field and therefore significantly biased measured solute concentrations. On the other hand, PCAPS can perform well in a field setting (Brandi-Dohrn, 1993). Due to the known surface area of a PCAPS, water fluxes can be easily determined. Boll et al. (1992) found that fiberglass wicks used in PCAPS had a small effect on the measurement of solute concentrations as well as on the dispersion of solutes. For the subsequent analysis of the variability of the leaching characteristics, we will therefore only use data obtained from the 32 PCAPS within the study site.

For the first seven months of the project, Brandi-Dohrn (1993) found that for each PCAPS sample volumes in its three subunits were strongly correlated. This relationship between sample volumes continued throughout the study (Table 7). Nevertheless, we found that Bottle 1 (i.e., the PCAPS subunit closest to the former trench) collected consistently less water than the other two bottles. For the first two years, the average deviation of the collected percolation into Bottle 1 from the PCAPS mean was -10.8%. Over time, this below average collection of Bottle 1 was reduced, while the above average collection of Bottles 2 and 3 decreased correspondingly. In this manner, we observed that the overall variance of each subunit from the corresponding PCAPS mean diminished over time (Table 8 and Figure 8).

Table 7. Mean of correlation coefficient r for water flux into three subunits of all PCAPS over the first two years of the project.

	Bottle 1	Bottle 2	Bottle 3
Bottle 1	1		
Bottle 2	0.887	1	
Bottle 3	0.856	0.895	1

The above results indicate that it is appropriate to combine the water collection of the three bottles and to consider a PCAPS as one sampling unit. Next, we observed the variability of the collected water flux into the 32 PCAPS. It is apparent that the variance of the collected water flux within the 0.98 ha plot was inversely related to the amount of percolation (Figure 9). This relationship indicates that relatively low amounts of percolation (as

Table 8. Average deviation of collected percolation of bottles 1, 2 and 3 from PCAPS mean.

	Average deviation of single bottle from PCAPS mean		
Period	Bottle 1	Bottle 2	Bottle 3
		%	
days 1-214	- 16.2	+ 9.2	+ 7.0
days 404-727*	- 4.2	+ 1.3	+ 2.9
overall	- 10.8	+ 5.6	+ 5.2

* Note that for days 215-403 (summer and fall 1993) no meaningful values could be calculated due to lack of percolation.

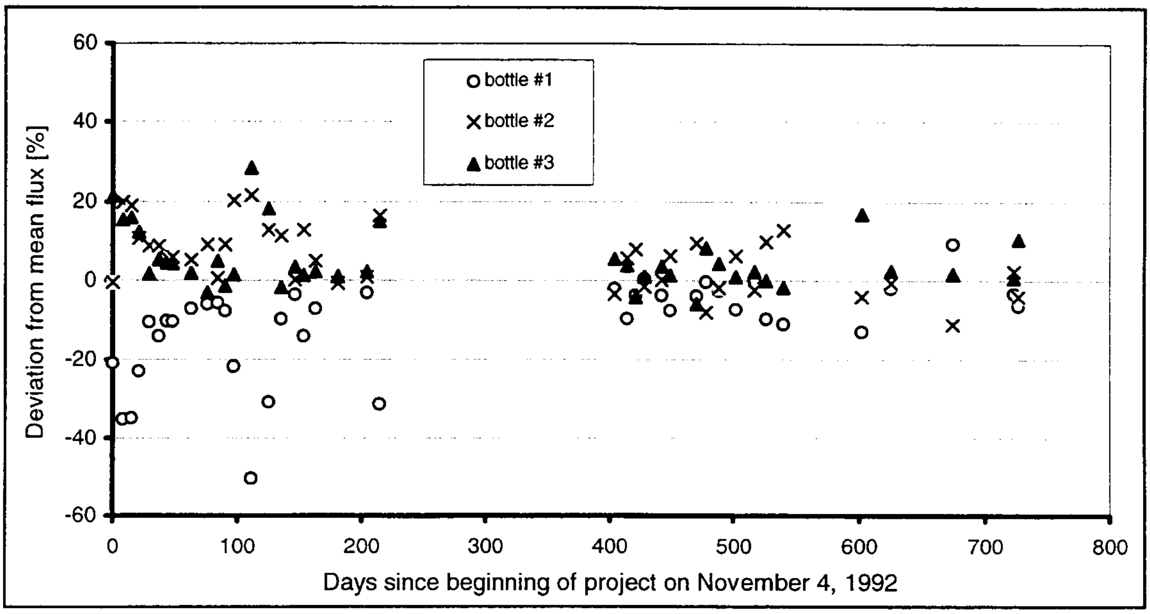

Figure 8. Deviation of collected percolation in the three subunits from PCAPS mean.

with summer time irrigation) are associated with greater variances. This was expected, since preferential flow paths become more important under low flux and high matric potential conditions (Figure 10).

A further approach to assess spatial variability is to rank the 32 PCAPS by the amount of collected percolation. This will reveal if sites were consistent in the relative amount of percolation obtained. In order to receive meaningful results, we selected sampling events conforming to the following three criteria:

(1) all 32 PCAPS were accessible,
(2) none of the 32 PCAPS had overflowed,
(3) a maximum of one PCAPS was empty.

Sixteen out of 47 sampling events met these criteria and were therefore selected for this analysis. For each sample date, rank number 32 was allocated to the PCAPS with the highest water collection, rank number 31 to the one with the second highest and so on. Consequently, the PCAPS with the lowest collection at any given date received rank number 1. The result of this analysis shows that the ranking between PCAPS remained fairly consistent, even though regular rank changes were common (Figure 11). It is

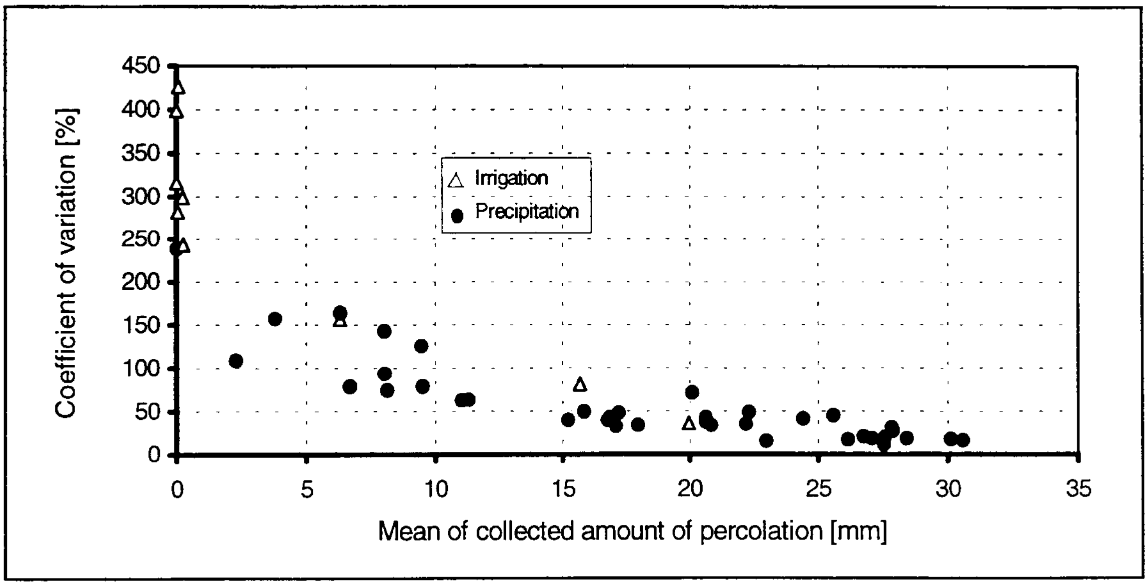

Figure 9. Scatterplot of mean percolation as collected with 32 PCAPS against the coefficients of variation among the samplers.

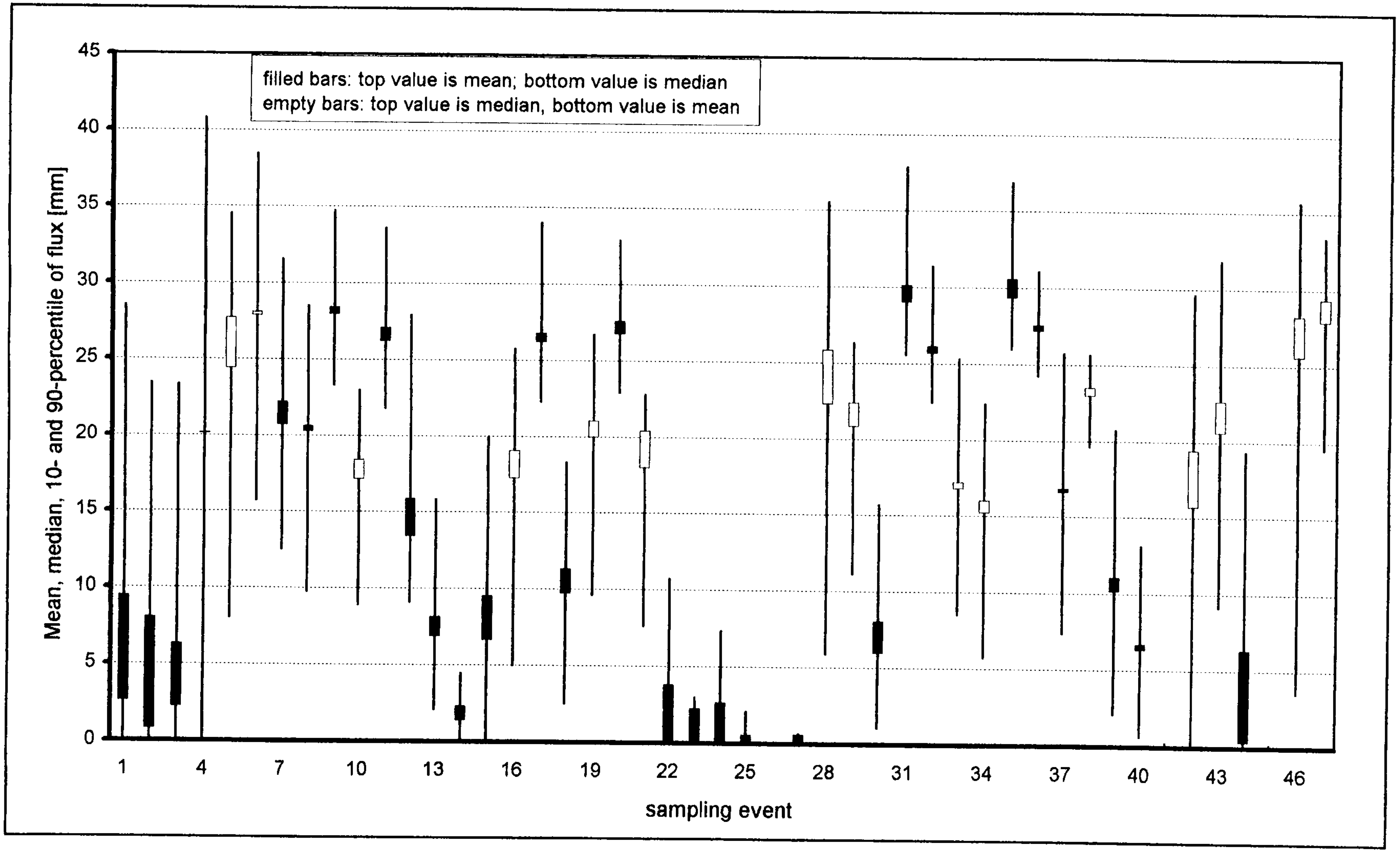

Figure 10. Mean, median, 10- and 90-percentile of collected percolation over the first two years of the project.

important to take into account that most of the 16 sampling events used for this analysis were during winter, when high amounts of precipitation caused consistent water flux collection among samplers. For the 16 selected sampling events, the average coefficient of variation between all samplers was only 46%. This low variation indicates that absolute changes in water flux collection were also low. Therefore, the observed average change in rank between two subsequent sampling events of about one quartile (6.9 ranks) lies within the expected limits. A few PCAPS ranked very consistently in the same range. For example, the PCAPS at C3 North N1 was ranked one in 14 out of 16 events. This ranking analysis indicates that the relative amount of water collected by each PCAPS was consistent over time. Since the percolation characteristics are unlikely to undergo rapid changes with time, the ranking analysis suggests that the PCAPS provide a stable long term collection method. As a result, we believe that the percolation process within our field site was mainly influenced by local soil characteristics and topography.

In the final analysis of the water flux variability, the semi-variogram in respect to the amount of percolation was computed. The semi-variogram value γ as a function of distance is described by:

$$\gamma(|h|) = [\frac{1}{2n(|h|)}] \sum_{i=1}^{n(|h|)} [Z(x_i + h) - Z(x_i)]^2 \qquad (11)$$

where x [L] and h [L] represent the location and distance of samplers, Z the amount of percolation [L], and n(h) the number of data pairs separated by a distance h (Delhomme, 1978). In between all 32 PCAPS within the 0.98 ha study site, the maximum number of cross comparisons were performed using the entire water flux data set for the first two years of the experiment. This

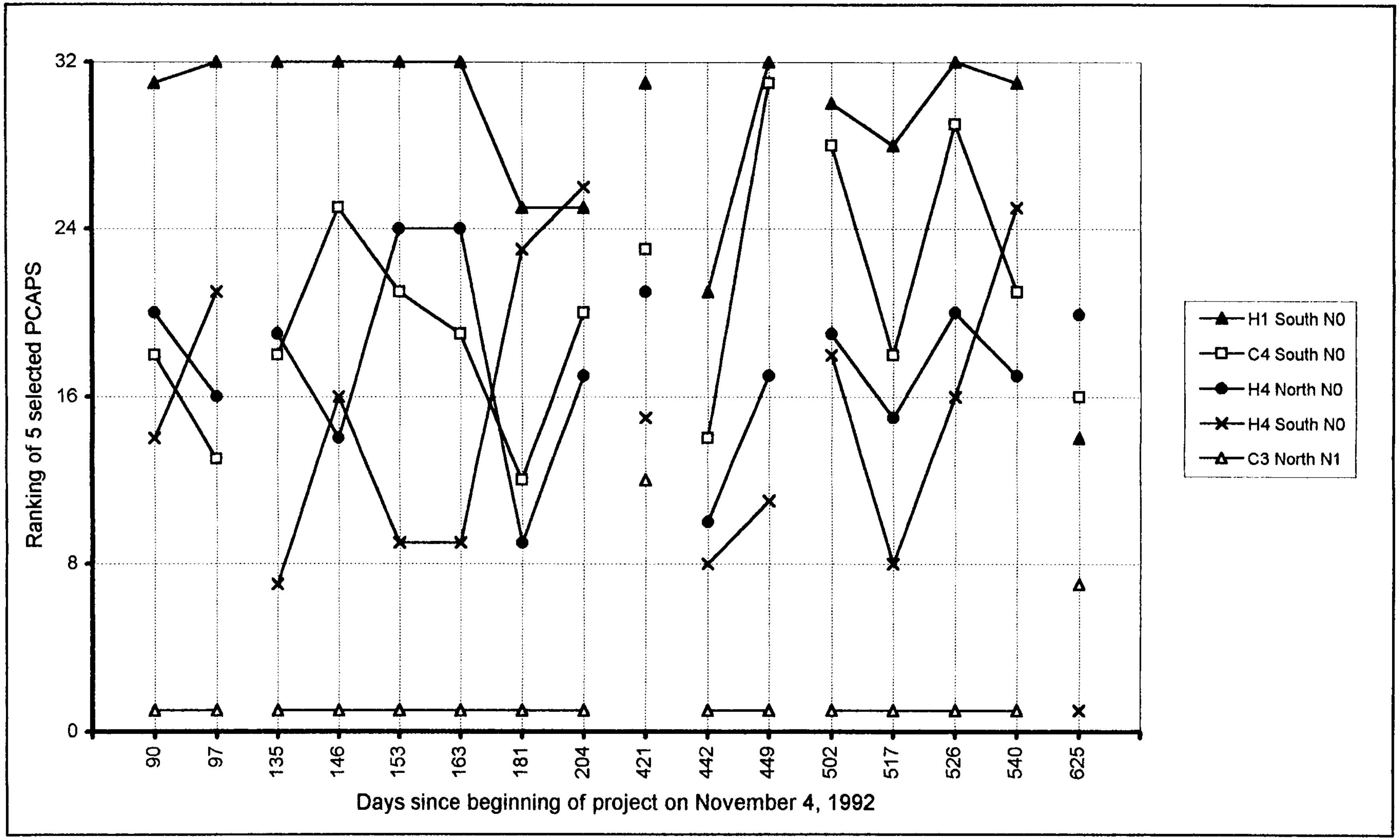

Figure 11. Change in rank of water flux collection between all 32 PCAPS at 16 selected sampling events for the five PCAPS ranked on average at top, 75-percentile, median, 25-percentile and bottom.

procedure resulted in 496 semi-variogram values at distances between 2.0m and 102.5m (Figure 12). Figure 12 indicates that observed values for percolation become random at distances beyond about 20 meters. PCAPS within two meters of each other exhibited some spatial correlation with regard to water flux collection. At each of the 16 former trench sites, this distance encompasses the 16 neighboring PCAPS pairs. It is important to note that no distinction between treatment categories (different N fertilizer application rates; cover crop/no cover crop) was made. Therefore, actual semi-variogram values for these 16 data pairs are likely to be lower than those computed because they all relate to different N fertilizer application rates. In an attempt to categorize semi-variogram values, two additional semi-variograms were created. The first has 21 categories based on five meter distance intervals (Figure 13). In the second, we used equal bin sizes of 20 points (Figure 14). Both plots indicate that there is evidence of correlation with respect to water collection at the two meter distance and a weak correlation between ten to forty meters. Beyond 40 meters, no spatial association is seen.

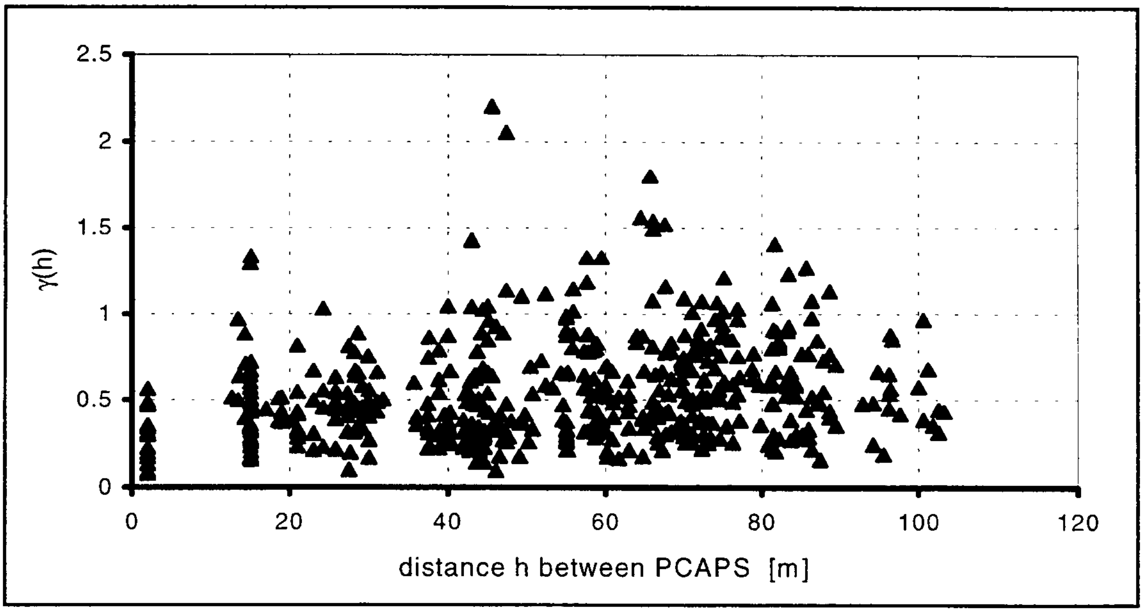

Figure 12. Semi-variogram of water flux.

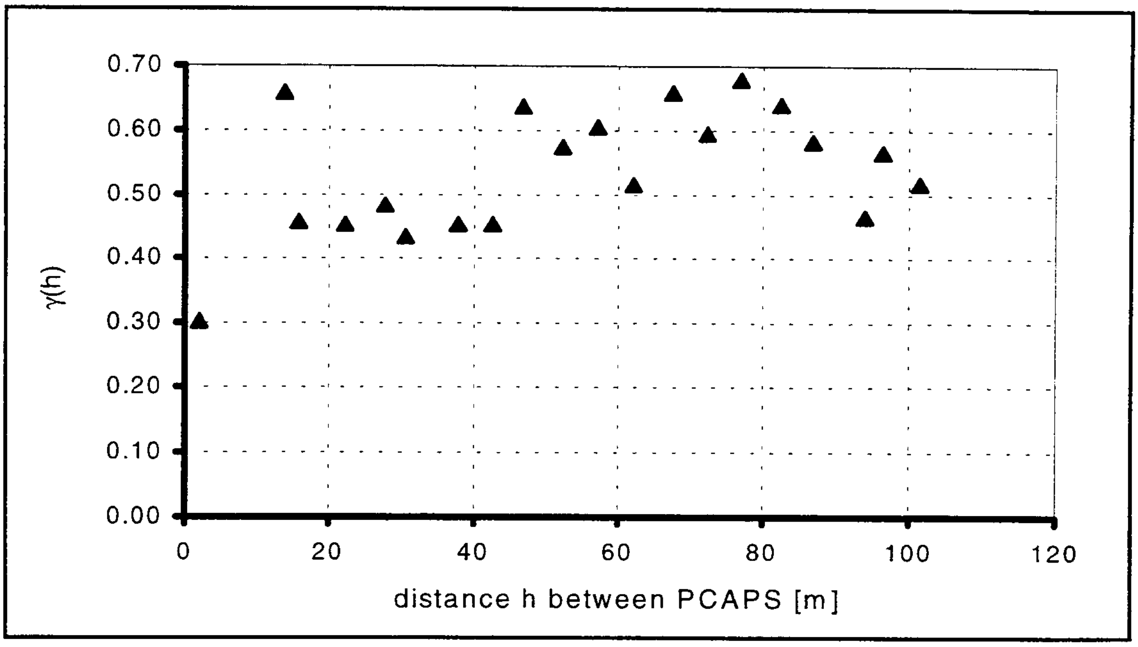

Figure 13. Semi-variogram of water flux with 21 categories based on five meter distance intervals.

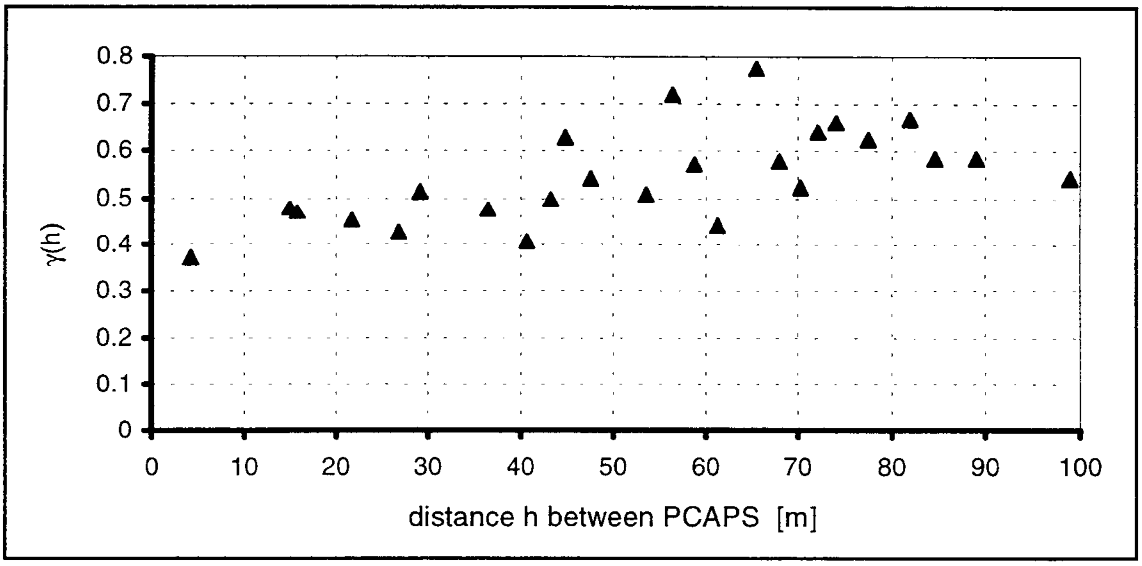

Figure 14. Semi-variogram of water flux with 25 categories of equal bin size.

3.2.2. Variability of the breakthrough of applied tracers

Throughout the first two years of the project, measured Brilliant Blue FCF and Rhodamine WT concentrations were extremely low or even below the detection limit. Subsequently, none of the PCAPS collected enough of these two retarded tracers to allow us to construct a continuous breakthrough curve. Maximum values of dye concentrations were 0.015% of the initial concentration of Brilliant Blue FCF and 0.03% of the initial concentration of Rhodamine WT (Figures 15 and 16). We observed that it takes about one year at this site for one pore volume to reach the depth of the samplers. Brilliant Blue FCF and Rhodamine WT are known to be moderately to strongly adsorbed to the soil matrix (Flury and Flühler, 1995; Everts and Kanwar, 1994). Therefore, their peak breakthrough might not be seen for two or three more years. However, observed concentrations seemed to decrease rather than increase over the second year of the experiment. This indicates that there is a possibility that both dye tracers were biodegraded (Tonogai et al., 1978; Flury and Flühler, 1994). Future observations will be required to reveal the fate of the applied Brilliant Blue FCF and Rhodamine WT.

Bromide proved to be the most useful of the three applied tracers. All 64 samplers (PCAPS and suction cup samplers) were able to detect bromide well. A summary of the flow-weighted bromide concentrations (as measured with 32 PCAPS) is given in Appendix A. For all 32 locations, PCAPS-measured flow-weighted bromide concentrations were plotted against pore volumes as time variable (Figure 17). This plot revealed that the bromide breakthrough past the root zone to the depth of the samplers portrayed a normal distribution over time. Peak concentrations were observed at roughly one pore volume, as one would expect for a conservative tracer.

We then determined the mass recovery of bromide. A bromide mass recovery ratio was calculated by dividing the collected mass of bromide by the applied mass of 3.88 g per PCAPS. The recovery ratio ranged from 5.3% to 76.7% (Appendix B). Its mean was found to be 29.0%, with a standard deviation of 14.9%. This percentage is well below the standard assumption that there would be a high recovery ratio through vertical transport. There are three processes which might have caused the loss of bromide. First, plant uptake was not measured, but might have contributed to the bromide loss (Owens et al., 1985; Kung, 1990; Steenhuis et al., 1990). It is interesting to note that the effect of bromide uptake by the winter cover crop was minor, since the recovery ratio differed by only 1.3% between the fallow and the cover crop treatment plots. The other two processes might have been lateral water movement and lateral diffusion of bromide.

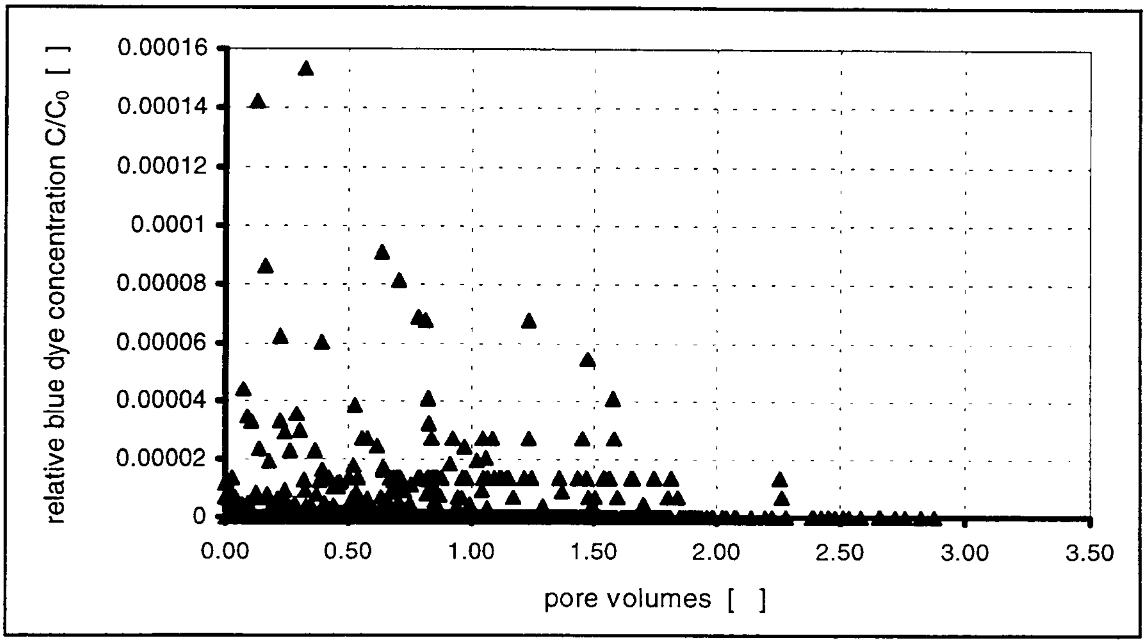

Figure 15. Relative concentrations of Brilliant Blue FCF for all PCAPS throughout the first two years of the experiment.

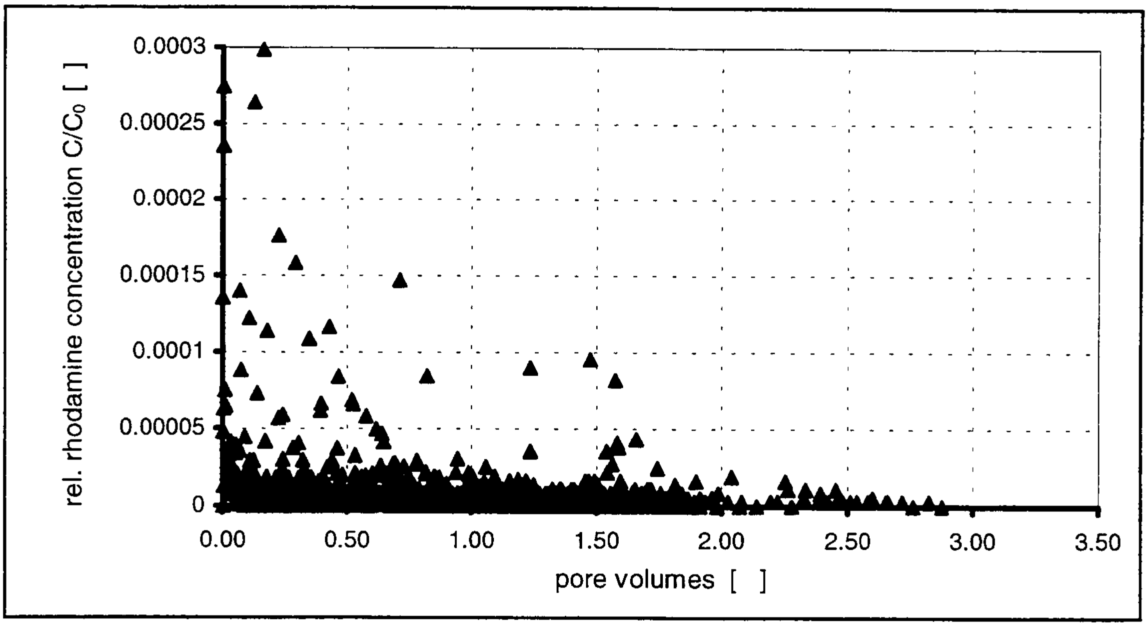

Figure 16. Relative concentrations of Rhodamine WT for all PCAPS throughout the first two years of the experiment.

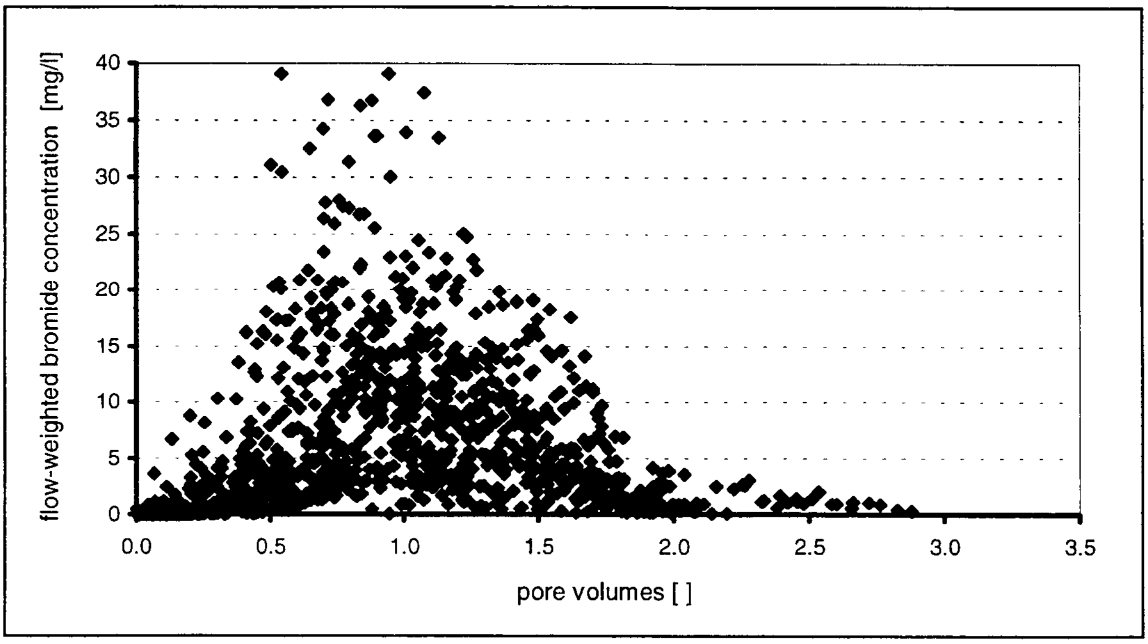

Figure 17. Bromide breakthrough curve as observed with 32 PCAPS.

For the spatial variability analysis, we determined values for the longitudinal hydrodynamic dispersion coefficient for each of the 32 PCAPS by fitting observed breakthrough curves to the convection-dispersion equation using Parker and van Genuchten's CXTFIT computer program (Parker and van Genuchten, 1984). Its procedure is based on the least-squares inversion method to fit the appropriate analytical solution for the flux concentration to the observed concentrations (Marquardt, 1963). In our case, we assumed decay and production of solute during the transport to be zero, since bromide is known to conform with these two assumptions (Flury and Papritz, 1993). The initial concentration of bromide was also assumed to be zero. Furthermore, we reduced the concentrations of bromide, and used pore volumes as the time variable. Due to the highly variable bromide mass recovery between individual PCAPS, reduced concentrations were based on the amount of bromide which had actually been collected in each sampler. The short bromide pulse, calculated as the ratio of the estimated thickness of the mixing zone (i.e., 2 cm) over the depth of the PCAPS (i.e., 120 cm), had a reduced duration of 0.01667. Under these conditions, the convection-dispersion equation (Equation 10) becomes:

$$R\frac{\partial \hat{C}}{\partial \hat{t}} = \left(\frac{D}{vz}\right)\frac{\partial^2 \hat{C}}{\partial \hat{x}^2} - \frac{\partial \hat{C}}{\partial \hat{x}} \qquad (12)$$

R = retardation factor [ ],

$\hat{C}$ = solute concentration [M L^{-3}],

$\hat{t}$ = number of pore volumes passed through the soil [ ],

D = hydrodynamic dispersion coefficient[L^2 T^{-1}],

v = pore water velocity [L T^{-1}],

z = estimated depth of one pore volume (i.e., 41.3 cm),

$\hat{x}$ = dimensionless distance (i.e., depth of PCAPS/z).

Due to our non-dimensional time variable, the pore water velocity v is one. CXTFIT's output value for the hydrodynamic dispersion coefficient (i.e., D/vz) is dimensionless as well. For this specific set-up of the convection-dispersion equation, the analytical solution used by CXTFIT is:

$$\hat{C}\left(\hat{x},\hat{t}\right) = A(\hat{x},\hat{t}) - A(\hat{x},\hat{t}-t_0) \tag{13}$$

with

$$A\left(\hat{x},\hat{t}\right) = \frac{1}{2}\operatorname{erfc}\left[\frac{R\hat{x}-v\hat{t}}{2\sqrt{DR\hat{t}}}\right] + \frac{1}{2}\exp\left(\frac{v\hat{x}}{D}\right)\operatorname{erfc}\left[\frac{R\hat{x}+v\hat{t}}{2\sqrt{DR\hat{t}}}\right] \tag{14}$$

where t_0 [T] denotes the applied pulse duration, erfc the error function, and exp the exponential function. By using pore volumes rather than time, we a priori assumed that mechanical dispersion dominates molecular diffusion. However, it is important to note that we did not know for certain that the time-dependent diffusion process can actually be neglected. Using the Einstein equation, we estimated the single effect of molecular diffusion on the root mean square displacement of bromide in all directions as:

$$\sigma = \sqrt{2D_{diff}t} \tag{15}$$

where σ [L] represents the root mean square displacement of bromide due to diffusion, D_{diff} [L^2T^{-1}] the molecular diffusion coefficient of bromide, and t [T] the time of the peak bromide breakthrough. Using the molecular diffusion coefficient for bromide in aqueous solution of $2x10^{-5}$ cm^2s^{-1} (Weast, 1987) and one year as the time of average peak breakthrough, the displacement of bromide in all directions solely due to diffusion would be approximately 40 cm. The observed spreading was approximately 60 cm. Since the samplers were installed at a depth of 120 cm, the use of pore volumes as the time variable appeared to be justified.

Due to parametrization (reduced concentrations, pore volumes as time variable), pore water velocity was fixed and could not be fitted. The only variables which were fitted by the CXTFIT model, were the hydrodynamic dispersion coefficient D and the retardation factor R. The retardation factor R was kept variable in order to match the model breakthrough curves to the observed breakthrough as accurately as possible. If the retardation factor R had been fixed at one (expected value for conservative tracer), all bromide peaks would have been forced to occur at one pore volume. Since observed breakthrough curves peaked between 0.5 and 1.5 pore volumes, the fitting of the parameter R allowed for a more flexible and more accurate model. Fitted values of R ranged from 0.69 to 1.63 with a mean of 1.11, indicating that the breakthrough curve peak occurred before or after one pore volume had reached the PCAPS (Figure 18). Appendix C displays a summary of the numerical output of all CXTFIT runs. Resulting fitted bromide breakthrough curves for all 32 PCAPS sites are shown in Appendix D.

For the early tracer breakthrough (i.e., pore volumes smaller than half the peak pore volume), most breakthrough curves show that fitted bromide concentrations are much lower than those actually observed. Closer analysis revealed that fitted bromide concentrations, in fact, deviated from observed concentrations on average by -72% for this period. Since the convection dispersion equation is based upon transport through unstructured media, it cannot account for spatial heterogeneities (e.g., macropores) affecting the actual bromide transport. It is therefore not surprising that the model failed to predict the observed early bromide breakthrough. The early breakthrough likely stemmed from preferential flow captured by the PCAPS.

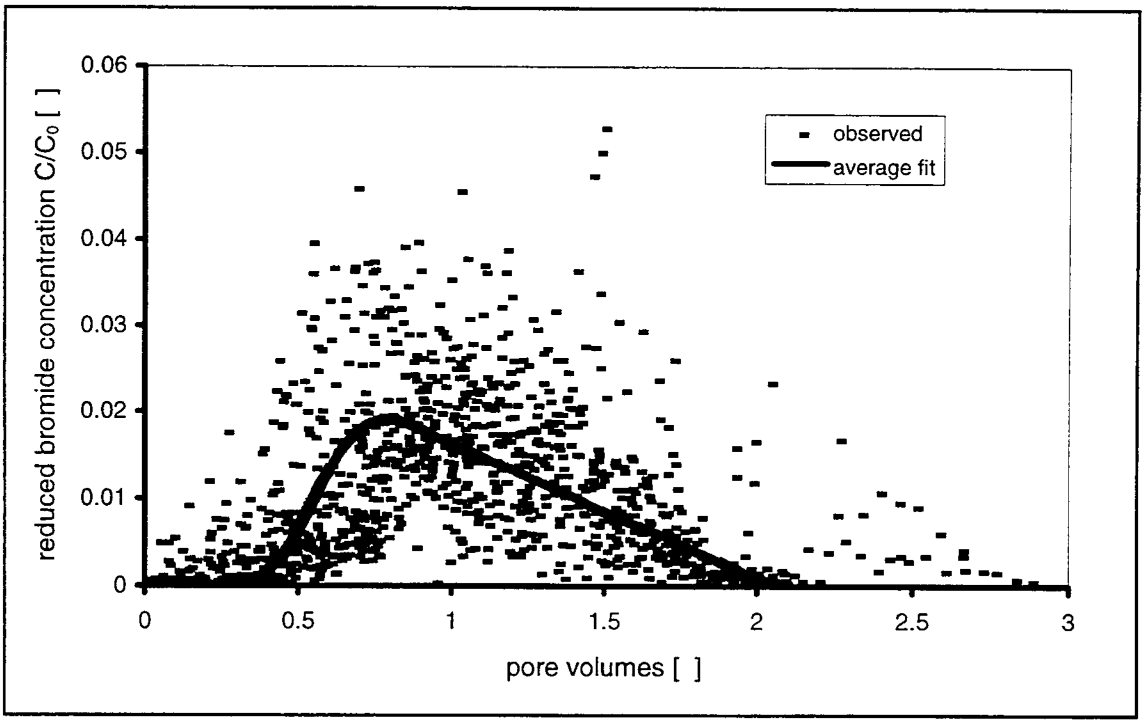

Figure 18. Observed bromide concentrations from all 32 PCAPS and their average fit using CXTFIT.

Next, we estimated the average pore water velocity for each PCAPS by dividing the depth of the PCAPS (i.e., 120 cm) by the time of the fitted bromide breakthrough peaks (in days since bromide application). This method resulted in average pore water velocities ranging from 0.25 to 1.58 cm day^{-1}, with a mean of 0.47 cm day^{-1} and a coefficient of variation of 66.7% (Appendix E).

In order to calculate values of the hydrodynamic dispersion coefficient (in units of cm^{2}s^{-1}), CXTFIT output values, D/vz, were multiplied with the estimated pore volume z (i.e., 41.28 cm) and the corresponding average pore water velocities. Resulting values of the hydrodynamic dispersion coefficient had a mean of 1.82x10^{-3} cm^{2}s^{-1} with a coefficient of variation of 153.3% (Appendix E). The lowest calculated value was 1.72x10^{-4} cm^{2}s^{-1} (for PCAPS at

C1 South N1), which is about one order of magnitude higher than the molecular diffusion coefficient for bromide.

We then plotted the fitted values of the hydrodynamic dispersion coefficient D/vz against the bromide peak breakthrough time in days since bromide application (Figure 19). This plot revealed that for early peak breakthrough times (i.e., before day 300) the spreading of the plume was significantly greater than for late peak breakthrough times (i.e., after day 400; Table 9 and Appendix E). Due to the natural setting of this long-term field experiment, the interpretation of this behavior is complex.

Table 9. Comparison of characteristics of the hydrodynamic dispersion coefficient D/vz as influenced by the actual peak breakthrough time.

	Characteristics of values for D/vz at times of	
	Early peak breakthrough (i.e., before day 300)	Late peak breakthrough (i.e., after day 400)
Mean of D/vz [ ]	8.68	4.80
Std. deviation of D/vz [ ]	6.50	1.55
C.V. [%]	74.97	32.26
Max./Min. [ ]	32.22	2.91

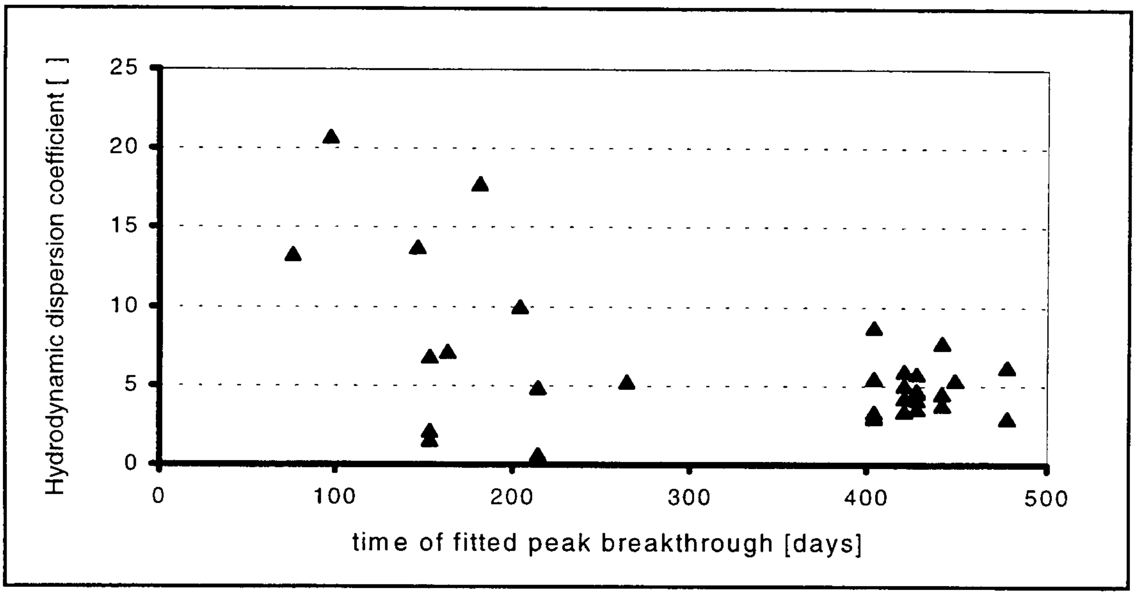

Figure 19. Scatterplot of values of the hydrodynamic dispersion coefficient D/vz against the corresponding peak breakthrough times.

The Peclet number is a useful indicator of the importance of mechanical dispersion versus diffusion on the solute spreading. The Peclet number is defined as:

$$Pe = \frac{vd}{D} \tag{16}$$

where Pe [ ] represents the Peclet number, v [LT^{-1}] the pore water velocity, d [L] the average grain size diameter, and D [L^2T^{-1}] the molecular diffusion coefficient (Fetter, 1993). With an estimated mean pore water velocity of 0.47 cm day^{-1} for all 32 PCAPS, a mean particle size diameter of 0.001 cm (i.e., silt), and a molecular diffusion coefficient for bromide of $2x10^{-5}$ cm^{2}s^{-1}, the Peclet number with respect to soil particle size computes to $3x10^{-4}$. At such a low Peclet number, diffusion should dominate mechanical dispersion (Fetter, 1993). On the other hand, we know that the soil is highly structured and that preferential flow occurs. Therefore, mechanical dispersion around soil peds should strongly affect the flow. Assuming a ped size of 5.0 cm and using this as the effective "grain" size diameter, the Peclet number with respect to soil ped size changes to 1.4. Peclet numbers in this range indicate the combined effects of mechanical dispersion and diffusion on solute spreading. The actual flow paths are unknown and effective ped sizes can only be estimated roughly, hence Peclet numbers can only be used to show that both, diffusion and mechanical dispersion, are contributing to solute spreading. Clearly it is necessary to re-examine the nature of these two processes in order to interpret these data.

Diffusion is a time-dependent process: from Fick's law (Equation 9) we know that the extent of spreading of a solute is directly related to time. But this relationship is only true in a system where diffusion is the only process by which solute spreading occurs (e.g., injection of a tracer pulse into a static body of water). In our porous soil system (with air, multi-sized particles, and moving water), mechanical dispersion becomes an important factor for solute spreading. Mechanical dispersion is independent of time so long as the Reynolds number is less than one: it is solely a function of soil structure (i.e., grain size and distribution, soil layering, ped size and distribution, macropores) and hydraulic flow paths. With an average count of only 0.8 macropores per PCAPS area and the seldom occurrence of ponded field conditions, macropore flow was found to be a minor means of water transport (Brandi-Dohrn, 1993). Nevertheless, we observed the occurrence of preferential flow at our site, which demonstrates the importance of relatively large soil peds (size range 10^{-1} to 10^{1} cm) on water and solute movement in our natural field setting.

On the basis of these characteristics, we drew a schematic diagram of the possible effects of peak breakthrough time on diffusion and mechanical dispersion (Figure 20). It is helpful to note that the time of peak tracer breakthrough is inversely proportional to the flow rate, meaning that early peak breakthrough times correspond with high flow rates and vice versa. The diagram indicates that diffusion is likely to cause more spreading at high flow rates, since in this case solute diffuses in and out of soil peds, causing severe retardation of some solute. In other words, diffusion increases the further spreading of the plume. At successively lower flow rates, the effect of diffusion on solute spreading continuously decreases. At some point, the flow rate will be so low that diffusion in and out of soil peds cannot add any more spreading to the downward-moving plume. The system, in respect to diffusion through soil peds, has reached an equilibrium. For flow rates at such a low level, dispersion will be the dominating process, by which solute is spread. Mechanical dispersion is unaffected by changes in flow rates and therefore remains constant. Finally, at sufficiently low flow rates bulk molecular diffusion again dominates (i.e., at flow rates approximately one tenth those seen in our experiment).

Comparing the schematic diagram (Figure 20) with the observed situation at our site (Figure 19) shows that the above concept fits our system rather well. Therefore, we think that for soil profiles at our site where the bromide peak occurred before day 300, diffusion in and out of soil peds is likely the key process of solute spreading. At low flow rates (bromide peaks occurring after day 400), the effects of diffusion have significantly decreased. In these cases, mechanical dispersion appears to be the key factor of solute spreading.

Numerous field experiments have shown that the hydrodynamic dispersion coefficient D is log-normally distributed in respect to space (e.g., Biggar and Nielsen, 1976; van de Pol, 1977). In previous cases, authors have not accounted for the fact that D was a function of the time of travel, and therefore of the experimental procedure employed. Here we would like to compare the distribution of our data with that found by previous authors, understanding that this distribution is a function of both the soil and the particular experiment performed. In our experiment, values for D were tested for possibly underlying normal or log-normal distributions using the Filiben test (Filiben, 1975). Since we observed the median for D to be significantly lower than its mean (Appendix E), a log-normal distribution was considered. The degree of linearity of the probability plot, as indicated by the value of the coefficient of correlation, is indicative of the fit of the distribution (Figure 21 and 22).

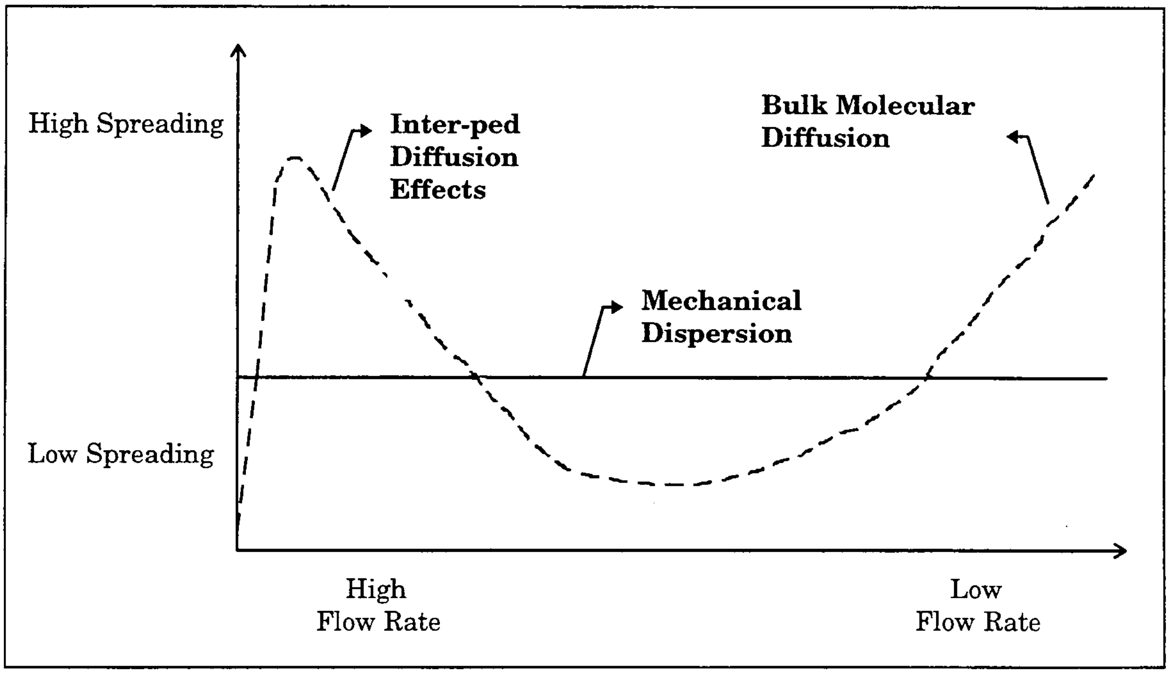

Figure 20. Schematic diagram of the effects of different flow rates on the amount of solute spreading due to diffusion and dispersion in a soil system experiencing preferential flow (Note that high flow rates correspond with early peak breakthrough times and low flow rates with late peak breakthrough times).

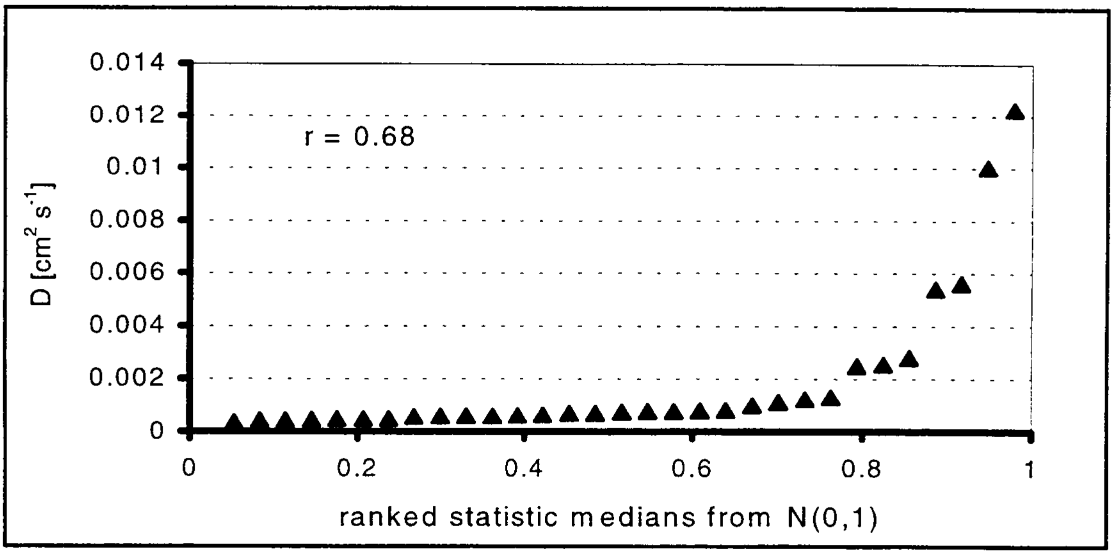

Figure 21. Normal probability plot testing for normal distribution of D.

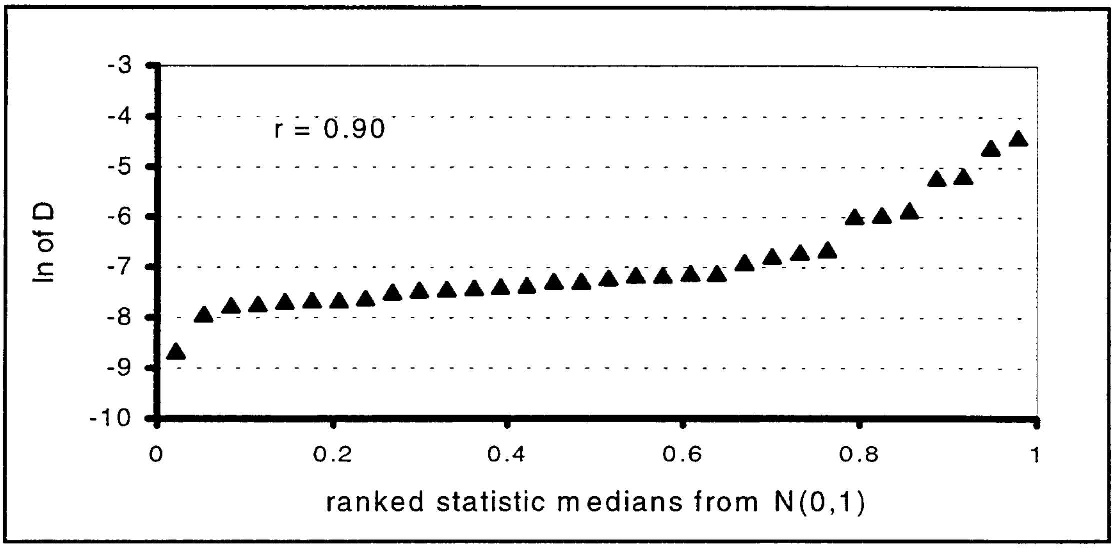

Figure 22. Normal probability plot testing for log-normal distribution of D.

With 32 data points (i.e., the number of samplers), the threshold value of a Type I error for the probability plot correlation coefficient is r=0.939, at the α=0.5% significance level. If r is less than this critical value, then there is

≤ 0.5% probability that D was indeed normally (log-normally) distributed, but was incorrectly rejected. Our data yielded r values of 0.677 (D) and 0.902 (ln D). On the basis of this r-test, we can be 99.5% confident that the hydrodynamic dispersion coefficient D is neither normally nor log-normally distributed. Neither distribution provided an excellent fit, yet the fit of lognormal was considerably better than the normal.

Finally, we analyzed the 32 values of the hydrodynamic dispersion coefficient for spatial variability. Here units of cm^2day^{-1} for the hydrodynamic dispersion coefficient were used. The data was transformed using $\log_{10}$ of the resulting semi-variogram values $\gamma(h)$. The semi-variogram shows that there is no spatial correlation in respect to D within the 0.98 ha field (Figure 23). Even for the two meter distance, the hydrodynamic dispersion coefficient D varies largely indicating a more or less random distribution of D throughout the field.

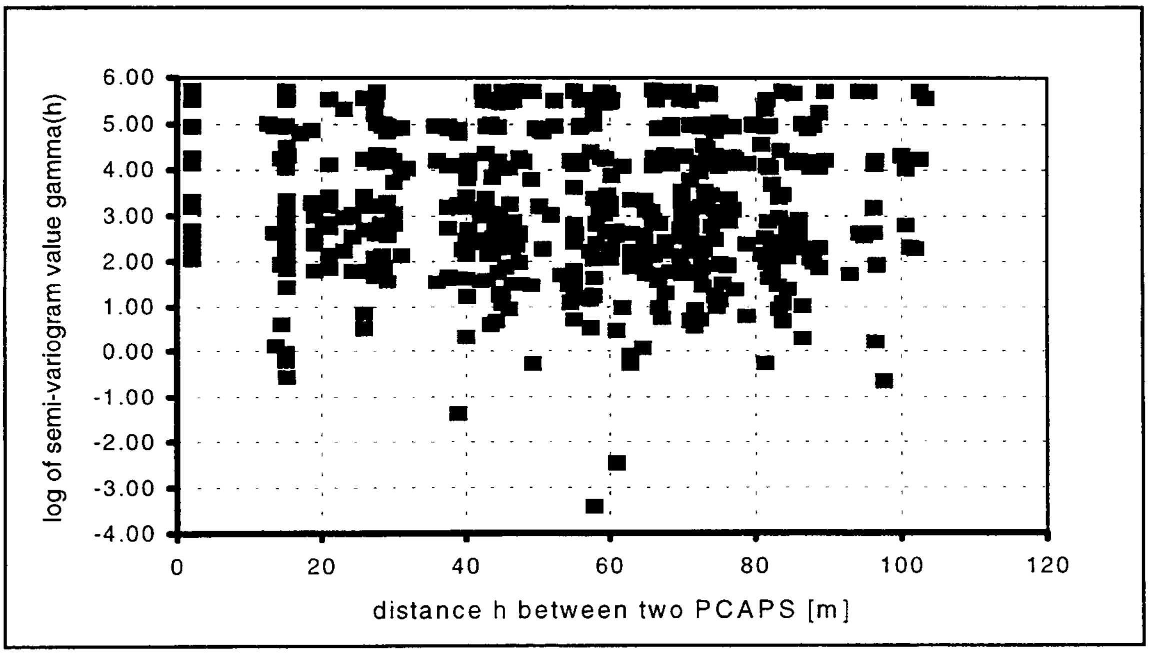

Figure 23. Semi-variogram of the hydrodynamic dispersion coefficient.

3.3 Conclusions

Water flux and hydrodynamic dispersion coefficient were analyzed for their spatial variability. For the water flux, we found that there is a significant correlation at the two meter distance. Beyond this distance, water fluxes are not correlated. The semi-variogram for the hydrodynamic dispersion coefficient D indicates that there is no spatial correlation between PCAPS in respect to D.

In spite of equivalent soil type and climatic conditions throughout the site, leaching characteristics were highly variable in respect to spatial position within the 0.98 ha site. The high spatial variability points out the importance of small scale features (i.e., soil peds) and preferential flow on the leaching process.

During the first year of the experiment, we found that Bottle 1 (i.e., the bottle closest to the trench) significantly undersampled relative to the other two bottles. This undersampling indicates that even though PCAPS were installed with extreme care, some flow paths were disrupted. Throughout the second year of the experiment, differences in water collection between bottles decreased considerably. Therefore, it appeared to be appropriate to combine the three bottles to receive flow-weighted solute concentrations for each PCAPS. The equalization of the separate bottles over time also suggests that Brandi-Dohrn's conjecture stating the declining importance of the preferential flow path system with decreasing infiltration intensities was not accurate (Brandi-Dohrn, 1993). Since the disparity in collection between bottles was independent of the amount of infiltration over the second year of the experiment, it seems that a new preferential flow path system, unaffected by the former trench, developed over time.

Brilliant Blue FCF and Rhodamine WT were only recovered in extremely low concentrations. This indicates the possibility that both tracers were biodegraded before reaching the samplers. However, since they are retarded tracers, no final decision can be made at this point. Results from the third year of the experiment may reveal the fate of these tracers. If they were biodegraded, Brilliant Blue FCF and Rhodamine WT should be re-examined for their usefulness as indicators for the long-term leaching of retarded contaminants.

The hydrodynamic dispersion coefficient D was neither normally nor log-normally distributed at this site as indicated by the Filiben test. However, the lognormal model gave an improved fit over the normal. A more conclusive experiment might require more observations for D than the 32 present samplers were able to supply.

The bromide mass recovery ratio, based on the assumption of one-dimensional solute transport, averaged only 29.0%. The rye grain cover crop did not significantly contribute to the bromide loss. Uptake by the summer crops (broccoli for 1993 and sweet corn for 1994) might have accounted for some of the tracer loss. However, literature values would indicate that a maximum of 20% might have been lost to summer crops, since the peak of the bromide tracer on average had already reached the depth of the samplers by summer 1993. Bromide uptake by sweet corn in the summer of 1994 can be considered negligible, as it was completely out of the root zone by this time. We believe that lateral water movement accounted for the majority of the bromide loss. The presence of a fragipan and perched water table could explain significant horizontal transport (Brandi-Dohrn, 1993).

Despite the bromide losses, all 32 PCAPS were able to detect the bromide breakthrough well. The majority of the PCAPS showed significantly higher bromide concentrations on the rising branch of the breakthrough curve than predicted by a best-fit solution to the convection dispersion equation. This both corroborates the occurrence of preferential flow at this site and demonstrates the PCAPS's ability to collect preferential flow. With a fitted retardation factor R ranging from 0.69 to 1.63 and a mean of 1.11, we conclude that bromide is an appropriate tracer of the movement of soil water. Finally, the CXTFIT modeling output indicates that spreading of the bromide plume occurred due to the joint processes of diffusion and mechanical dispersion. The two processes were found to be intertwined, greatly complicating the solute leaching pattern in this, and by implication most other, field experiment conducted under natural conditions.

In conclusion, it is of the utmost importance to conduct long-term field experiments under natural conditions to be able to accurately evaluate the actual leaching process. Day- or week-long experiments under artificial conditions (e.g., pre-experiment ponding of the soil, extremely high water input rates) alter the pre-experiment moisture conditions of a field site. By modifying the soil system, control over secondary variables (e.g., D, v) describing the leaching process is lost. Extrapolations of field-scale solute leaching from such experiments are liable to provide an inaccurate assessment of natural leaching processes.

4. Assessment of Saturated Hydraulic Conductivity and Precipitation as Factors of Percolation Past the Root Zone

4.1 Introduction and Literature Review

The percolation of water beyond the root zone is the primary carrier of pollution to ground water. Thus, to estimate root zone leaching losses of nutrients and ground water contamination, it is essential to understand percolation through the vadose zone. This deep percolation can be influenced by several factors, especially the soil's physical properties and the amount of water supply. In situations where hydraulic conductivity is the most important factor controlling percolation, the system is said to be conductivity-controlled. On the other hand, some systems are supply-controlled, meaning that the amount of water supplied by precipitation or irrigation is the key factor in percolation. The goal of this chapter is to assess whether percolation past the root zone at our site is conductivity- or supply-controlled.

The effects of hydraulic conductivity on percolation have been studied extensively throughout the world. Rose and Stern (1965) evaluated the drainage component of the water balance equation, and found that it is necessary to know the moisture characteristic curve, saturated hydraulic conductivity and the relationship between hydraulic conductivity and water content in order to estimate drainage for a specific soil. Warrick et al. (1977) simulated the water flux distribution in a clay loam soil under steady-state conditions using the Monte Carlo method. Based on measured values for steady-state hydraulic conductivity, they found the water flux to be log-normally distributed within a 150 ha study area . Fritton et al. (1986) used values of saturated hydraulic conductivity, k_{sat}, from 28 different locations to relate k_{sat} (determined by the shallow well pump-in method) to measured percolation times. They observed a positive linear relationship between these two parameters.

Besides actual field experiments, there is a great variety of models which assess the characteristics of percolation and solute leaching using k_{sat} as a decisive input parameters. Models such as "Oregon Water Quality Decision Aid" (Vogue et al., 1994), "Chemical Movement in Layered Soils" (CMLS), "Groundwater Loading Effects of Agriculture Management Systems" (GLEAMS), "Leaching Estimation and Chemistry Model" (LEACHM), "Method of Underground Solute Evaluation" (MOUSE), and "Pesticide Root Zone Model" (PRZM) represent just a few examples from this group (Pennell et al., 1990). Furthermore, numerous models have been produced for very specialized applications within the context of soil water percolation and solute transport. Kalita et al. (1992), for example, used a finite-difference model to predict vertical and lateral percolation losses under ponded field conditions. They found that k_{sat} was the key factor governing vertical percolation losses. All results from these field and modeling experiments indicate the importance of k_{sat} for percolation past the root zone.

The possibility of a supply-controlled percolation is intuitively appealing. One would assume that the output of a system (i.e., the extent of percolation past the root zone) is directly related to the input, which is typically from irrigation and precipitation.

Irrigation methods have improved tremendously over the last couple decades in order to allow the production of crops in dry areas while attempting to overcome adverse effects such as nutrient leaching and soil salinization. In view of these concerns, flood irrigation has become a less favorable technique, since significant amounts of water and nutrients may be lost via leaching. Freebairn et al. (1989) allude to this effect by showing that infiltration rates under ponded conditions are approximately one order of magnitude higher than under natural rainfall. In another field experiment, the impact of different irrigation methods (i.e., drip, intermittent flood, and continuous flood irrigation) on percolation and solute transport was assessed (Jaynes et al., 1988; Jaynes and Rice, 1993). The study showed that the method of irrigation, especially the amount and timing of water input, significantly affected leaching behavior.

As with irrigation, precipitation affects the amount of percolation and the related leaching of solutes. Only a few field experiments have been conducted to evaluate the effects of natural rainfall on percolation and leaching. Hall et al. (1989) studied the leaching of four different herbicides through a silty clay loam under natural conditions over a period of two years. They showed that leaching losses were strongly correlated with the precipitation pattern. In the same way, two experiments under simulated rainfall demonstrated that percolation is dependent upon rainfall intensities (Edwards et al., 1992; Sigua et al., 1993).

Our long-term experiment was conducted under natural (i.e., rain-fed) field conditions, except during the summer when drip irrigation was also applied. These study characteristics gave us the opportunity to compare PCAPS-measured percolation quantities at a depth of 120 cm with corresponding values for k_{sat} as well as with respective amounts of precipitation and irrigation.

4.2 Results

4.2.1 Field-saturated hydraulic conductivity as a factor of percolation

Field-saturated hydraulic conductivity, k_{fsat}, was measured with a well permeameter at a depth of 100 cm as outlined in chapter two. Resulting values for k_{fsat} ranged from 10.0 to 100.1 mm day^{-1} with a mean of 44.3 mm day^{-1} and a coefficient of variation of 73%. Since we wanted to avoid conducting the infiltration test at any position within the former trench, we selected a location on the N fertilizer application rate division line 1.2 m away from the edge of each trench (Figure 3). The distance between the position of the infiltration test and each PCAPS was 2.4 m. Subsequently, only one infiltration test was performed per trench, which assumes that one value of k_{fsat} is able to represent both of the PCAPS at a specific trench. There are two arguments justifying this assumption: first, values for water flux were positively correlated at the 2.0 m distance (Figure 13). Second, Russo and Bresler (1981), assessing the spatial variability within a field soil in respect to k_{fsat}, found that k_{fsat} had a range of 14.0 m at the 90 cm depth.

To evaluate k_{fsat} as a factor of percolation, two contour maps for the 99 by 99 m site were produced. The first (Figure 24) was based on the cumulative amounts of percolation over two years as measured by each of the 32 PCAPS. The second (Figure 25) was based on measured values of k_{fsat}. These contour maps gave a visual indication regarding the correlation between percolation and k_{fsat}. With black areas representing the highest values and white areas representing the lowest values for both variables, the maps indicate no apparent correlation between percolation amount and k_{fsat}.

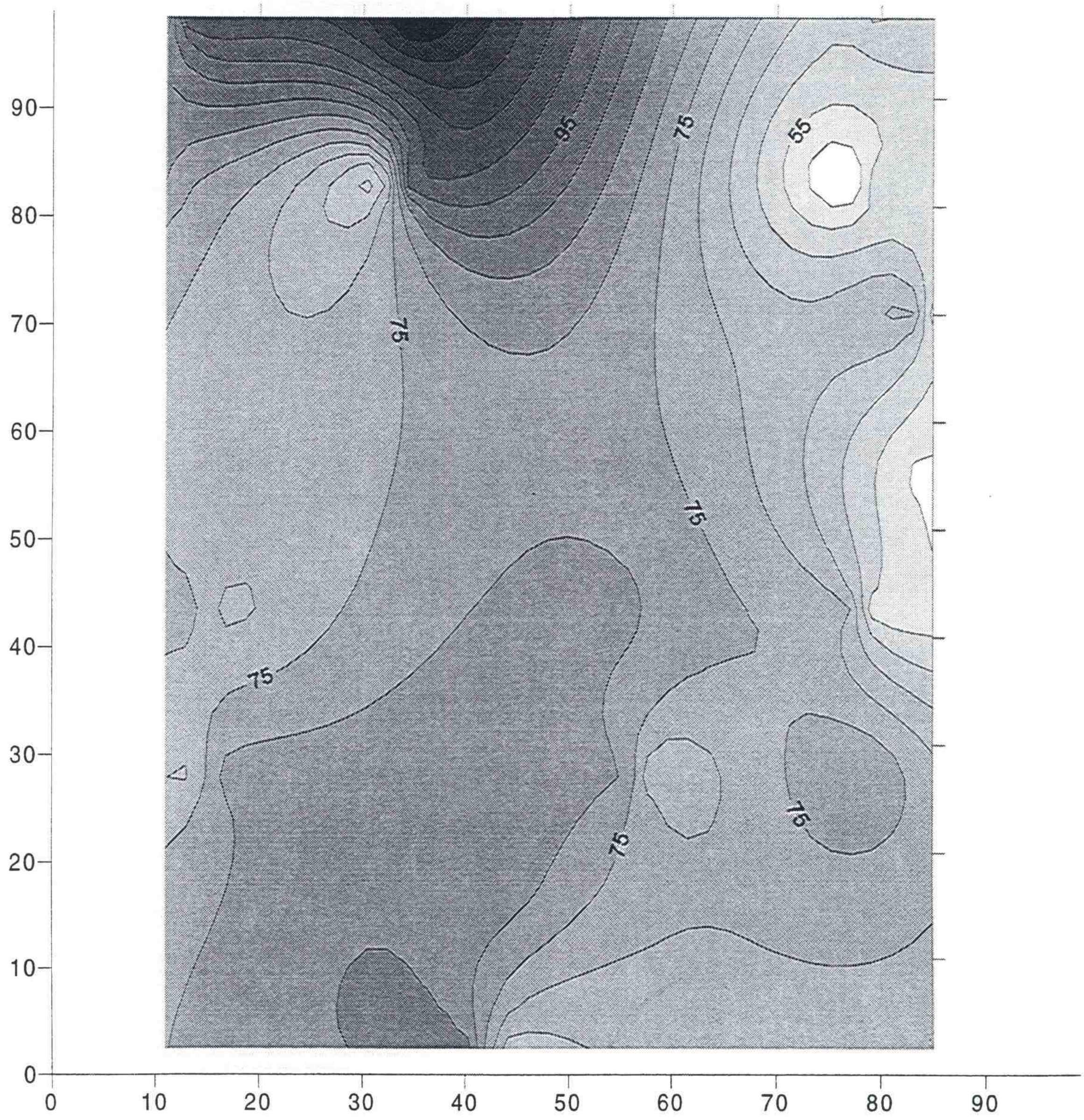

Figure 24. Contour map of our site in respect to cumulative percolation [cm].

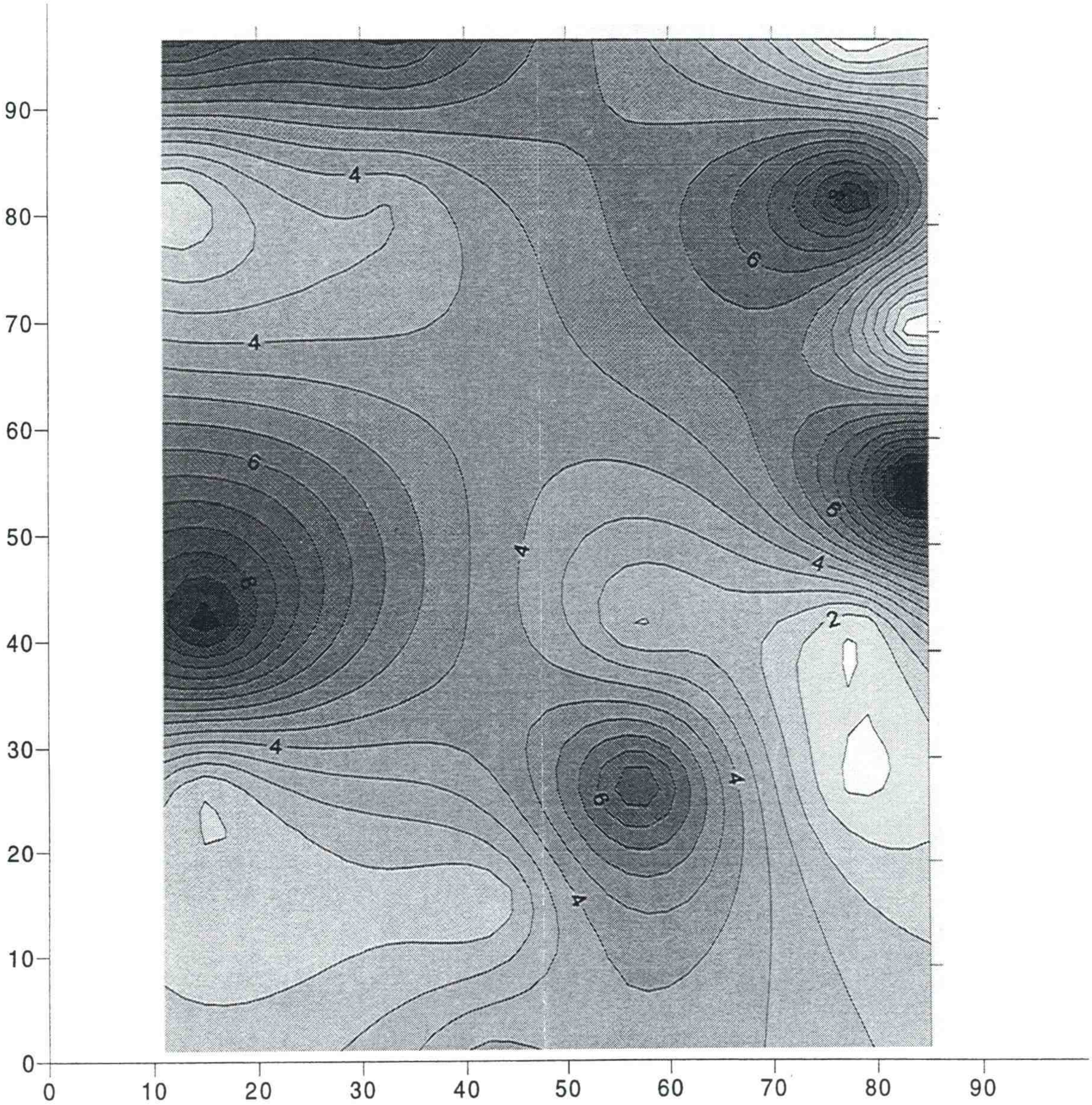

Figure 25. Contour map of our site in respect to k_{fsat} [cm day^{-1}].

This observation was confirmed with a calculated correlation coefficient r of -0.007. Note that we averaged flux values into both PCAPS at each trench before comparing with corresponding k_{fsat} values. The significance of this correlation coefficient can be assessed using a t-statistic (Hirsch et al., 1993):

$$t = \frac{r\sqrt{n-2}}{\sqrt{1-r^2}} \qquad (17)$$

with n-2 degrees of freedom (n = 16; i.e., number of data pairs). The null hypothesis for this test is that the two data sets are independent from each other (i.e., r = 0). In the above case, the value for r of -0.007 was highly significant (2-sided p-value = 0.978). This t-statistic demonstrates that there was no significant correlation between measured amounts of percolation and values of k_{fsat} at our site (Figure 26).

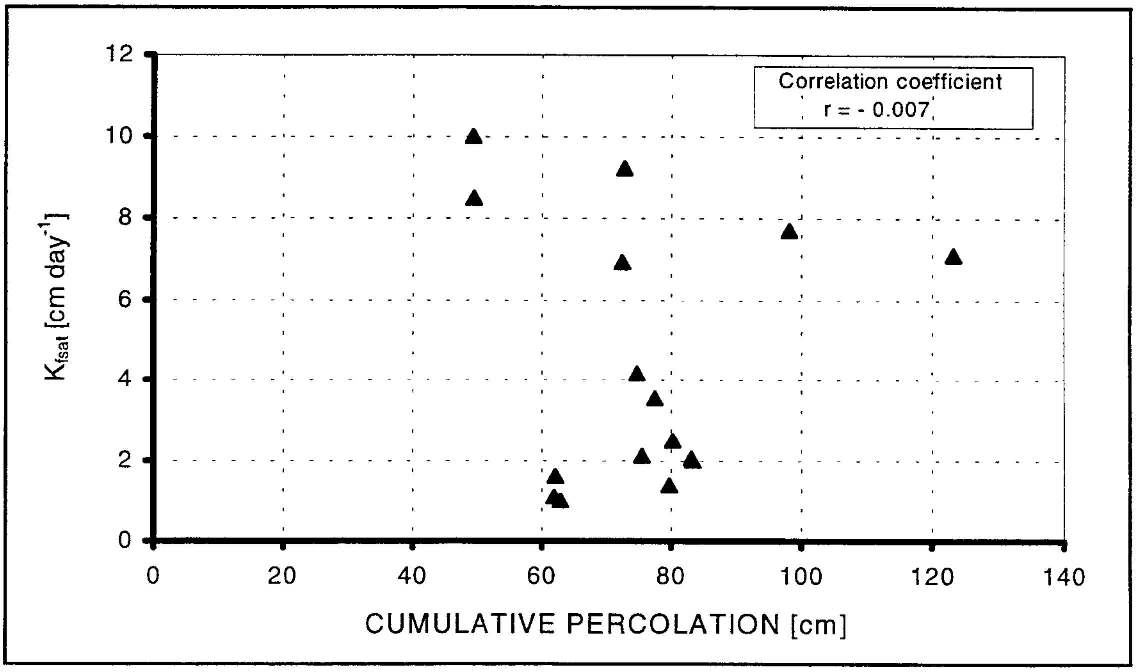

Figure 26. Scatterplot of cumulative amounts of percolation over two years as measured with 32 PCAPS against corresponding values of k_{fsat}.

Our finding is at odds with the assumption of conductivity controlled percolation employed in simple vadose zone models, as well as with the findings of many field studies (e.g., Fritton et al., 1986; Kalita et al., 1992). There are several possible explanations for a lack of correlation between k_{fsat} and percolation amount. Most importantly, it is essential to point out that our study was conducted under natural rain-fed conditions where fully saturated soil conditions throughout the profile were rare. Hence, we did not expect saturated flow to be a key factor for water transport. Unlike our unsaturated field conditions, almost all other studies, including those cited above took place under percolation rates far in excess of those occurring outside of the research setting, which has a dramatic impact upon the percolation process. This reasoning leads us to the next explanation: the importance of soil structure at our site. All infiltration tests were conducted at a depth of 100 cm, unaffected by the percolation characteristics between the soil surface and the 100 cm depth. The presence of a plowed surface horizon and multiple-sized peds within this depth at the study site could not affect the outcome of the infiltration tests. Furthermore, unsaturated flow (which occurred predominantly throughout our long-term experiment) probably followed different pathways than saturated flow (which was present during our infiltration tests).

Hence, values for k_{fsat} were not informative with respect to estimating true percolation volumes past the root zone. Analogous to findings in the previous chapter, this analysis demonstrates the importance of conducting experiments under natural conditions in order to assess actual field percolation past the zone of major biological activity.

4.2.2 Quantity of supplied water as a factor of percolation

Percolation due to irrigation only occurred twice during our study, both times during the 1994 summer when sweet corn was grown: 15.7 mm and 20.6 mm of mean PCAPS-measured percolation on June 29, 1994 and July 22, 1994, respectively. This observation indicates the possibility of percolation losses and nutrient leaching due to irrigation practices. Further investigations into the relationship between irrigation and percolation were inconclusive because: (1) drip irrigation does not lend itself well to accurate quantitative measurements, and (2) we observed that most of the water applied never passed the root zone.

By far the most important source of water for percolation originated from precipitation. Significant percolation occurred between November and May, which coincides with the period of high precipitation in the Willamette Valley. Therefore, we selected the extended winter periods of 1992/93 and 1993/94 to see if there was evidence that percolation past the root zone was supply-controlled.

Using precipitation and evaporation data, we constructed a simple water balance. By assuming that changes in storage even out in the long term and that runoff and interflow are negligible as well, we estimated percolation by subtracting the amount of evaporation from the corresponding precipitation to estimate the water surplus. Since evaporation was generally low within the two observation periods, values for water surplus often corresponded with the amount of precipitation itself. Naturally, this analysis technique could not account for collection variability between the 32 PCAPS at a given date (Appendix F). Therefore, we calculated mean percolation values from the 32 PCAPS at each sampling event and compared these values with the cumulative amounts of water surplus.

We found that the amount of water surplus is a good indicator for percolation quantities. The correlation coefficients between mean PCAPS-measured percolation and water surplus were 0.72 for 1992/93 (p-value = 0.0004) and 0.60 for the 1993/94 winter period (p-value = 0.03). Knowing that precipitation clearly exceeds evaporation during the winter, these correlation coefficients demonstrate that precipitation was a statistically significant factor for percolation past the root zone at our site (Figures 27 and 28).

It is important to note that the two correlation coefficients would have been higher if we had eliminated days with intense precipitation from the analysis. During such periods, the collection capacity of the PCAPS (i.e., 43.5 mm of percolation, corresponding with a volume of 3780 ml) was exceeded, in some cases vastly. For example, 54.1 mm of precipitation were measured at our site on February 24, 1994. At this time, the soil was fairly wet and cumulative precipitation since the most recent sampling event on February 17, 1994 had already amounted to 33.8 mm. Even though emptied on February 25, 1994, more than half of the samplers had reached their maximum capacity. Hence, the entire amount of actual percolation past the 120 cm depth was not obtained. Beside the PCAPS capacity problem, there was strong visual evidence suggesting that surface runoff and interflow occurred on days experiencing such strong rain storms (e.g., 39.6 mm on January 1, 1994 or the above mentioned 54.1 mm on February 24, 1994). Of course, on these few occasions soil conductivity may have limited percolation. Since surface runoff and interflow were not considered in the above analysis, the gap between the measured percolation and the water surplus curves would have been even smaller (Figures 27 and 28). These considerations reinforce our finding of a precipitation- or supply-controlled percolation process. Furthermore, they indicate a shortcoming in PCAPS design, suggesting the implementation of larger inside collection vessels to avoid capacity problems at times of high precipitation.

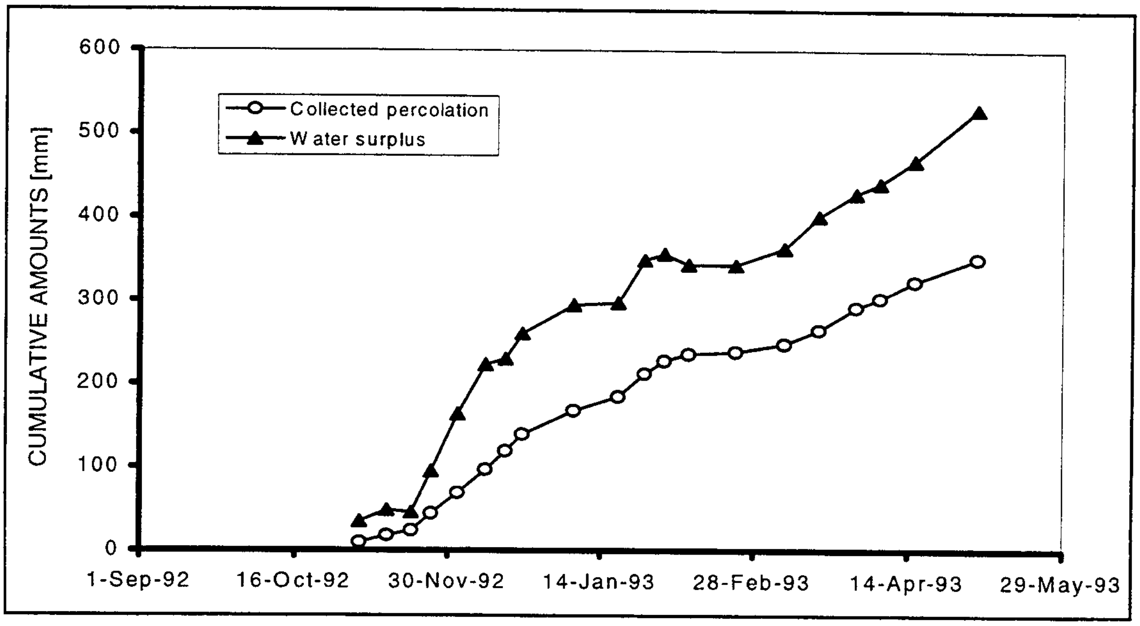

Figure 27. Comparison of cumulative amounts of collected percolation with corresponding values for water surplus during the 1992/93 winter period.

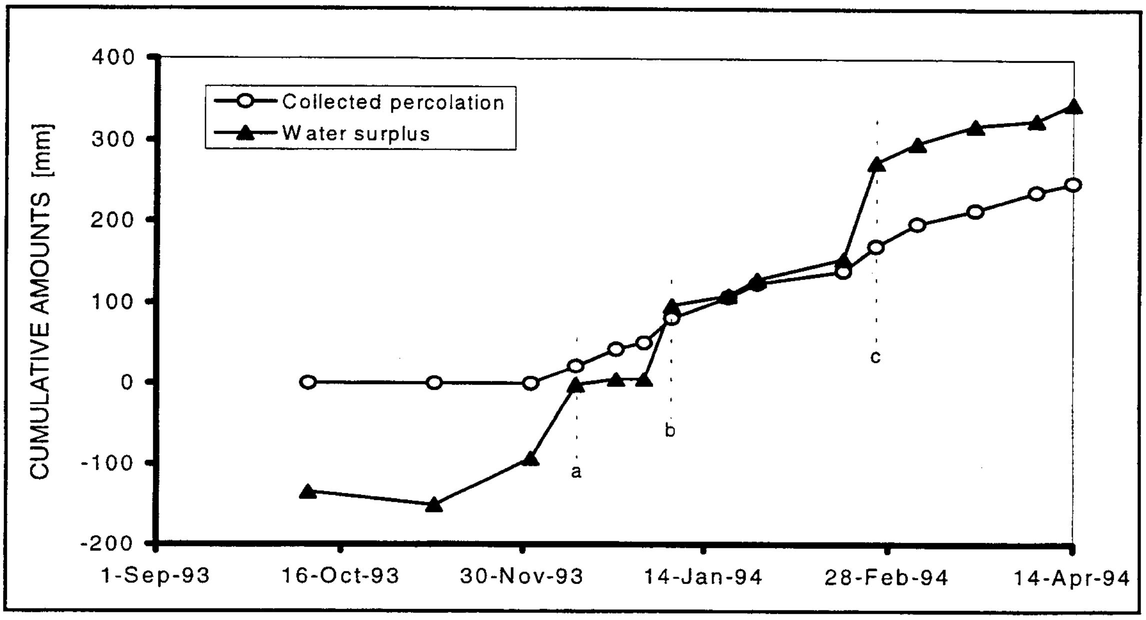

Figure 28. Comparison of cumulative amounts of collected percolation with corresponding values for water surplus during the 1993/94 winter period ("a": approximately 200 mm of "water surplus" was required to refill the soil profile to field capacity above the samplers; "b": 4 out of 32 PCAPS overflowed; "c": 10 out of 32 PCAPS overflowed).

4.3 Conclusions

Our two year long field study revealed that field-saturated conductivity, k_{fsat}, was an inappropriate indicator to assess percolation. We found that the quantity of water input, particularly by precipitation, significantly affected percolation. We therefore conclude that the percolation system at our site under natural field conditions was supply- rather than conductivity-controlled. This observation raises two issues in respect to water and contaminant transport in the vadose zone: the importance of proper irrigation management practices to avoid water losses and subsequent contaminant leaching, and the susceptibility of agricultural soils within a winter rain dominated region such as the Willamette Valley to exhibit percolation past the root zone likely combined with contaminant leaching towards the ground water. Given the modest conductivity of the soil and very humid conditions which prevail at this site (both of which would favor conductivity-controlled percolation), our observations challenge the validity of the widely held view that soil conductivity is a useful determinant of susceptibility to ground water contamination.

5. Assessment of Nitrate Leaching Under Cover Crop Management

5.1 Introduction and Literature Review

The leaching of nitrate is a common threat to the contamination of ground water resources worldwide (Gambrell et al., 1975; Chichester, 1977; Bergström and Brink, 1986; Macdonald et al., 1989; Ritter, 1989; Ritter et al., 1993; Owens et al., 1994). Nitrate pollution poses a serious health risk, since many countries depend on ground water as their primary drinking water source (Gabel et al., 1982; Hallberg, 1987; Moody, 1990). Consuming nitrate-laden water may cause the death of infants by methemoglobinemia and may lead to cancer due to the formation of nitrosamines (Bruning-Fann and Kaneene, 1993). The U.S. Environmental Protection Agency set a drinking water quality standard for nitrate-N of 10.0 mg/l (U.S. Environmental Protection Agency, 1990). In the United States, where 53% of the nation's population and 97% of the rural population drink ground water, 6.4% of domestic wells exceeded this standard for nitrate-N in 1984 (Madison and Brunett, 1984).

This water pollution originated in particular from intensive agriculture using N fertilizers to increase crop yields. Therefore, it is not surprising that states with intensive agriculture had a higher percentage of contaminated wells than the nation's average: 9.3% in Nebraska, 11.8% in Oklahoma, and 20.0% in Kansas (Madison and Brunett, 1984). The agricultural community is faced with finding ways to reduce nitrate contamination in order to prevent pollution of ground water resources. Among various other agricultural practices (Hamlett and Epp, 1994), the use of a winter cover crop may be an effective tool to decrease ground water contamination by nitrate leaching (Martinez and Guiraud, 1990). The goal of this chapter is to evaluate the effects of a winter cover crop and different N fertilizer application rates on the leaching of nitrate.

Nitrogen is an abundant element on our planet and is stored in three major reservoirs: the atmosphere, the oceans and terrestrial ecosystems. More than 99.9% of the earth's nitrogen is present as diatomic nitrogen, N_2, and is therefore inaccessible to almost all living organisms. In order to be used by crops, atmospheric N must be fixed into nitrate and other compounds by the agricultural-soil ecosystem.

Nitrogen is an essential nutrient for plants. Major biological forms of N include proteins, microbial cell walls and nucleic acids. Nitrogen exists in various oxidation states within the agricultural-soil ecosystem; transformations between compounds are common. Therefore, we can formulate the concept of a terrestrial N cycle, which consists of four major pools and five major processes between the reservoirs (Kinzig and Socolow, 1994). The four pools are plants, soil microorganisms (i.e., bacteria and fungi), dead organic matter and inorganic N (i.e., ammonium and nitrate). The five major processes by which N is transformed within the ecosystem include decay of plants and microorganisms, mineralization, nitrification, immobilization, and assimilation by plants (Figure 29).

Prior to the Industrial Revolution, N could only enter the agricultural-soil ecosystem by atmospheric fixation, which depends mainly on the activity of N-fixing bacteria. In this way, the global N balance was maintained by bacteria which carried out the processes of nitrification and denitrification. Since the advent of industrialization, however, N fixation quantities have more than doubled, offsetting the earth's geochemical N cycle momentously (Kinzig and Socolow, 1994). This development is due to the vast amounts of anthropogenic N fixation. Fertilizer production accounts for roughly two thirds of this additional N fixation. The increased N input into the agricultural-soil ecosystem via fertilizers directly relates to output mechanisms by which this ecosystem loses N. For the agricultural-soil ecosystem, there are four output mechanisms: denitrification, ammonia volatilization, harvesting of plant material and leaching.

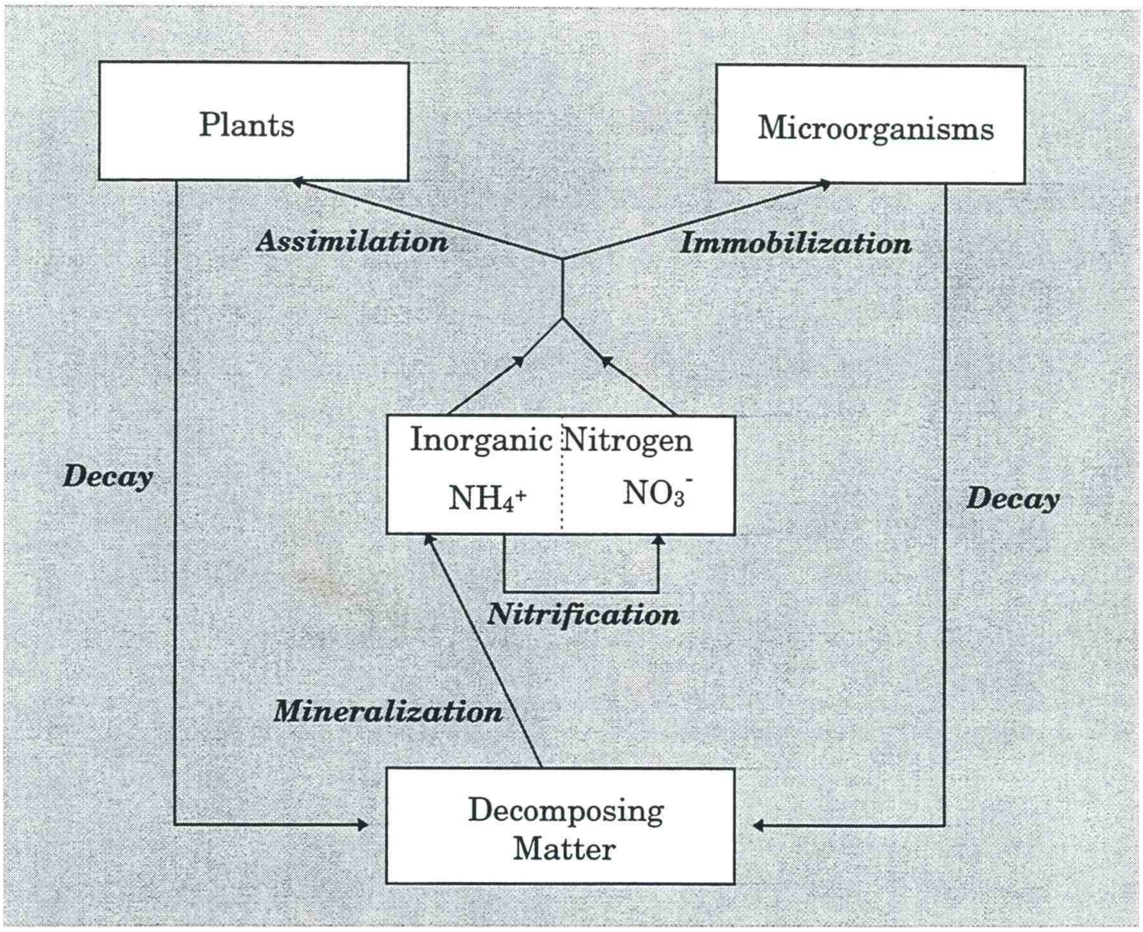

Figure 29. Terrestrial nitrogen cycle.

Agricultural crops depend on inorganic forms of N (i.e., nitrate and ammonium) for their nutrition. For crops to assimilate N, nitrate and ammonium have to be in solution with the soil water. Fertilizers can increase N losses via all four output mechanisms. Nitrogen fertilizers have been a major factor in the dramatic increase in yield since the 1950s. However, if fertilizer application is not managed well, the leaching of nitrate past the root zone can occur, causing ground water pollution.

Nitrate that leaches below the root zone is very likely to reach the ground water because it readily moves with percolating water. Therefore, it is desirable to monitor nitrate concentration directly below the root zone. Such measurements would be helpful indicators of future ground water contamination problems caused by nitrate leaching, especially since changes in fertilizer or crop management practices can produce effects which may not become evident for several years (Haith, 1982; Owens, 1990).

In order to minimize the amount of nitrate leaching, it is crucial that nitrates which are not taken up by the plants remain within the root zone for as long as possible. Proper fertilizer and irrigation management practices represent key factors with respect to the residence time of inorganic N within this zone (Silvertooth et al., 1992; Barry et al., 1993; Jemison and Fox, 1994). After crop harvest, residual inorganic fertilizer N and recently mineralized N become susceptible to leaching, especially when the fallow period coincides with the wet season. In this case, the use of a winter cover crop to assimilate excess inorganic N and thereby prevent its leaching can be an efficient management practice (Shennan, 1992).

The potential of winter cover crops to decrease the amount of nitrate leaching by crop uptake has been shown in various studies (Dowdell and Webster, 1980; Lord and Shepherd, 1990; Martinez and Guiraud, 1990;

Shipley et al., 1992; Ditsch et al., 1993; McCracken et al., 1994). Besides decreasing nitrate leaching, other beneficial effects of winter cover crops (as opposed to fallow management) can include the reduction of soil erosion (Tisdale et al., 1993) and allow for higher infiltration rates in the spring (McVay et al., 1989). However, plowing down some winter cover crops has resulted in reduction of growth for the subsequent spring crop (Martinez and Guiraud, 1990; Karlen and Doran, 1991).

In this study, a complete block split plot design was used to simultaneously assess the effects of a cereal rye cover crop and three different N fertilizer application rates on the leaching of nitrate throughout the 1993/94 period.

5.2 Results

5.2.1 Nitrate leaching due to irrigation

In the summer of 1993, broccoli was planted in all eight plots of this experiment (Figure 2). During the three months of irrigation (i.e., from the end of May until the end of August), three sampling events took place: June 6, July 26, and August 26. For these three events we measured (via the 32 PCAPS) average nitrate-N concentrations of 6.8, 5.7, and 5.7 mg/l, respectively. The PCAPS-measured percolation during this period of 91 days accumulated to 0.9 cm, with about half of the PCAPS empty at each sampling event. In light of this low percolation, the cumulative N loss was very low, only 0.5 kg ha^{-1}. Therefore, losses of N due to irrigation during the summer of 1993 were negligible.

During the summer of 1994, sweet corn was grown on all plots. Increased irrigation over the last year lead to substantial percolation at the depth of the PCAPS. We sampled water three times (June 29, July 22 and September 9) and collected average amounts of percolation of 1.6, 2.1 and 0.6 cm on the respective dates. With average nitrate-N concentrations of 6.1, 8.1 and 5.5 mg/l, respectively, the cumulative N loss was 3.0 kg ha^{-1} over a period of 110 days. This N loss demonstrated the possibility of nitrate leaching due to summer time irrigation.

5.2.2 N fertilizer effect on nitrate leaching

In order to evaluate the effects of the three different N fertilizer application rates (i.e., N0, N1, and N2), we selected a sampling period during which at least 75% of the PCAPS collected percolation. In view of the dry 1993 fall, our selection period was from December 3, 1993, until April 28, 1994, and included 13 sampling events (Appendix G provides a two-year summary of PCAPS-measured nitrate-N concentrations). To avoid complications due to the occurrence of flooded PCAPS, we calculated one flow-weighted nitrate-N concentration for the entire time span per PCAPS. Treatment effects on nitrate-N leaching were assessed using a paired t-test (Hirsch et al., 1993):

$$t = \frac{D}{S/\sqrt{n}}, \qquad (18)$$

where D denotes the mean difference in nitrate-N concentration between treatments (i.e., different fertilizer application rates), S the standard deviation of D and n the number of data pairs. The null hypothesis is that the difference between two treatments is zero. For the N0 plots, we combined the two PCAPS within each subplot to determine a flow-weighted average concentration. Using this simplification, we had the same number of PCAPS for each treatment category.

Greater N fertilizer application rates during the summer of 1993 resulted in higher nitrate-N leachate concentrations within all treatment combinations during the following months. However, none of the mean differences in nitrate-N leachate concentrations between treatments was significant at the 95% level (Table 10).

Table 10. Effects of the three different N fertilizer application rates on nitrate-N leaching concentrations during the 1993/94 winter period.

	Difference in nitrate-N concentrations between application rates	
	N1 - N0	N2 - N1
Within fallow plots		
Mean difference [mg N/l]	5.44	10.98
Standard deviation [mg N/l]	7.17	11.39
Number of data pairs	4	4
1-sided p-value	0.113	0.075
Within cover crop plots		
Mean difference [mg N/l]	1.23	5.70
Standard deviation [mg N/l]	2.45	7.12
Number of data pairs	4	4
1-sided p-value	0.194	0.104

This test indicated that 1993/94 amounts of winter nitrate leaching were positively related to mid-1993 N fertilizer application rates. In fact, soil testing in late summer of 1993 showed that nitrate-N concentrations in all three N treatment categories differed significantly from each other (p-values < 0.05), with N2 plots containing the highest and N0 plots the lowest near surface concentrations (Kauffman, 1994). Kauffman also observed large flushes of ammonium at the site during August and September.

5.2.3 Cover crop effect on nitrate leaching

Wheeler rye (*secale cereale*) was planted as a winter cover crop at all H-plots on September 30, 1993. Analogous to the previous analysis, we assessed the effects of the cereal rye cover crop on nitrate leaching throughout the period from December 3, 1993, until April 28, 1994. We found that the cover crop was able to reduce nitrate-N leaching concentrations at all three N fertilizer application levels (Figures 30, 31 and 32). All reductions were significant at the 95% level (Table 11). At the recommended N application rate (N2), the flow-weighted nitrate-N leachate concentration under fallow treatment was on average 22.2 mg/l, more than twice the EPA water quality standard of 10.0 mg/l.

Under the cover crop treatment, however, the flow-weighted nitrate-N concentration was maintained below the EPA standard, averaging 9.9 mg/l. This result demonstrates the ability of the Wheeler rye cover crop to considerably reduce nitrate-N leachate concentrations and thereby help prevent the contamination of ground water resources in the long term.

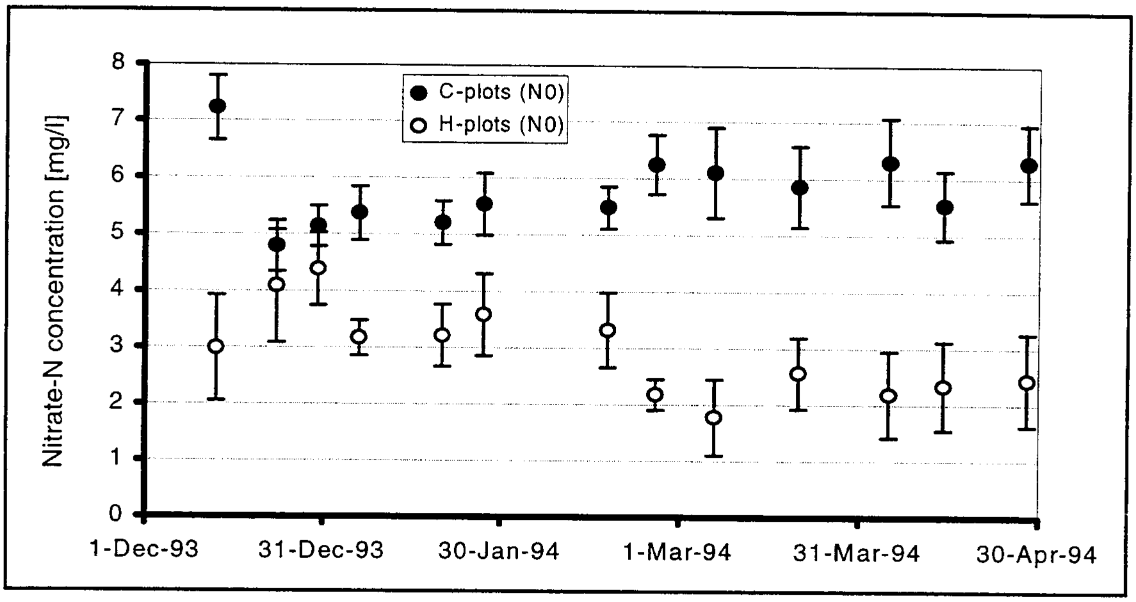

Figure 30. Cover crop effect on nitrate-N leachate concentrations at zero N fertilizer application rate (error bar represents one standard error).

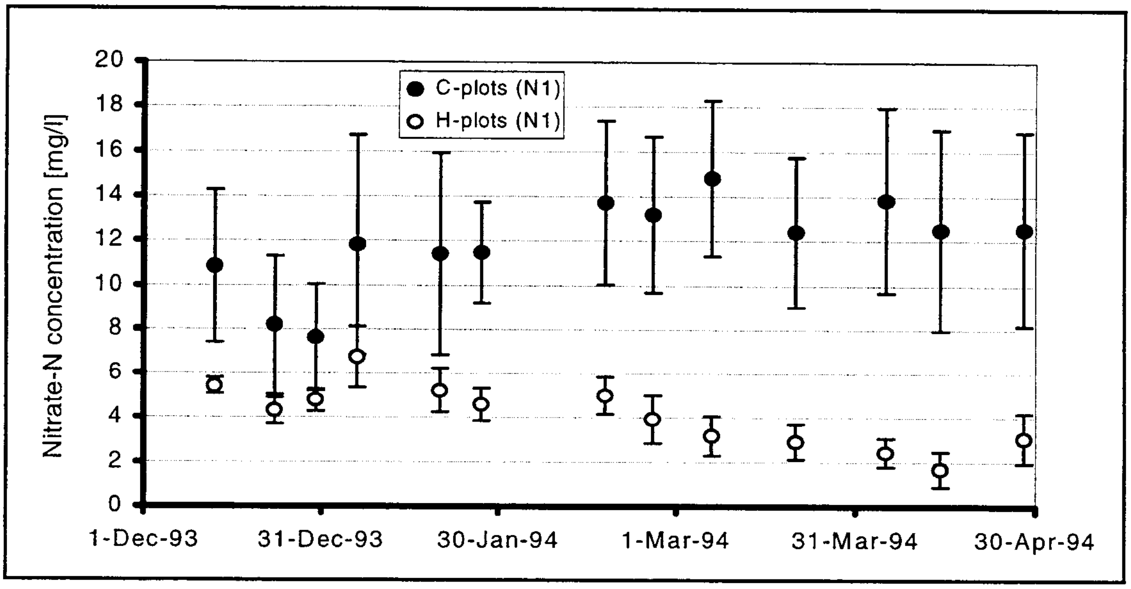

Figure 31. Cover crop effect on nitrate-N leachate concentrations at medium N fertilizer application rate (error bar represents one standard error).

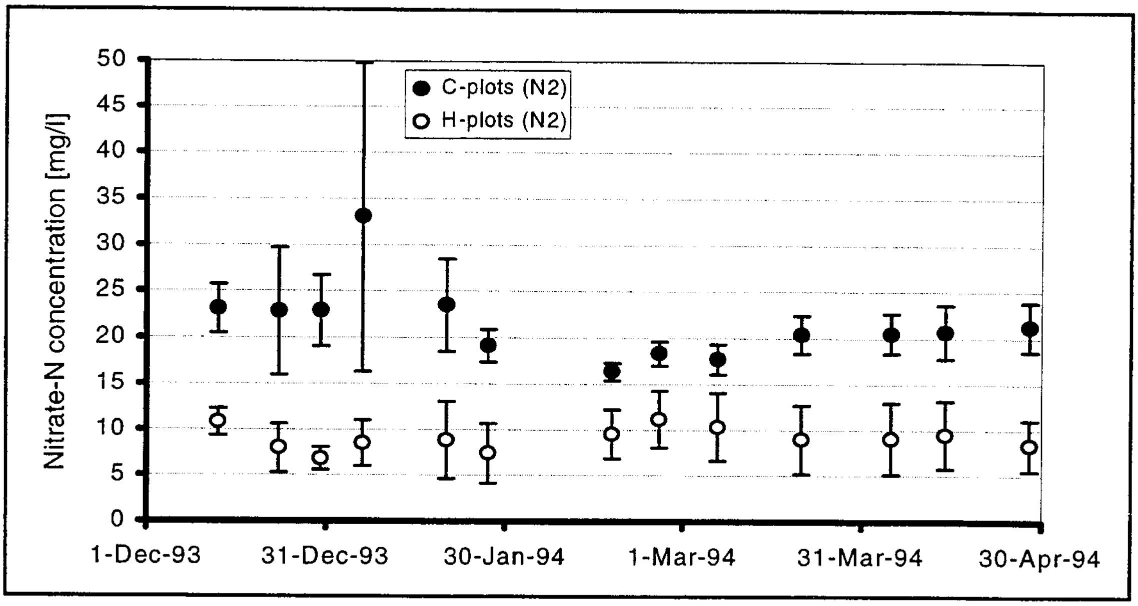

Figure 32. Cover crop effect on nitrate-N leachate concentrations at high N fertilizer application rate (error bar represents one standard error).

Table 11. Effect of fallow (C) and cover crop (H) treatment on nitrate-N leachate concentrations at all three N rates.

	Difference in nitrate-N leachate concentrations between fallow (C) and cover crop (H) treatment			
N rate	Mean difference C - H	Standard deviation	n[†]	1-sided p-value
	mg NO_3-N/l			
N0	2.89	1.84	4	0.026
N1	7.10	5.76	4	0.045
N2	12.38	8.55	4	0.031

[†] Number of data pairs within same treatment category.

5.2.4 N mass losses due to nitrate leaching

For the second year of the experiment (October 1993 until October 1994), the nitrate-N flux for each PCAPS was calculated at each sampling event by multiplying the flow-weighted nitrate-N concentration with the observed percolation. In this way, we were able to measure N mass losses on a kg ha^{-1} basis. The measurement of N losses below the root zone indicates to what extent different treatment practices might contaminate underlying ground water resources. The majority of the N losses from the soil ecosystem occurred during the period of high precipitation from early December 1993 until late April 1994. During these five months, more than 85% of the cumulative N losses took place, demonstrating the susceptibility of agricultural fields to nutrient leaching during wet winters.

At the recommended fertilizer rate (N2), N leaching losses amounted to 61.5 kg ha^{-1} under fallow and 23.2 kg ha^{-1} under cover crop treatment. Therefore, the cereal rye cover crop prevented the leaching of 38.3 kg N ha^{-1} within a one-year period. The decrease in N losses due to cover crops was significant at the 95% level under all three N fertilizer treatments (Table 12). Cumulative N losses, which will likely contribute to future pollution of the underlying ground water, were on average reduced by 55% due to the presence of the cereal rye cover crop (Figure 33, 34 and 35).

The second treatment variable, N fertilizer rate, also affected N leaching losses. We found that higher N fertilizer rates were associated with greater N losses (Table 13). Under fallow treatment, the cumulative N loss for the N2 rate was 61.5 kg ha^{-1} in comparison to 32.6 kg ha^{-1} for the N1 and 17.0 kg ha^{-1} for N0 rate. Although mean differences between N treatments were considerable within fallow and cover crop plots, only the differences between N2 and N0 (under fallow and cover crop treatment) were significant at the 95% confidence level (Table 13).

Table 12. Nitrate-N mass losses due to leaching from October 8, 1993, until October 5, 1994, under fallow and cover crop treatment.

N rate reduction	Total mass lost fallow (C)	Total mass lost cover crop (H)	Difference C - H	1-sided p-value	loss due to cover crop
	kg N ha^{-1}				%
N0	17.0	8.8	8.2	0.015	48
N1	32.6	14.8	17.8	0.037	55
N2	61.5	23.2	38.3	0.018	62

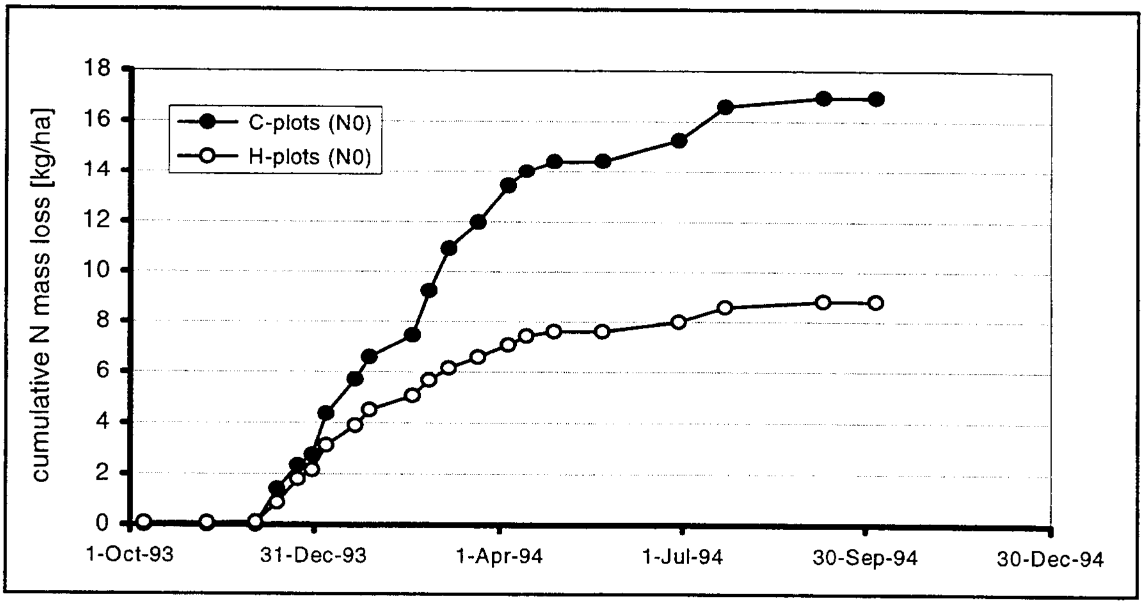

Figure 33. Cumulative N mass loss as affected by cover crop at N0 rate.

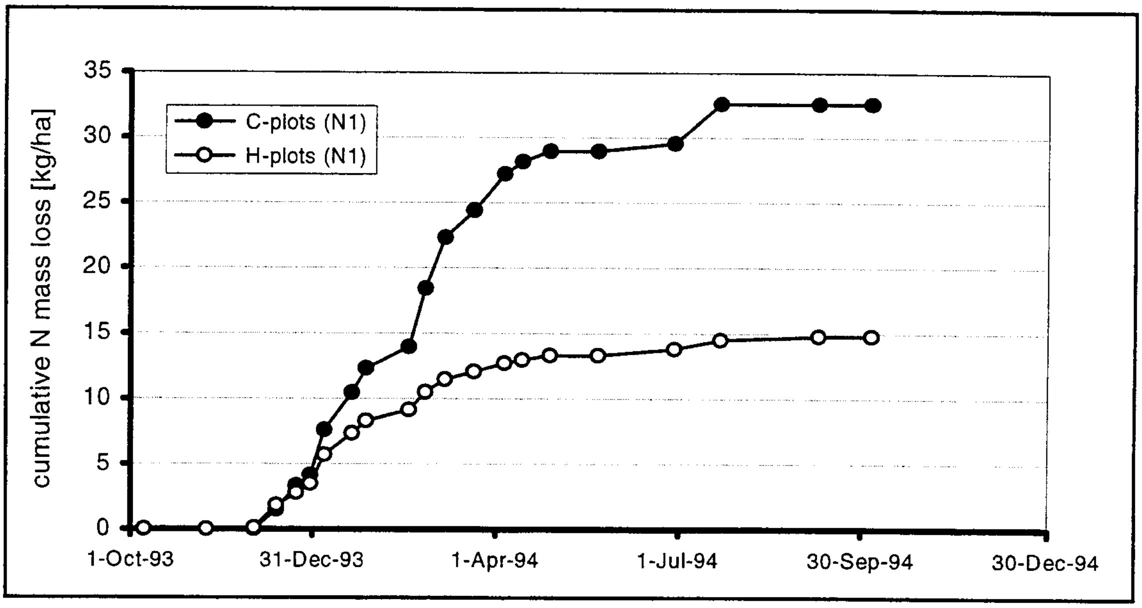

Figure 34. Cumulative N mass loss as affected by cover crop at N1 rate.

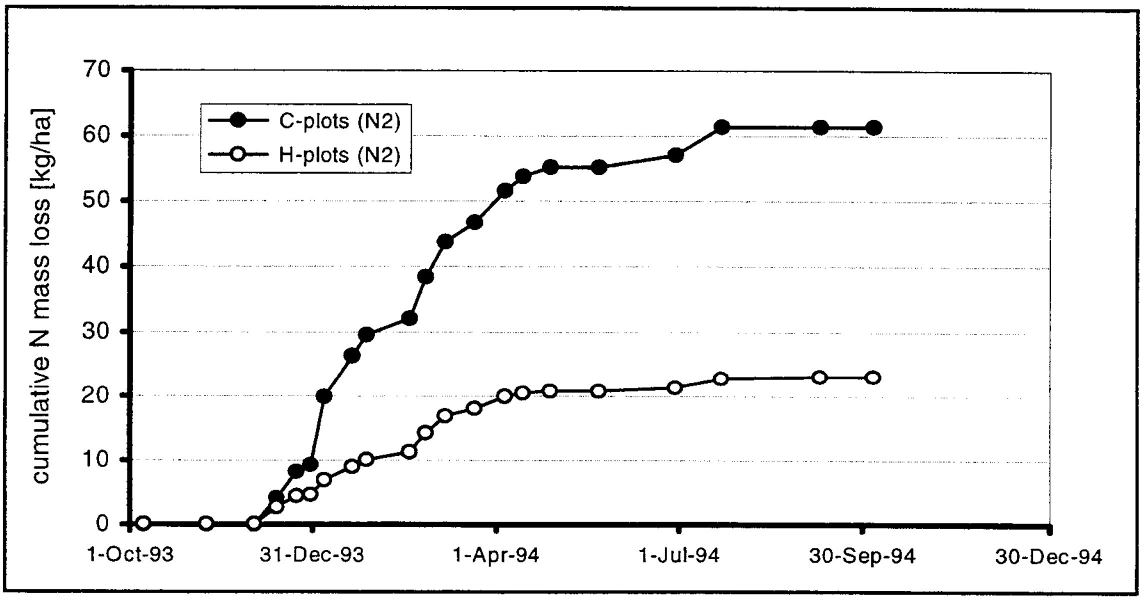

Figure 35. Cumulative N mass loss as affected by cover crop at N2 rate.

Table 13. Effects of the three different N fertilizer application rates (N0, N1, and N2) on cumulative N mass losses from October 8, 1993, until October 5, 1994.

	Differences in cumulative N mass losses as affected by N rate		
	N1 - N0	N2 - N1	N2 - N0
Within fallow plots			
Mean difference [kg N ha^{-1}]	15.7	28.8	44.5
Std. deviation [kg N ha^{-1}]	17.1	26.0	21.1
Number of data pairs	4	4	4
1-sided p-value	0.082	0.057	0.012
Within cover crop plots			
Mean difference [kg N ha^{-1}]	5.9	8.4	14.4
Standard deviation [kg N ha^{-1}]	6.9	13.3	11.42
Number of data pairs	4	4	4
1-sided p-value	0.091	0.147	0.043

5.3 Conclusions

At our experiment site, nitrate leaching and N mass losses due to irrigation throughout the summer months were minor in comparison to winter leaching. We measured cumulative mass losses of 0.5 kg N ha^{-1} and 3.0 kg N ha^{-1} over the summer periods of 1993 and 1994, respectively. These small N losses indicate that proper management practices can largely prevent the leaching of nitrate due to summer time irrigation.

The amount of N fertilizer (applied in June and July of 1993) had a major influence on nitrate leaching throughout the following year. Using only half the recommended N fertilizer rate (N1) reduced cumulative N losses from August 1993 until May 1994 on average by 48% under winter fallow plots and by 36% under cover crop plots. In view of these observations, application rates of spring fertilizers should be calculated with extreme care to avoid nitrate leaching.

Finally, there was convincing evidence that the cereal rye cover crop reduced the leaching of nitrate at all three fertilizer application rates. At the recommended rate (N2), nitrate-N concentrations were lowered on average from 22.2 to 9.9 mg/l (December 1993 through April 1994), which is below the EPA's water quality standard of 10.0 mg/l. Simultaneously, cumulative N mass losses were cut by 62% due to plant uptake by the cereal rye cover crop. These results demonstrate that, given similar climatic conditions, cover crops can recover residual inorganic N and thereby prevent adverse environmental impacts of nitrate leaching.

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Appendices

Appendix A

Flow-weighted bromide concentrations as measured with PCAPS (November 1992 - November 1994)

	# of sample set				# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	# 9	# 10
	date of sample set				4-Nov-92	12-Nov-92	19-Nov-92	25-Nov-92	3-Dec-92	11-Dec-92	17-Dec-92	22-Dec-92	6-Jan-93	19-Jan-93
	# of days since Br-application				0	8	15	21	29	37	43	48	63	76
# of sampler	*Management*	*N - rate*	*Placement*		*Concentration*	*Concentration*	*Concentration*	*Concentration*	*Concentration*	*Concentration*	*Concentration*	*Concentration*	*Concentration*	*Concentration*
					[mg/l]	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*
25	*C1*	*N0*	*North*		0.00	0.00	0.00	1.10	0.87	1.62	4.93	7.20	8.66	14.85
23	*C1*	*N0*	*South*		flooded	0.00	0.00	flooded	flooded	flooded	flooded	flooded	flooded	flooded
31	*C2*	*N0*	*North*		0.00	0.00	0.00	0.76	0.39	0.36	0.35	0.42	0.55	0.64
29	*C2*	*N0*	*South*		empty	empty	0.00	0.19	0.37	1.83	1.70	0.79	0.64	0.70
17	*C3*	*N0*	*North*		0.00	0.00	0.00	0.00	0.00	0.04	0.19	0.49	0.80	2.28
19	*C3*	*N0*	*South*		0.00	0.00	0.00	0.68	1.76	5.21	8.13	10.33	13.57	16.22
5	*C4*	*N0*	*North*		0.00	0.00	0.00	1.02	4.44	4.10	4.39	2.73	2.47	2.31
9	*C4*	*N0*	*South*		0.00	0.00	0.00	0.50	4.10	4.11	3.61	1.73	2.01	2.07
27	*H1*	*N0*	*North*		flooded	1.00	0.57	flooded	flooded	flooded	flooded	5.03	3.48	2.83
21	*H1*	*N0*	*South*		flooded	flooded	0.00	flooded	flooded	flooded	flooded	flooded	flooded	flooded
1	*H2*	*N0*	*North*		empty	empty	empty	0.09	0.00	0.00	0.03	0.06	0.06	0.00
3	*H2*	*N0*	*South*		empty	0.00	empty	0.00	0.09	0.72	2.08	2.45	3.33	6.31
13	*H3*	*N0*	*North*		empty	empty	empty	0.00	0.00	0.00	0.00	0.00	0.02	0.00
15	*H3*	*N0*	*South*		0.00	0.00	0.00	0.54	0.14	0.07	0.07	0.11	0.41	0.36
7	*H4*	*N0*	*North*		0.00	0.00	0.00	0.00	0.03	0.32	0.61	1.08	1.73	2.03
11	*H4*	*N0*	*South*		empty	empty	empty	empty	0.00	0.00	0.00	0.00	0.00	0.06
24	*C1*	*N1*	*South*		flooded	0.00	0.00	flooded	flooded	flooded	flooded	flooded	flooded	flooded
32	*C2*	*N1*	*North*		empty	empty	0.00	0.83	1.21	2.29	2.52	3.01	2.38	3.27
18	*C3*	*N1*	*North*		empty	empty	empty	0.85	0.28	0.34	0.27	0.19	0.16	0.10
10	*C4*	*N1*	*South*		0.01	0.00	0.00	0.37	0.17	2.27	5.31	3.32	1.96	1.73
22	*H1*	*N1*	*South*		flooded	flooded	0.00	flooded	flooded	flooded	flooded	flooded	flooded	flooded
4	*H2*	*N1*	*South*		empty	empty	empty	empty	0.11	0.05	0.04	0.06	0.07	0.00
16	*H3*	*N1*	*South*		0.00	empty	empty	empty	0.04	0.00	0.00	0.01	0.00	0.00
8	*H4*	*N1*	*North*		0.00	empty	empty	0.61	0.56	0.62	0.82	0.67	0.87	0.97
26	*C1*	*N2*	*North*		empty	empty	0.48	0.82	0.49	0.73	1.07	1.34	1.56	1.83
30	*C2*	*N2*	*South*		empty	empty	empty	0.49	2.44	3.28	2.33	1.63	1.50	1.46
20	*C3*	*N2*	*South*		0.00	0.00	0.00	0.00	0.07	0.14	0.16	0.13	0.11	0.06
6	*C4*	*N2*	*North*		empty	empty	empty	empty	3.64	6.68	8.77	5.56	3.34	2.87
28	*H1*	*N2*	*North*		flooded	0.26	0.02	flooded	flooded	flooded	flooded	1.99	0.90	1.00
2	*H2*	*N2*	*North*		0.00	0.00	0.00	1.62	0.94	1.13	1.89	4.82	3.42	5.04
14	*H3*	*N2*	*North*		0.00	empty	empty	0.39	0.42	0.83	2.64	3.46	4.71	6.86
12	*H4*	*N2*	*South*		0.00	0.00	1.13	1.13	0.84	1.03	1.09	0.85	0.96	1.17

Note: "empty" means that PCAPS did not collect any water;
"flooded" means that irrigation box was inaccessible due to surface ponding.

	# of sample set				**# 11**	**# 12**	**# 13**	**# 14**	**# 15**	**# 16**	**# 17**	**# 18**	**# 19**	**# 20**
	date of sample set				**27-Jan-93**	**2-Feb-93**	**9-Feb-93**	**23-Feb-93**	**9-Mar-93**	**19-Mar-93**	**30-Mar-93**	**6-Apr-93**	**16-Apr-93**	**4-May-93**
	# of days since Br-application				**84**	**90**	**97**	**111**	**125**	**135**	**146**	**153**	**163**	**181**
# of sampler	*Management*	*N - rate*	*Placement*		*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*
25	*C1*	*N0*	*North*		19.30	26.35	18.40	20.02	20.73	22.04	33.63	39.04	33.96	37.42
23	*C1*	*N0*	*South*		flooded	4.69	3.94	4.68	5.06	3.84	4.30	5.18	5.54	5.30
31	*C2*	*N0*	*North*		1.02	1.17	1.12	1.13	1.25	1.43	2.37	2.77	4.04	6.76
29	*C2*	*N0*	*South*		5.29	6.21	3.59	3.71	4.25	2.96	3.95	6.19	6.35	7.37
17	*C3*	*N0*	*North*		3.96	7.37	7.38	7.55	9.78	11.82	16.89	23.44	25.91	27.31
19	*C3*	*N0*	*South*		18.06	20.31	17.28	15.53	17.32	14.35	13.75	17.23	15.04	13.13
5	*C4*	*N0*	*North*		4.48	3.73	3.47	3.14	3.75	3.88	11.42	7.70	8.50	9.37
9	*C4*	*N0*	*South*		7.18	4.71	3.28	2.77	4.65	6.15	13.33	10.30	12.04	14.27
27	*H1*	*N0*	*North*		2.83	2.90	2.76	2.97	3.09	2.92	2.80	2.58	2.96	2.75
21	*H1*	*N0*	*South*		flooded	2.50	7.64	8.07	10.48	11.04	13.56	16.45	18.27	17.57
1	*H2*	*N0*	*North*		0.07	0.31	0.51	0.62	0.43	0.67	4.54	4.73	7.85	10.95
3	*H2*	*N0*	*South*		16.07	17.42	13.09	5.00	7.73	9.74	16.07	10.89	14.27	14.29
13	*H3*	*N0*	*North*		0.19	0.26	0.26	empty	empty	0.35	0.85	1.02	1.04	2.83
15	*H3*	*N0*	*South*		10.25	5.63	3.18	7.36	7.36	9.37	9.11	10.08	10.64	9.24
7	*H4*	*N0*	*North*		3.35	4.44	4.88	6.32	8.00	6.28	10.01	15.69	15.84	17.25
11	*H4*	*N0*	*South*		0.59	1.10	1.10	1.12	1.73	2.29	4.11	6.50	8.54	12.07
24	*C1*	*N1*	*South*		flooded	0.90	2.73	3.22	3.33	3.14	3.38	6.79	10.45	11.99
32	*C2*	*N1*	*North*		2.82	3.66	3.06	3.20	3.73	3.53	8.12	10.68	9.52	12.25
18	*C3*	*N1*	*North*		0.52	0.67	empty	empty	empty	empty	0.53	empty	empty	0.72
10	*C4*	*N1*	*South*		2.40	3.17	2.04	1.48	2.15	5.59	6.40	9.51	8.16	8.73
22	*H1*	*N1*	*South*		flooded	0.05	0.96	0.81	1.28	1.70	1.29	2.49	3.98	4.23
4	*H2*	*N1*	*South*		0.19	0.23	0.15	empty	0.16	0.17	0.37	0.56	0.96	1.85
16	*H3*	*N1*	*South*		0.10	0.21	0.20	empty	empty	0.51	1.11	1.68	1.56	1.27
8	*H4*	*N1*	*North*		2.45	4.02	3.38	2.61	5.61	5.26	10.80	10.29	11.09	15.69
26	*C1*	*N2*	*North*		2.32	3.74	3.09	3.09	3.49	2.89	5.81	9.03	9.26	10.25
30	*C2*	*N2*	*South*		5.77	4.28	3.37	3.63	3.08	3.47	7.10	9.19	8.68	9.50
20	*C3*	*N2*	*South*		0.43	0.40	0.36	empty	0.34	0.68	1.32	1.31	1.52	1.71
6	*C4*	*N2*	*North*		4.73	4.48	3.44	2.70	3.02	3.25	7.64	7.64	6.44	6.12
28	*H1*	*N2*	*North*		0.40	0.88	0.80	empty	empty	0.66	0.48	0.56	0.97	1.04
2	*H2*	*N2*	*North*		8.59	10.06	9.58	12.66	11.11	9.49	11.79	11.49	11.07	11.37
14	*H3*	*N2*	*North*		8.22	12.71	12.96	empty	15.24	16.30	12.14	20.76	17.28	16.16
12	*H4*	*N2*	*South*		1.44	1.38	1.39	1.27	1.89	2.00	2.23	3.15	4.00	4.05

	# of sample set				**# 21**	**# 22**	**# 23**	**# 24**	**# 25**	**# 26**	**# 27**	**# 28**	**# 29**	**# 30**
	date of sample set				**27-May-93**	**6-Jun-93**	**26-Jul-93**	**26-Aug-93**	**8-Oct-93**	**8-Nov-93**	**2-Dec-93**	**13-Dec-93**	**23-Dec-93**	**30-Dec-93**
	# of days since Br-application				**204**	**214**	**264**	**295**	**338**	**369**	**393**	**404**	**414**	**421**
# of sampler	*Management*	*N - rate*	*Placement*		*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*
25	*C1*	*N0*	*North*		33.47	empty	empty	empty	empty	empty	empty	22.84	25.05	24.76
23	*C1*	*N0*	*South*		4.72	5.30	3.04	5.68	empty	empty	empty	1.25	0.64	1.85
31	*C2*	*N0*	*North*		9.70	empty	5.42	empty	empty	empty	empty	10.38	13.12	11.59
29	*C2*	*N0*	*South*		10.81	13.32	11.95	10.35	empty	empty	empty	12.70	17.53	16.99
17	*C3*	*N0*	*North*		36.28	empty	22.32	empty	empty	empty	empty	26.79	36.72	33.64
19	*C3*	*N0*	*South*		11.81	10.87	empty	empty	empty	empty	empty	7.78	9.22	8.44
5	*C4*	*N0*	*North*		10.44	empty	empty	12.63	empty	empty	empty	10.75	12.45	13.28
9	*C4*	*N0*	*South*		15.62	14.99	12.08	empty	empty	empty	empty	9.83	10.82	14.28
27	*H1*	*N0*	*North*		2.57	2.54	1.93	1.49	empty	empty	empty	0.60	0.45	0.47
21	*H1*	*N0*	*South*		14.17	11.47	empty	10.90	9.08	2.34	empty	3.17	1.54	3.66
1	*H2*	*N0*	*North*		20.93	empty	9.43	empty	empty	empty	empty	20.95	20.64	20.79
3	*H2*	*N0*	*South*		14.01	22.93	empty	7.40	8.68	empty	empty	6.04	8.36	9.11
13	*H3*	*N0*	*North*		6.09	empty	empty	empty	empty	empty	empty	31.07	39.04	30.46
15	*H3*	*N0*	*South*		11.14	empty	9.28	9.53	empty	empty	8.39	8.56	9.74	9.60
7	*H4*	*N0*	*North*		19.22	6.24	8.81	empty	empty	empty	empty	18.78	20.64	21.21
11	*H4*	*N0*	*South*		17.56	18.39	14.82	14.52	27.76	6.96	empty	19.51	27.99	27.44
24	*C1*	*N1*	*South*		15.60	16.51	empty	17.43	empty	empty	empty	3.33	1.91	8.55
32	*C2*	*N1*	*North*		16.26	empty	empty	empty	empty	empty	empty	18.53	20.07	21.09
18	*C3*	*N1*	*North*		0.60	empty	empty	empty	empty	empty	empty	3.85	4.45	3.63
10	*C4*	*N1*	*South*		12.16	empty	empty	empty	empty	empty	empty	8.12	8.42	8.75
22	*H1*	*N1*	*South*		5.18	empty	empty	3.84	empty	empty	empty	3.42	1.09	2.14
4	*H2*	*N1*	*South*		3.44	empty	empty	empty	empty	empty	empty	12.58	17.75	8.22
16	*H3*	*N1*	*South*		1.62	empty	empty	empty	empty	empty	12.26	20.09	18.33	15.75
8	*H4*	*N1*	*North*		15.29	empty	12.84	8.80	empty	empty	empty	19.15	22.74	21.87
26	*C1*	*N2*	*North*		14.67	empty	15.04	13.92	10.20	empty	empty	15.97	20.95	20.32
30	*C2*	*N2*	*South*		9.91	13.95	14.38	empty	empty	empty	empty	6.40	10.42	10.23
20	*C3*	*N2*	*South*		1.81	empty	empty	empty	empty	empty	empty	2.97	4.17	2.94
6	*C4*	*N2*	*North*		6.19	5.37	4.56	empty	empty	empty	empty	11.78	14.99	14.44
28	*H1*	*N2*	*North*		1.18	empty	0.98	1.80	empty	empty	empty	5.20	2.07	1.67
2	*H2*	*N2*	*North*		13.36	19.82	13.96	empty	empty	empty	empty	10.75	14.99	14.29
14	*H3*	*N2*	*North*		21.79	17.90	12.34	empty	empty	empty	empty	12.27	17.85	9.94
12	*H4*	*N2*	*South*		5.32	5.92	1.65	5.68	11.14	empty	empty	9.16	11.67	13.37

	# of sample set				# 31	# 32	# 33	# 34	# 35	# 36	# 37	# 38	# 39	# 40
	date of sample set				6-Jan-94	20-Jan-94	27-Jan-94	17-Feb-94	25-Feb-94	7-Mar-94	21-Mar-94	5-Apr-94	14-Apr-94	28-Apr-94
	# of days since Br-application				428	442	449	470	478	488	502	517	526	540
# of sampler	*Management*	*N - rate*	*Placement*		*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*
25	*C1*	*N0*	*North*		15.32	14.79	13.82	19.14	14.12	5.46	6.66	7.17	5.75	6.96
23	*C1*	*N0*	*South*		flooded	1.10	1.13	flooded	flooded	0.68	0.25	0.13	0.22	0.24
31	*C2*	*N0*	*North*		11.70	12.44	5.72	11.66	10.84	5.55	4.26	5.05	4.04	4.07
29	*C2*	*N0*	*South*		14.71	19.17	16.60	23.36	21.37	12.89	13.41	13.77	11.90	11.67
17	*C3*	*N0*	*North*		30.06	23.07	19.73	24.46	18.81	10.92	8.41	8.68	7.08	5.42
19	*C3*	*N0*	*South*		7.50	7.06	6.56	7.90	6.93	4.11	3.98	4.35	4.21	4.14
5	*C4*	*N0*	*North*		9.71	10.15	7.33	10.65	8.36	2.00	2.81	4.31	3.14	2.23
9	*C4*	*N0*	*South*		6.74	10.10	6.39	9.36	4.27	1.36	4.43	3.23	3.66	3.55
27	*H1*	*N0*	*North*		0.32	0.16	0.46	0.54	flooded	0.48	0.34	0.37	0.31	0.25
21	*H1*	*N0*	*South*		flooded	2.50	2.29	3.07	flooded	2.02	0.93	1.07	1.02	0.90
1	*H2*	*N0*	*North*		16.02	13.80	8.81	11.98	10.58	4.41	2.42	3.53	2.07	1.95
3	*H2*	*N0*	*South*		7.09	7.88	5.36	8.00	6.48	3.50	4.09	3.45	2.66	2.87
13	*H3*	*N0*	*North*		32.54	34.24	19.78	36.76	31.35	19.40	17.46	16.38	13.03	10.57
15	*H3*	*N0*	*South*		8.78	9.08	7.33	9.30	8.08	6.15	5.53	5.73	4.95	4.59
7	*H4*	*N0*	*North*		20.94	17.92	13.72	19.86	18.96	12.84	14.54	14.61	13.29	12.16
11	*H4*	*N0*	*South*		26.76	25.56	17.79	21.24	22.05	16.16	16.45	14.56	13.80	12.44
24	*C1*	*N1*	*South*		flooded	4.13	3.91	flooded	flooded	2.67	1.15	0.57	1.03	1.13
32	*C2*	*N1*	*North*		18.01	14.22	10.26	14.94	13.86	8.43	8.71	8.79	9.30	8.77
18	*C3*	*N1*	*North*		5.11	4.66	4.68	3.22	6.26	6.43	5.35	5.93	3.35	2.68
10	*C4*	*N1*	*South*		8.96	7.28	8.21	10.38	6.65	2.92	5.61	5.93	5.80	5.26
22	*H1*	*N1*	*South*		flooded	2.42	2.54	3.59	flooded	2.57	1.27	1.65	1.46	1.39
4	*H2*	*N1*	*South*		18.49	15.05	9.51	12.88	13.07	9.97	10.07	8.79	8.61	9.42
16	*H3*	*N1*	*South*		16.46	16.03	11.85	15.57	12.44	6.32	6.72	5.42	4.37	5.13
8	*H4*	*N1*	*North*		13.94	15.21	10.15	15.99	10.95	3.51	6.12	6.27	2.93	2.82
26	*C1*	*N2*	*North*		20.32	14.32	18.47	18.68	12.49	5.49	9.38	11.04	11.17	9.70
30	*C2*	*N2*	*South*		7.03	8.53	9.02	9.25	10.04	7.57	7.58	8.51	5.86	5.64
20	*C3*	*N2*	*South*		5.55	4.30	3.32	4.28	5.11	5.05	4.92	5.21	5.30	4.37
6	*C4*	*N2*	*North*		13.89	14.43	15.35	14.94	11.86	4.48	11.00	13.03	14.56	14.46
28	*H1*	*N2*	*North*		1.63	0.49	2.31	3.05	flooded	5.18	3.49	4.20	3.12	2.36
2	*H2*	*N2*	*North*		12.04	12.65	6.45	10.54	9.93	6.48	3.20	3.21	1.04	0.43
14	*H3*	*N2*	*North*		18.75	16.90	13.51	18.06	18.11	11.70	9.83	11.31	10.39	0.00
12	*H4*	*N2*	*South*		8.73	7.55	5.38	7.95	6.04	4.41	4.44	3.90	3.74	3.32

	# of sample set			# 41	# 42	# 43	# 44	# 45	# 46	# 47
	date of sample set			22-May-94	29-Jun-94	22-Jul-94	9-Sep-94	5-Oct-94	28-Oct-94	1-Nov-94
	# of days since Br-application			564	602	625	674	700	723	727
# of sampler	*Management*	*N - rate*	*Placement*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*
25	*C1*	*N0*	*North*	2.00	1.43	2.08	2.08	1.01	0.86	1.05
23	*C1*	*N0*	*South*	empty	0.27	0.15	empty	empty	flooded	flooded
31	*C2*	*N0*	*North*	3.09	1.58	0.48	0.24	0.15	0.16	0.18
29	*C2*	*N0*	*South*	5.71	4.92	3.32	2.01	empty	1.88	1.41
17	*C3*	*N0*	*North*	4.04	empty	5.37	empty	empty	2.34	2.06
19	*C3*	*N0*	*South*	empty	2.53	3.88	empty	empty	2.62	2.14
5	*C4*	*N0*	*North*	0.24	2.23	1.28	0.94	1.36	0.53	flooded
9	*C4*	*N0*	*South*	empty	1.03	0.92	0.56	empty	0.44	flooded
27	*H1*	*N0*	*North*	empty	0.09	0.09	empty	empty	flooded	flooded
21	*H1*	*N0*	*South*	empty	0.40	0.31	empty	empty	flooded	flooded
1	*H2*	*N0*	*North*	3.25	0.77	0.97	0.48	empty	0.52	0.55
3	*H2*	*N0*	*South*	0.82	1.45	0.87	1.02	empty	0.41	0.57
13	*H3*	*N0*	*North*	empty	6.58	4.79	3.31	empty	2.72	3.37
15	*H3*	*N0*	*South*	empty	3.26	2.92	3.18	empty	1.82	1.77
7	*H4*	*N0*	*North*	empty	4.71	2.83	1.99	empty	0.58	flooded
11	*H4*	*N0*	*South*	empty	empty	empty	empty	empty	empty	7.71
24	*C1*	*N1*	*South*	empty	empty	0.92	empty	empty	flooded	flooded
32	*C2*	*N1*	*North*	5.50	4.39	6.86	4.15	empty	2.48	3.22
18	*C3*	*N1*	*North*	empty	empty	5.76	empty	3.25	2.91	2.71
10	*C4*	*N1*	*South*	empty	3.22	3.15	1.24	empty	1.44	0.71
22	*H1*	*N1*	*South*	empty	0.92	0.51	0.63	empty	flooded	flooded
4	*H2*	*N1*	*South*	9.18	4.06	3.73	3.28	2.65	0.78	0.94
16	*H3*	*N1*	*South*	empty	3.86	5.36	empty	empty	2.18	2.26
8	*H4*	*N1*	*North*	2.91	empty	4.79	4.73	empty	1.17	flooded
26	*C1*	*N2*	*North*	7.84	4.66	6.86	2.87	empty	2.12	2.98
30	*C2*	*N2*	*South*	empty	2.07	2.03	1.03	empty	0.74	0.99
20	*C3*	*N2*	*South*	empty	5.03	4.77	3.57	empty	3.97	2.79
6	*C4*	*N2*	*North*	empty	6.63	8.08	empty	empty	2.85	flooded
28	*H1*	*N2*	*North*	empty	0.89	1.10	0.60	empty	flooded	flooded
2	*H2*	*N2*	*North*	empty	1.33	1.29	0.32	empty	0.95	0.94
14	*H3*	*N2*	*North*	empty	6.41	7.36	5.07	empty	3.84	3.72
12	*H4*	*N2*	*South*	2.40	empty	2.71	1.08	empty	1.72	1.58

Appendix B

Bromide mass recovery ratios as measured with PCAPS

# of sampler	Management	N - rate	Placement		Total bromide	Total bromide	Mass recovery
					mass collected	mass applied	ratio
					[mg]	[mg]	[%]
25	*C 1*	*N 0*	*North*		2977	3880	76.7
23	*C 1*	*N 0*	*South*		263	3880	6.8
24	*C 1*	*N 1*	*South*		591	3880	15.2
26	*C 1*	*N 2*	*North*		1568	3880	40.4
31	*C 2*	*N 0*	*North*		899	3880	23.2
29	*C 2*	*N 0*	*South*		1340	3880	34.5
32	*C 2*	*N 1*	*North*		1384	3880	35.7
30	*C 2*	*N 2*	*South*		1118	3880	28.8
17	*C 3*	*N 0*	*North*		1662	3880	42.8
19	*C 3*	*N 0*	*South*		1555	3880	40.1
18	*C 3*	*N 1*	*North*		309	3880	8.0
20	*C 3*	*N 2*	*South*		349	3880	9.0
5	*C 4*	*N 0*	*North*		1044	3880	26.9
9	*C 4*	*N 0*	*South*		1119	3880	28.8
10	*C 4*	*N 1*	*South*		915	3880	23.6
6	*C 4*	*N 2*	*North*		1322	3880	34.1
27	*H 1*	*N 0*	*North*		329	3880	8.5
21	*H 1*	*N 0*	*South*		1076	3880	27.7
22	*H 1*	*N 1*	*South*		276	3880	7.1
28	*H 1*	*N 2*	*North*		204	3880	5.2
1	*H 2*	*N 0*	*North*		1024	3880	26.4
3	*H 2*	*N 0*	*South*		1387	3880	35.7
4	*H 2*	*N 1*	*South*		1204	3880	31.0
2	*H 2*	*N 2*	*North*		1449	3880	37.4
13	*H 3*	*N 0*	*North*		1771	3880	45.6
15	*H 3*	*N 0*	*South*		1216	3880	31.3
16	*H 3*	*N 1*	*South*		1001	3880	25.8
14	*H 3*	*N 2*	*North*		1259	3880	32.5
7	*H 4*	*N 0*	*North*		1806	3880	46.6
11	*H 4*	*N 0*	*South*		1585	3880	40.8
8	*H 4*	*N 1*	*North*		1328	3880	34.2
12	*H 4*	*N 2*	*South*		719	3880	18.5
		Mean (only C-plots)			1151		29.7
		Mean (only H-plots)			1102		28.4
		Mean (all plots)			1126		29.0
		Std. Deviation (all plots)			579		14.9

Appendix C

Summary of numerical output of CXTFIT runs

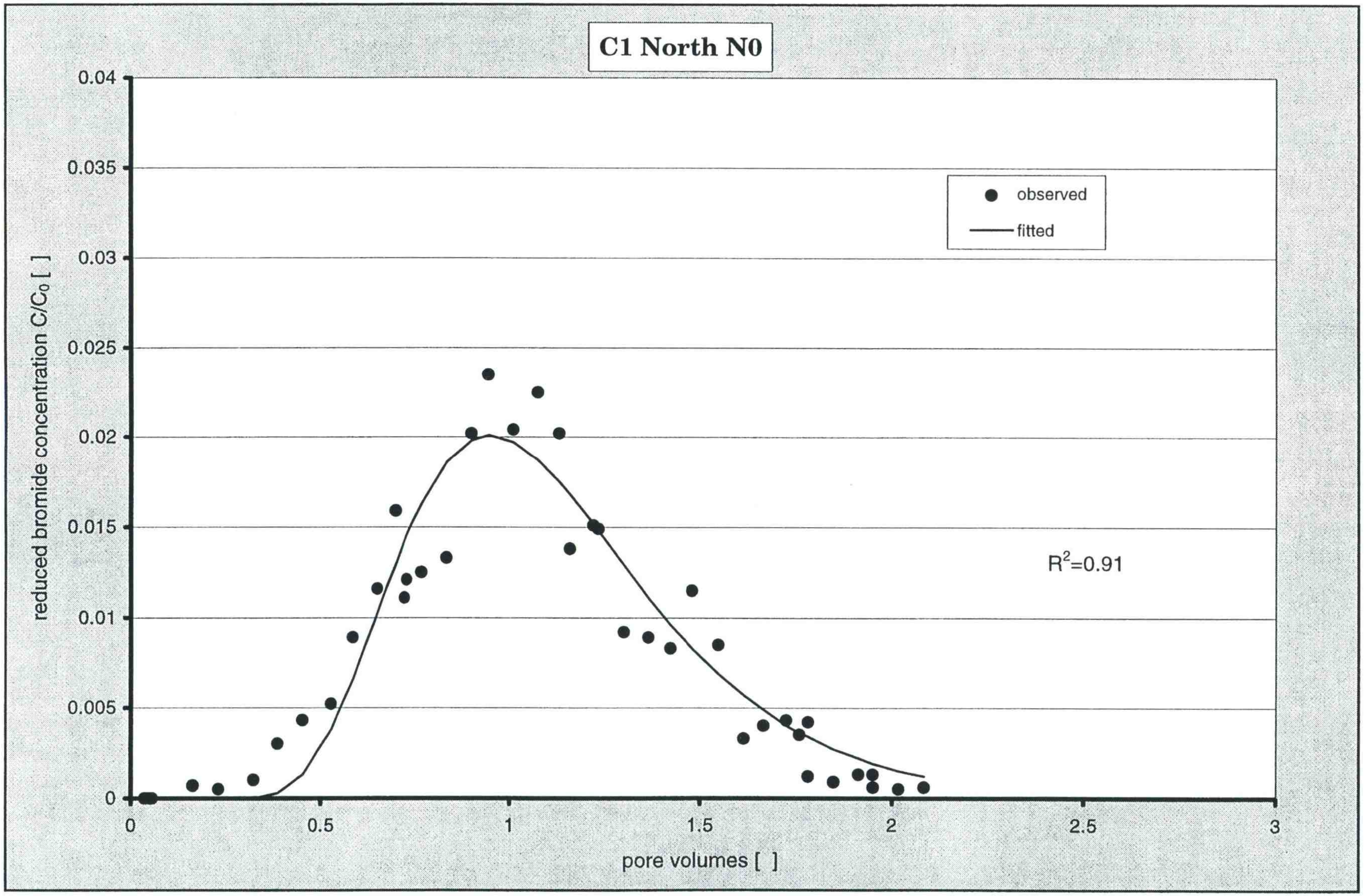
					Retardation factor R			Hydrodynamic dispersion coefficient D/vz				
# of sampler	Management	N - rate	Placement		R	95 % confidence limits		D/vz	95 % confidence limits			R^2 of model fit
						lower	upper		lower	upper		
					[ ]	[ ]	[ ]	[ ]	[ ]	[ ]		[ ]
25	C 1	N 0	North		1.12	1.08	1.15	6.85	5.73	7.96		0.91
23	C 1	N 0	South		1.02	0.98	1.06	2.18	1.32	3.05		0.84
31	C 2	N 0	North		1.20	1.17	1.22	3.56	2.95	4.18		0.91
29	C 2	N 0	South		1.10	1.07	1.13	3.80	2.96	4.64		0.86
17	C 3	N 0	North		0.91	0.90	0.93	3.11	2.76	3.46		0.95
19	C 3	N 0	South		0.83	0.80	0.87	20.73	18.40	23.07		0.96
5	C 4	N 0	North		1.20	1.16	1.25	4.87	3.80	5.95		0.79
9	C 4	N 0	South		1.14	1.10	1.19	5.24	4.20	6.29		0.83
27	H 1	N 0	North		0.96	0.87	1.06	13.30	9.13	17.46		0.80
21	H 1	N 0	South		1.49	1.45	1.53	1.61	1.14	2.08		0.85
1	H 2	N 0	North		0.78	0.76	0.80	4.27	3.60	4.94		0.93
3	H 2	N 0	South		1.00	0.90	1.09	13.77	9.26	18.29		0.71
13	H 3	N 0	North		0.69	0.67	0.71	4.63	3.79	5.47		0.93
15	H 3	N 0	South		1.07	0.99	1.15	17.75	14.15	21.35		0.87
7	H 4	N 0	North		1.30	1.24	1.36	5.95	4.52	7.38		0.81
11	H 4	N 0	South		0.95	0.92	0.98	4.77	3.58	5.96		0.87
24	C 1	N 1	South		1.45	1.41	1.50	0.64	0.39	0.89		0.79
32	C 2	N 1	North		1.11	1.07	1.14	5.06	4.19	5.93		0.90
18	C 3	N 1	North		0.74	0.69	0.79	6.21	4.38	8.04		0.77
10	C 4	N 1	South		1.26	1.20	1.32	5.50	4.17	6.84		0.77
22	H 1	N 1	South		1.63	1.49	1.78	3.03	1.17	4.89		0.60
4	H 2	N 1	South		1.20	1.15	1.25	4.55	3.43	5.67		0.87
16	H 3	N 1	South		0.74	0.71	0.76	5.80	4.82	6.79		0.93
8	H 4	N 1	North		1.30	1.26	1.34	3.37	2.65	4.09		0.85
26	C 1	N 2	North		1.33	1.30	1.36	4.17	3.36	4.98		0.88
30	C 2	N 2	South		1.19	1.12	1.26	8.71	6.56	10.86		0.75
20	C 3	N 2	South		1.22	1.18	1.25	2.99	2.37	3.61		0.92
6	C 4	N 2	North		1.19	1.08	1.30	7.72	4.70	10.75		0.56
28	H 1	N 2	North		1.00	0.87	1.13	5.39	1.98	8.81		0.36
2	H 2	N 2	North		1.24	1.18	1.30	7.15	5.53	8.76		0.81
14	H 3	N 2	North		0.79	0.74	0.83	10.03	7.67	12.39		0.79
12	H 4	N 2	South		1.30	1.25	1.35	3.42	2.48	4.35		0.77
				Mean	1.11	1.05	1.16	6.25	4.72	7.79		0.82

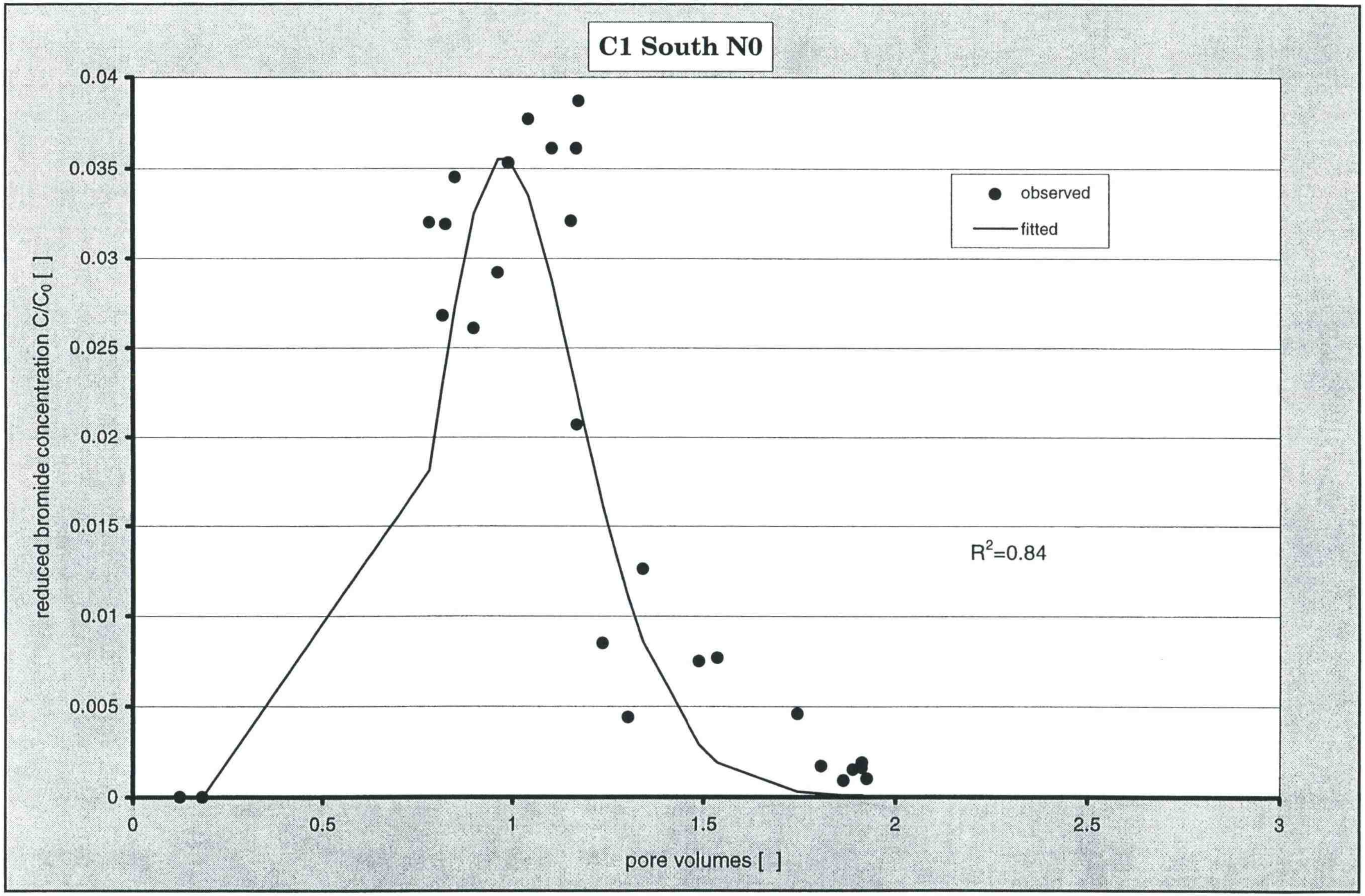
Appendix D

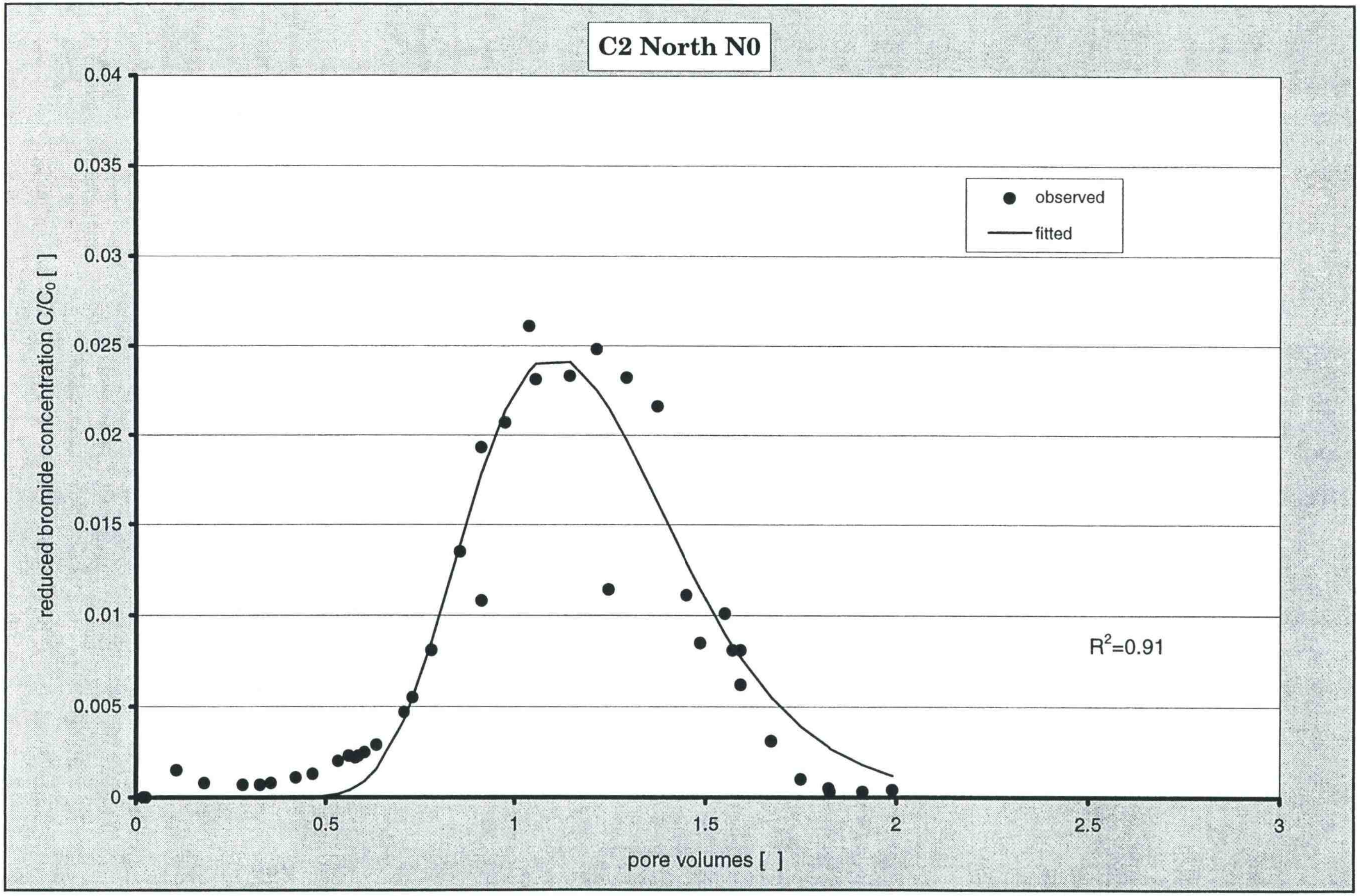
Bromide breakthrough as fitted with CXTFIT for all 32 PCAPS

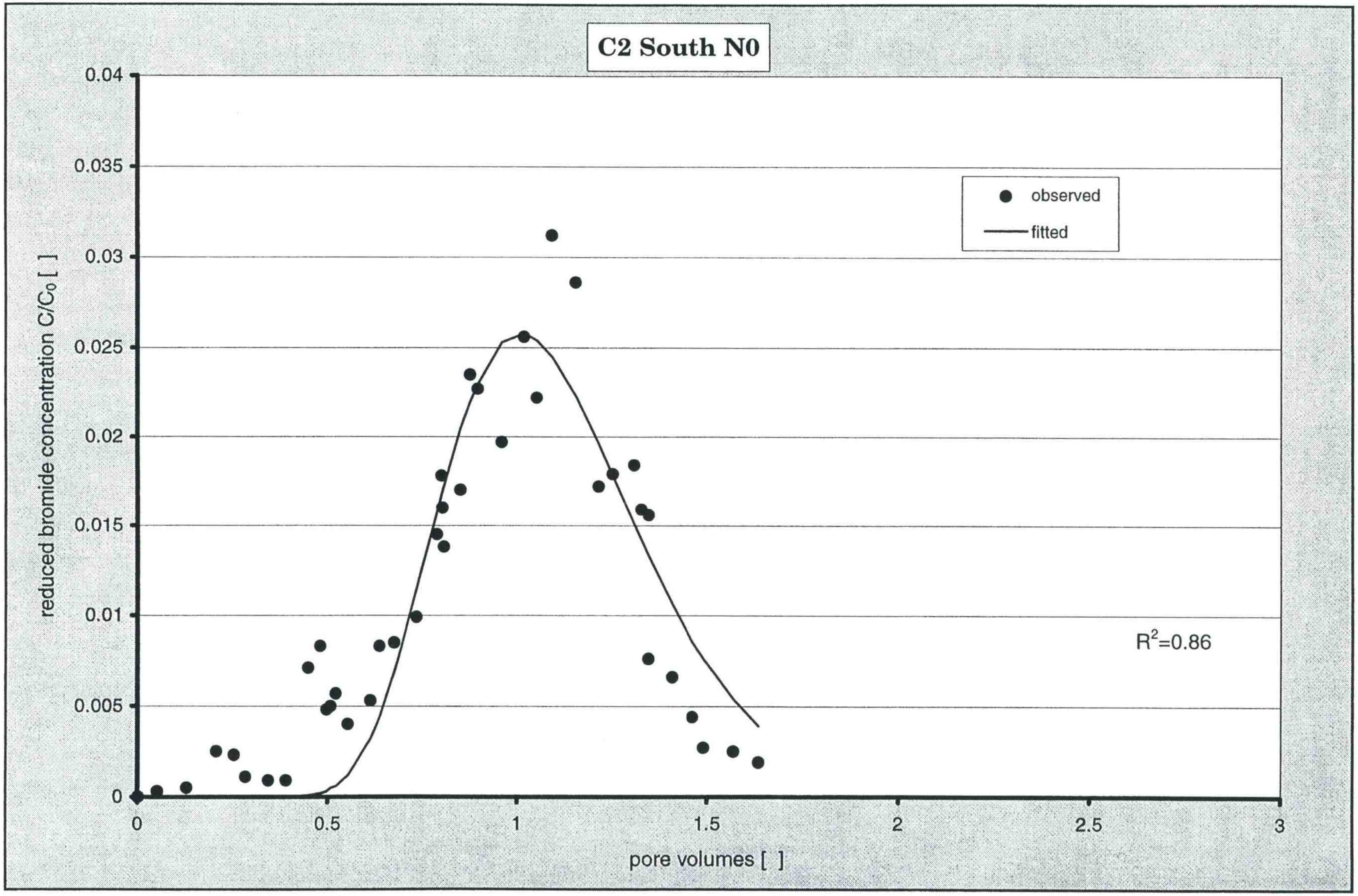
Note

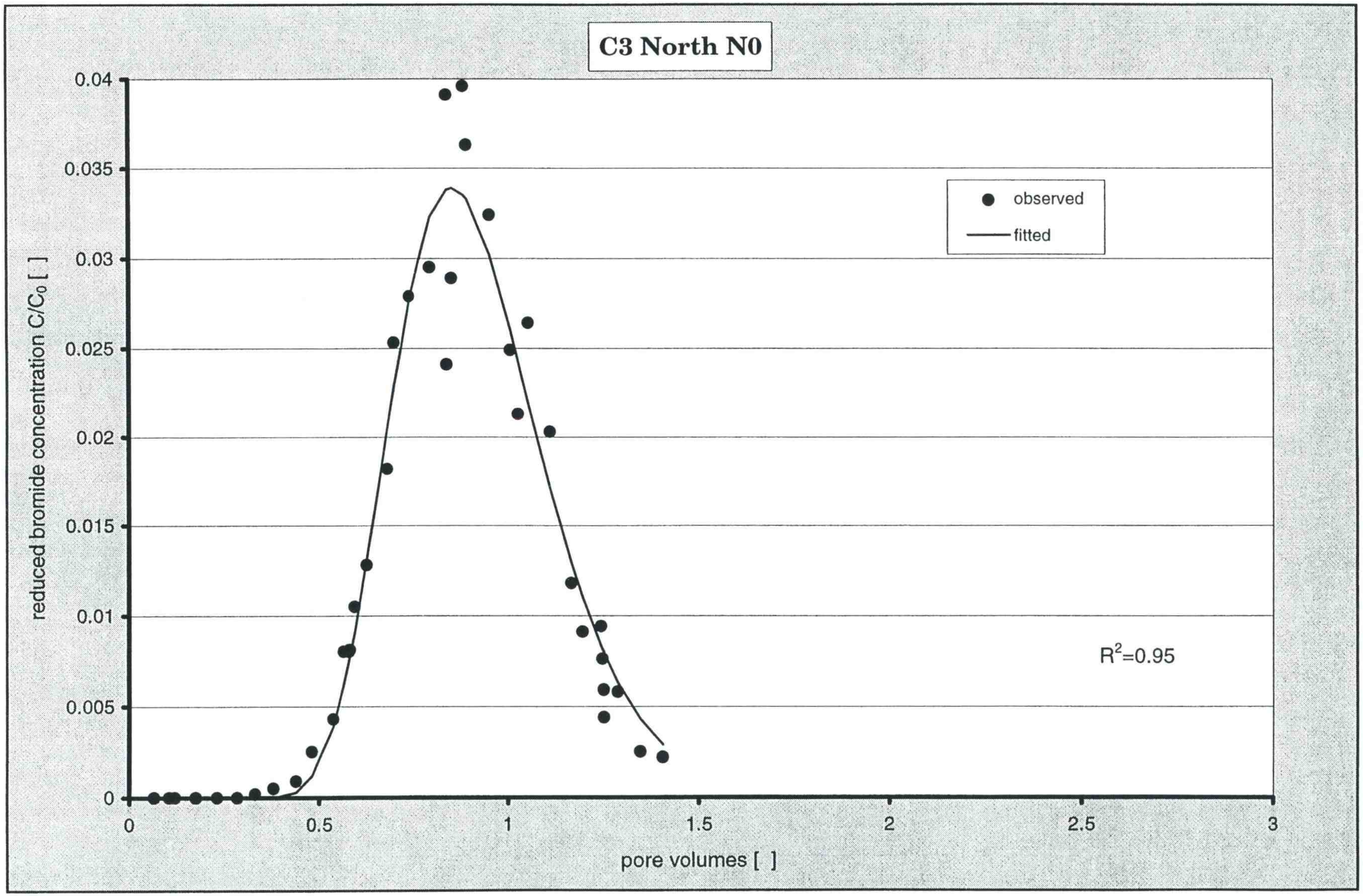
Some of the following 32 bromide breakthrough curves show outliers lowering the accuracy of the fit. We attribute some of the occurrence of outliers to the temporal variability in leaching (e.g., halting flow). Further research will be required to reveal the physical basis for deviations from the convection-dispersion equation.

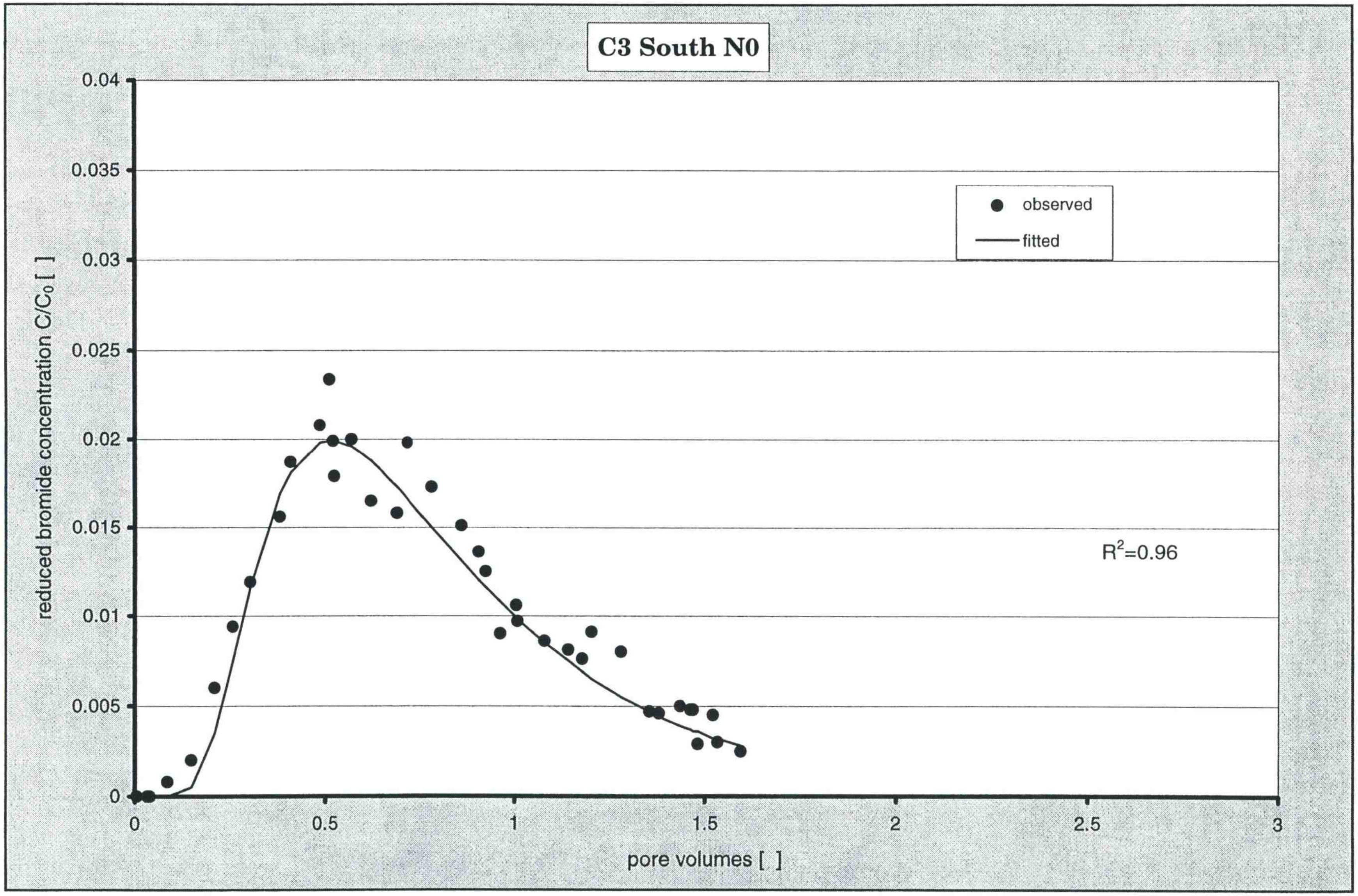

C1 North N0
reduced bromide concentration C/C$_0$ [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
observed
fitted
R^2=0.91

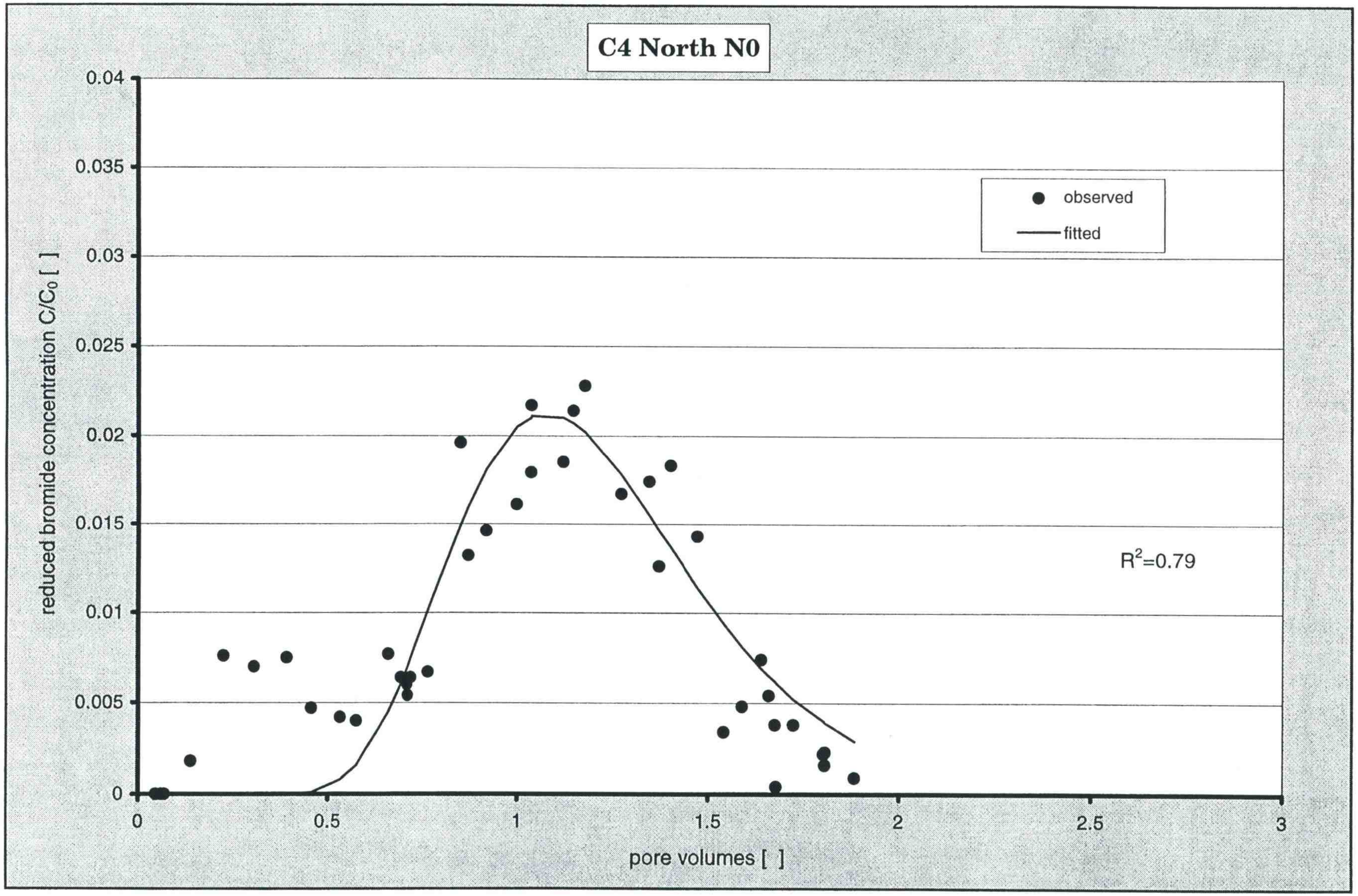

C1 South N0
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
reduced bromide concentration C/C₀ [ ]
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
observed
fitted
R²=0.84

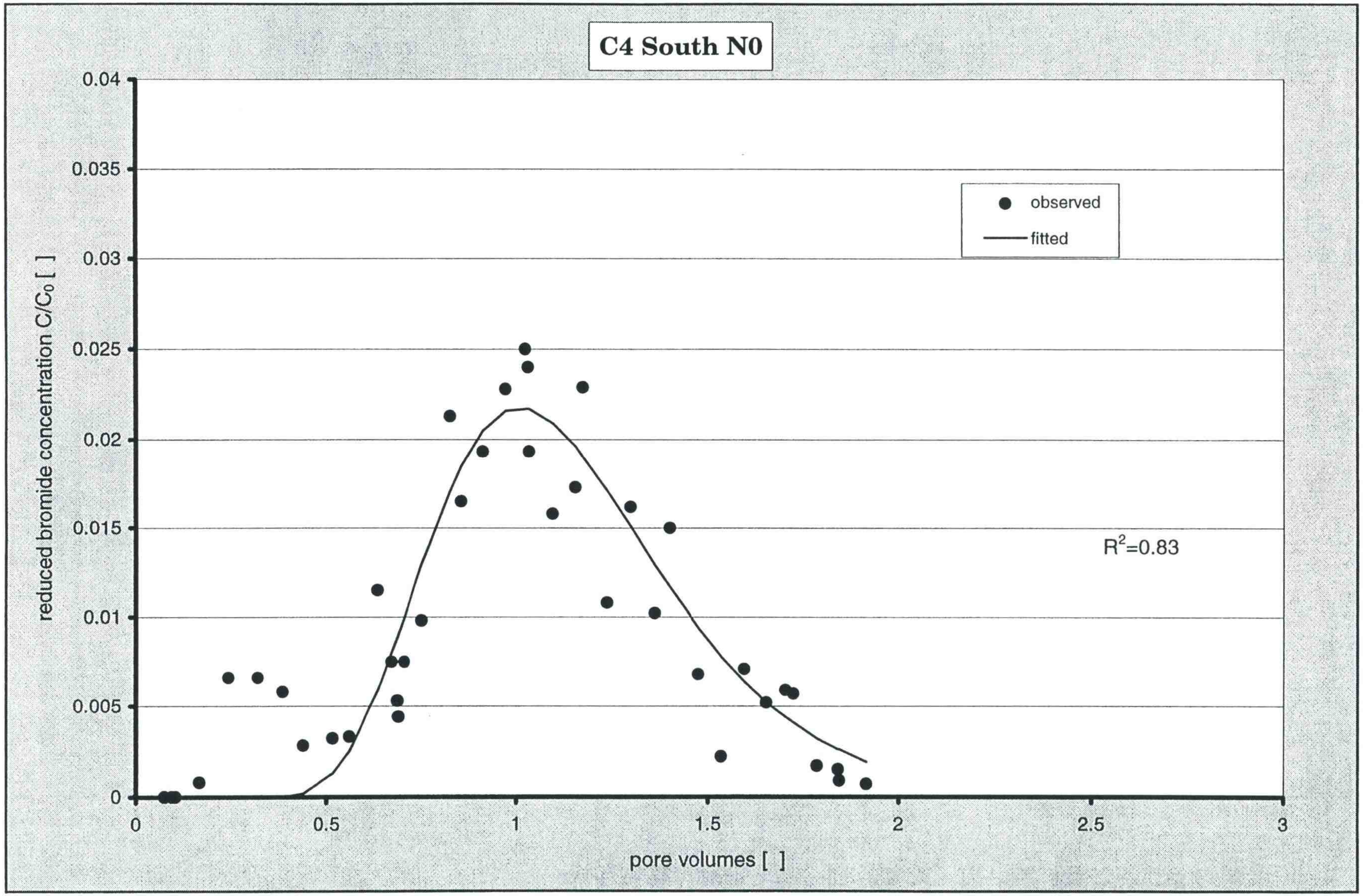

C2 North N0
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
reduced bromide concentration C/C_0 [ ]
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
R^2=0.91

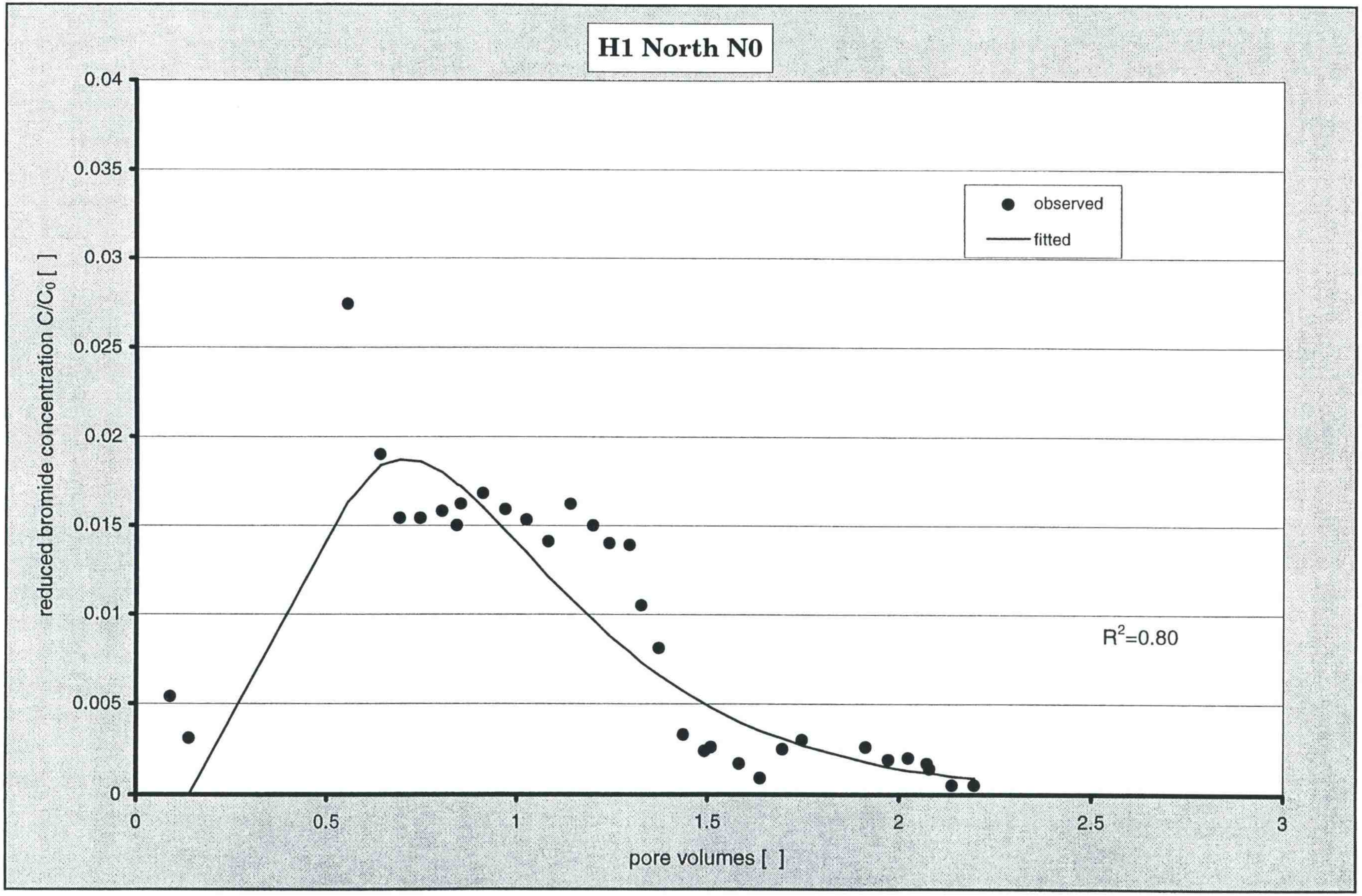

C2 South N0
reduced bromide concentration C/C_0 [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
R^2=0.86

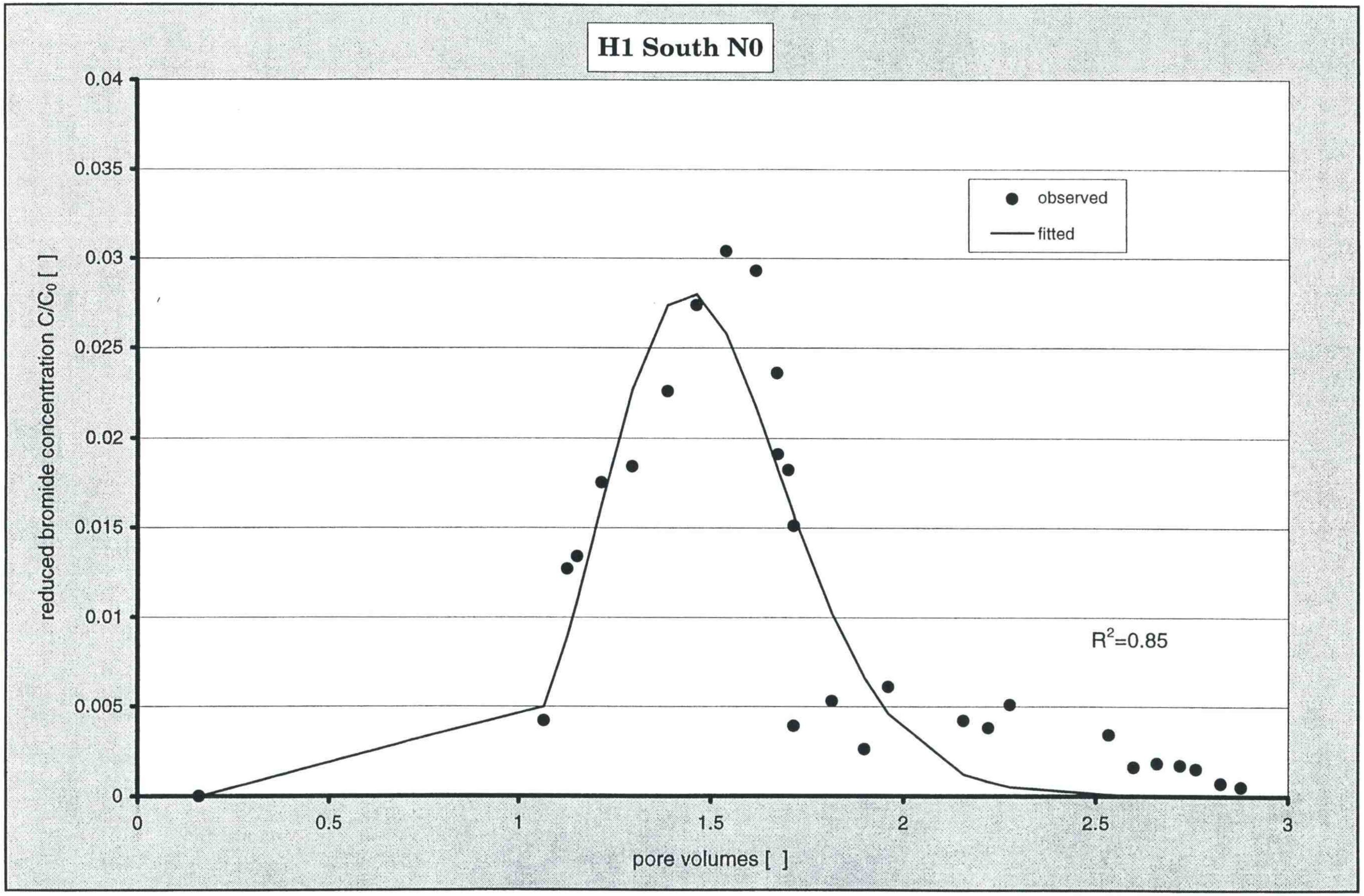

C3 North N0
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
reduced bromide concentration C/C_0 [ ]
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
$R^2=0.95$

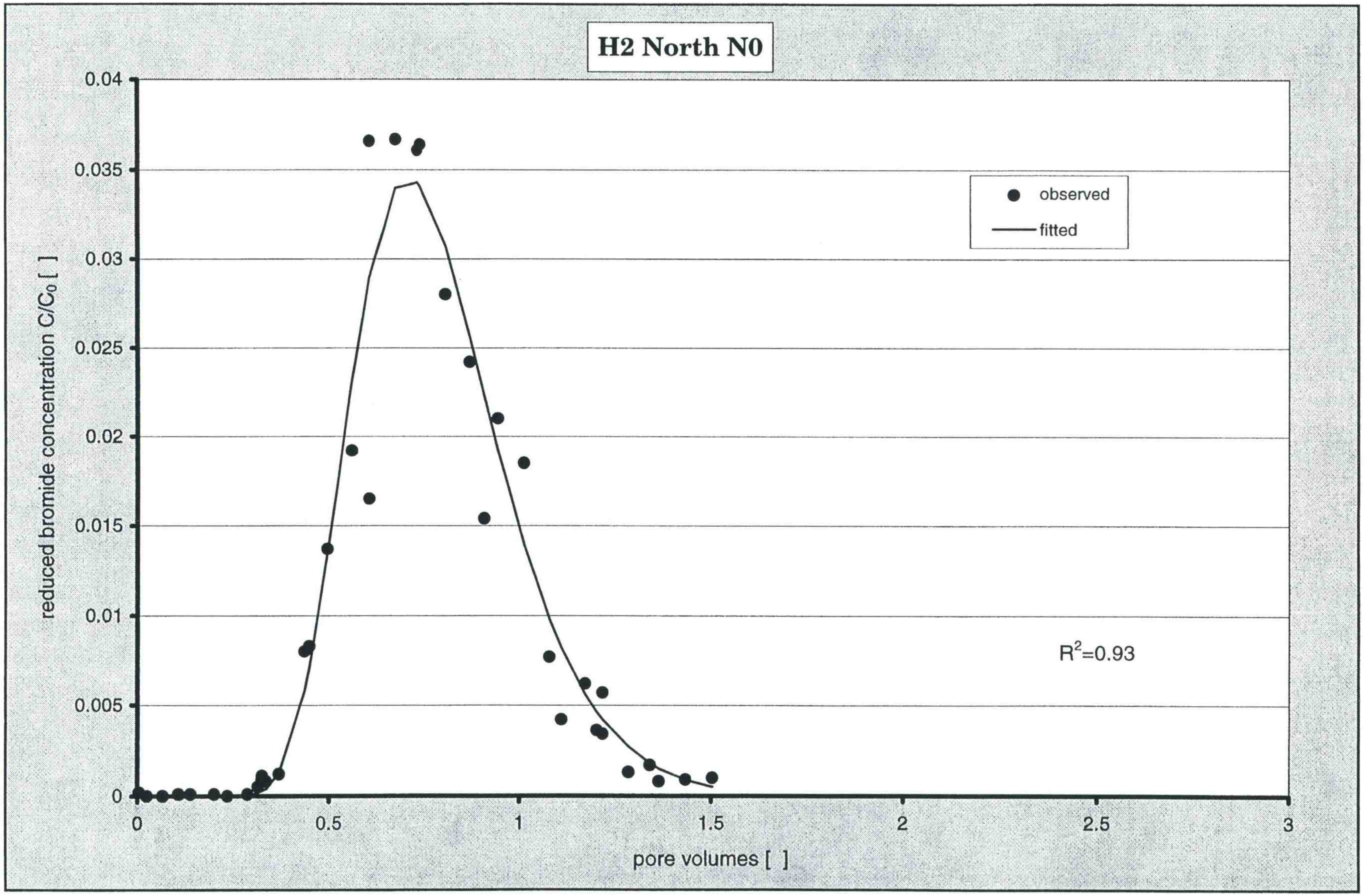

C3 South N0
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
reduced bromide concentration C/C₀ [ ]
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
R²=0.96

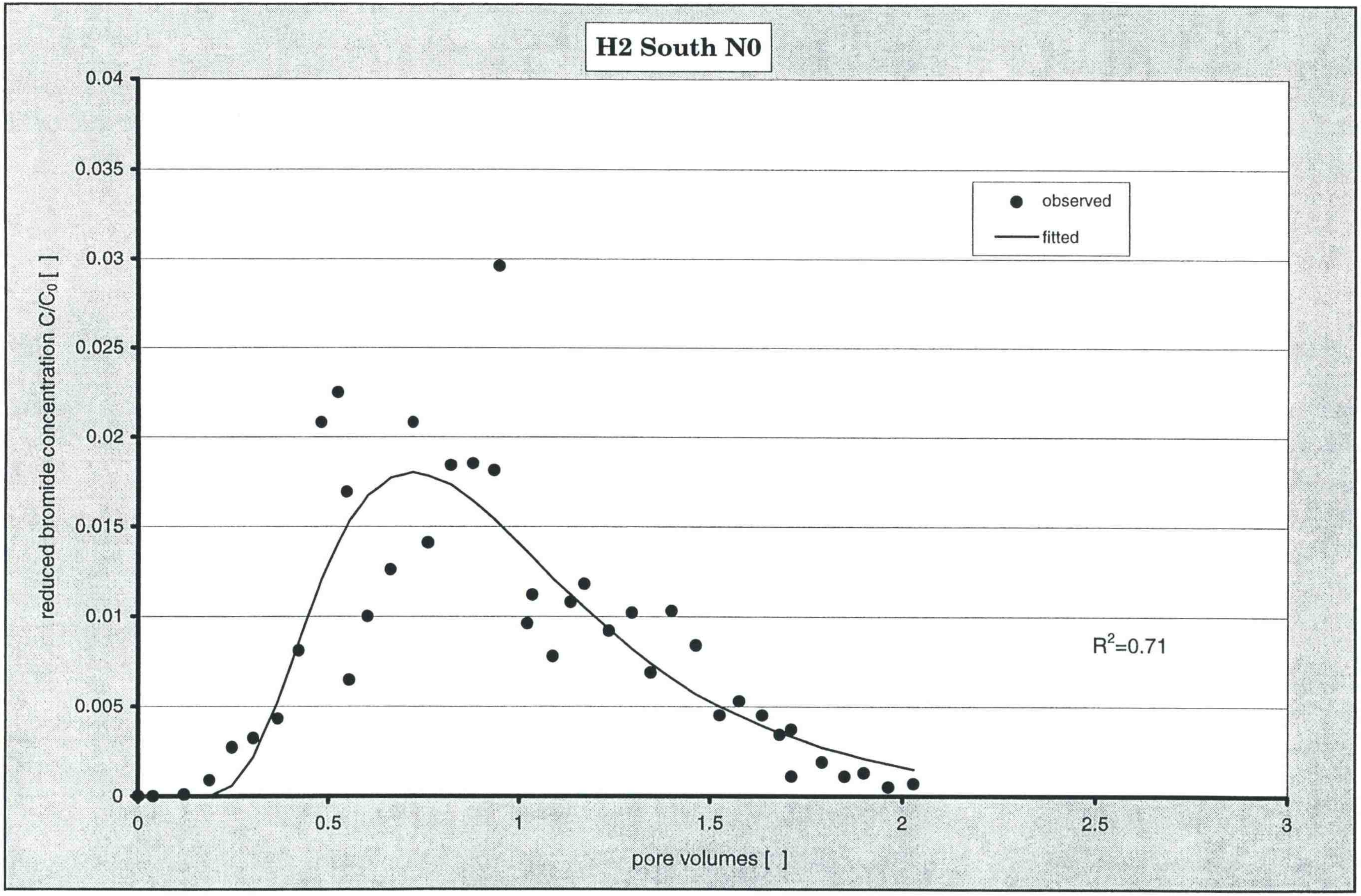

C4 North N0
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
reduced bromide concentration C/C_0 [ ]
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
R^2=0.79

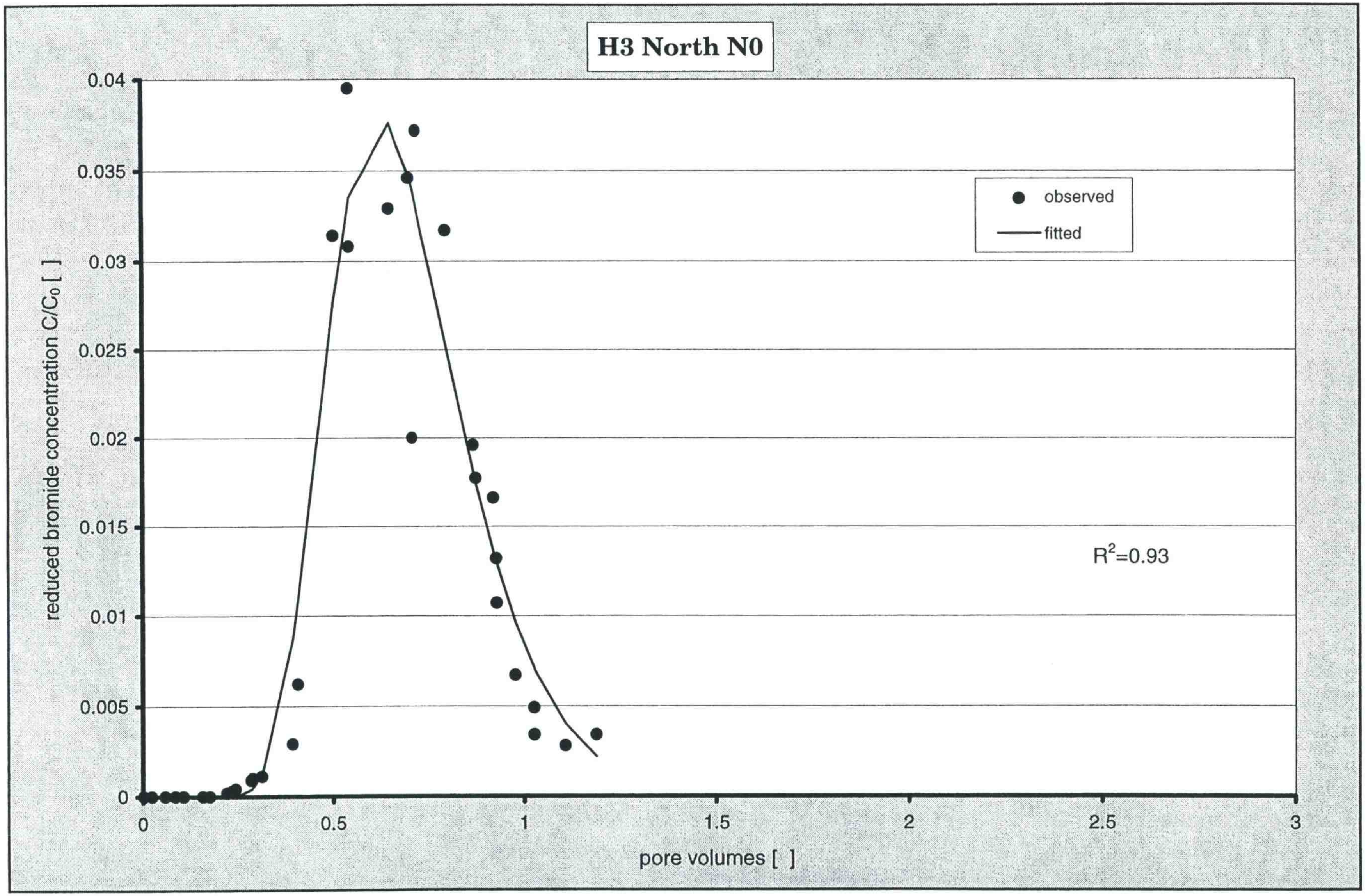

C4 South N0
reduced bromide concentration C/C_0 [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
R^2=0.83

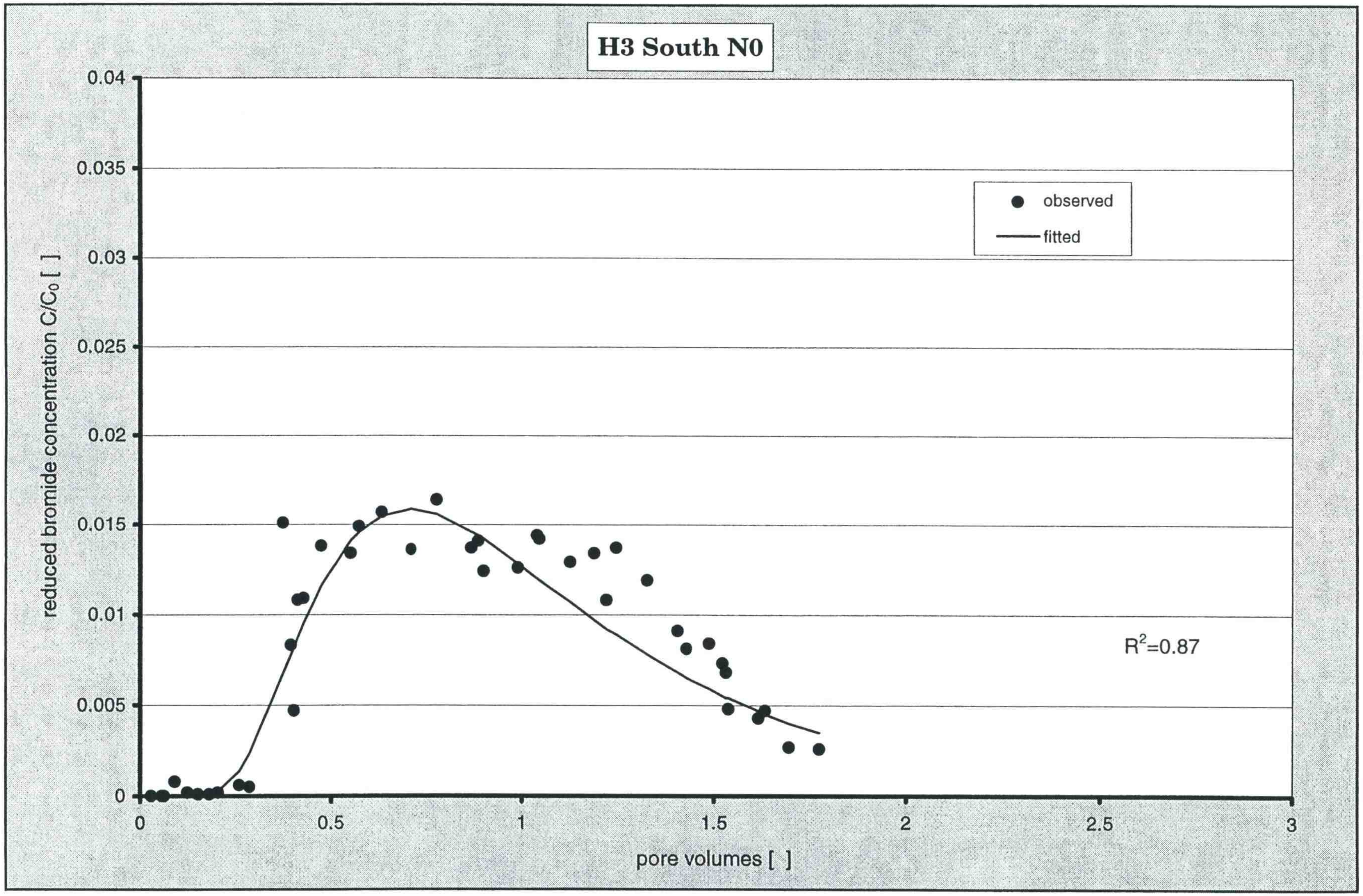

H1 North N0
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
reduced bromide concentration C/C0 [ ]
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
—— fitted
R2=0.80

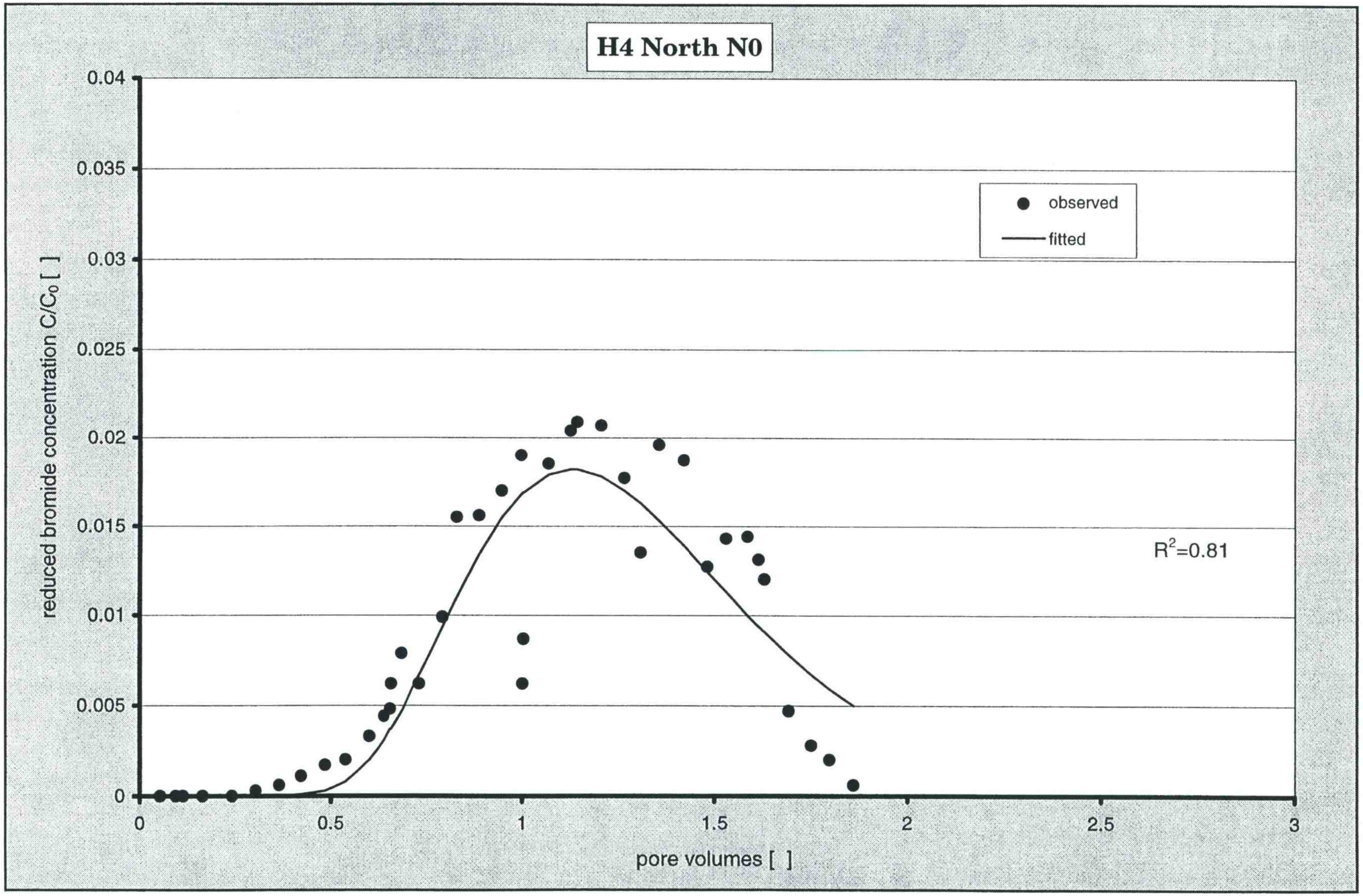

H1 South N0
reduced bromide concentration C/C₀ [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
R²=0.85

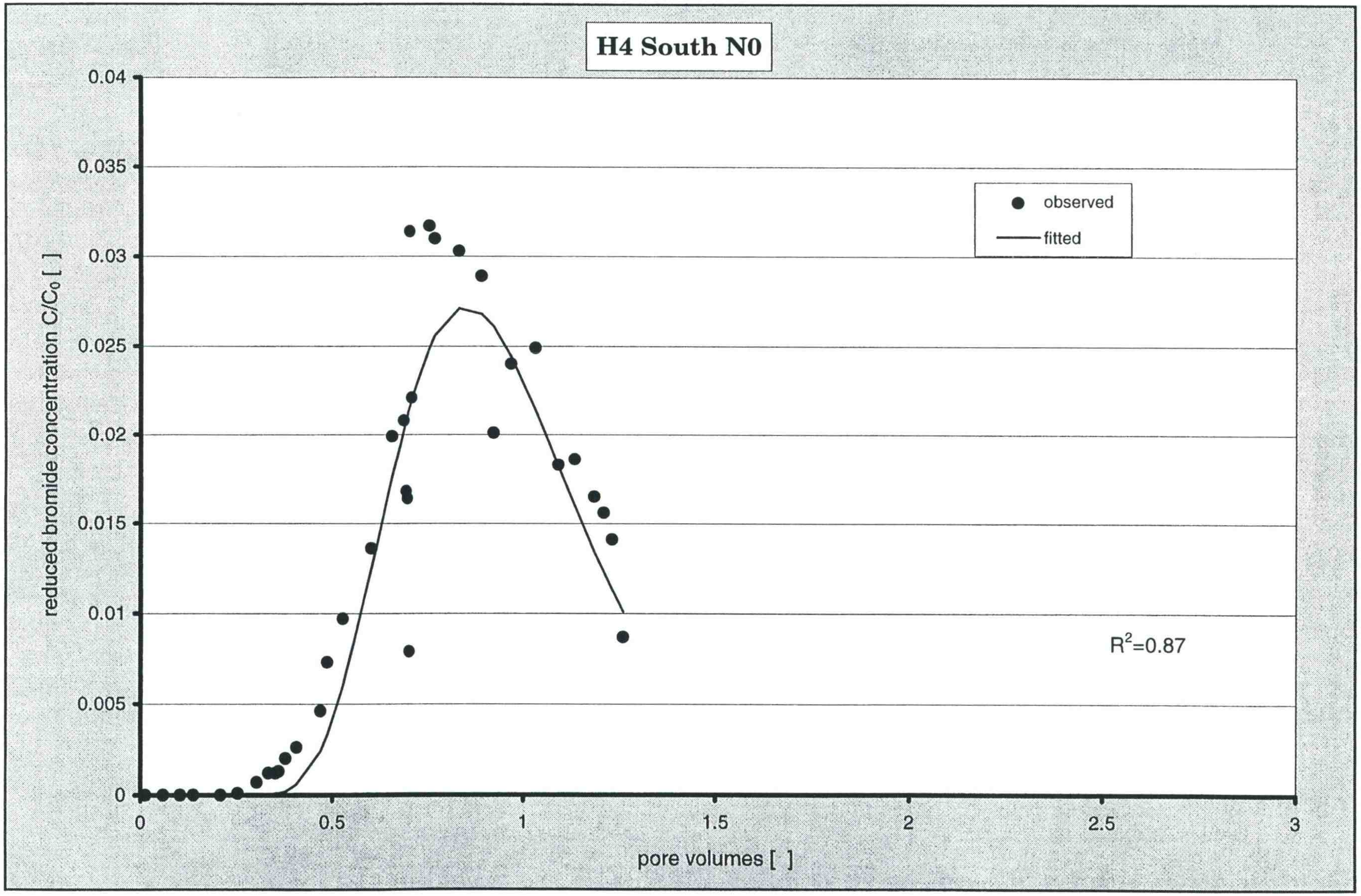

H2 North N0
reduced bromide concentration C/C₀ [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
R²=0.93

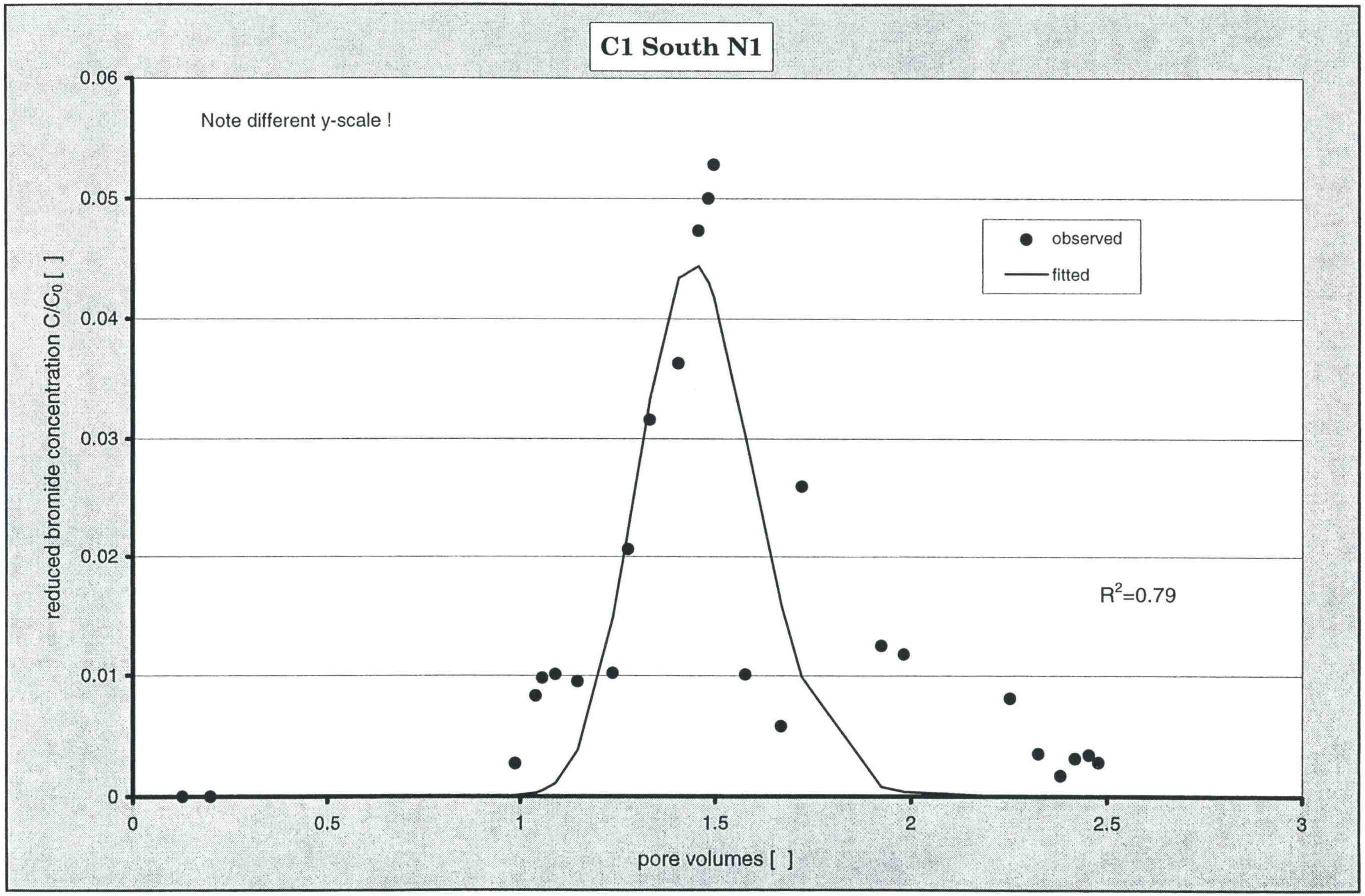

H2 South N0
reduced bromide concentration C/C$_0$ [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
observed
fitted
R^2=0.71

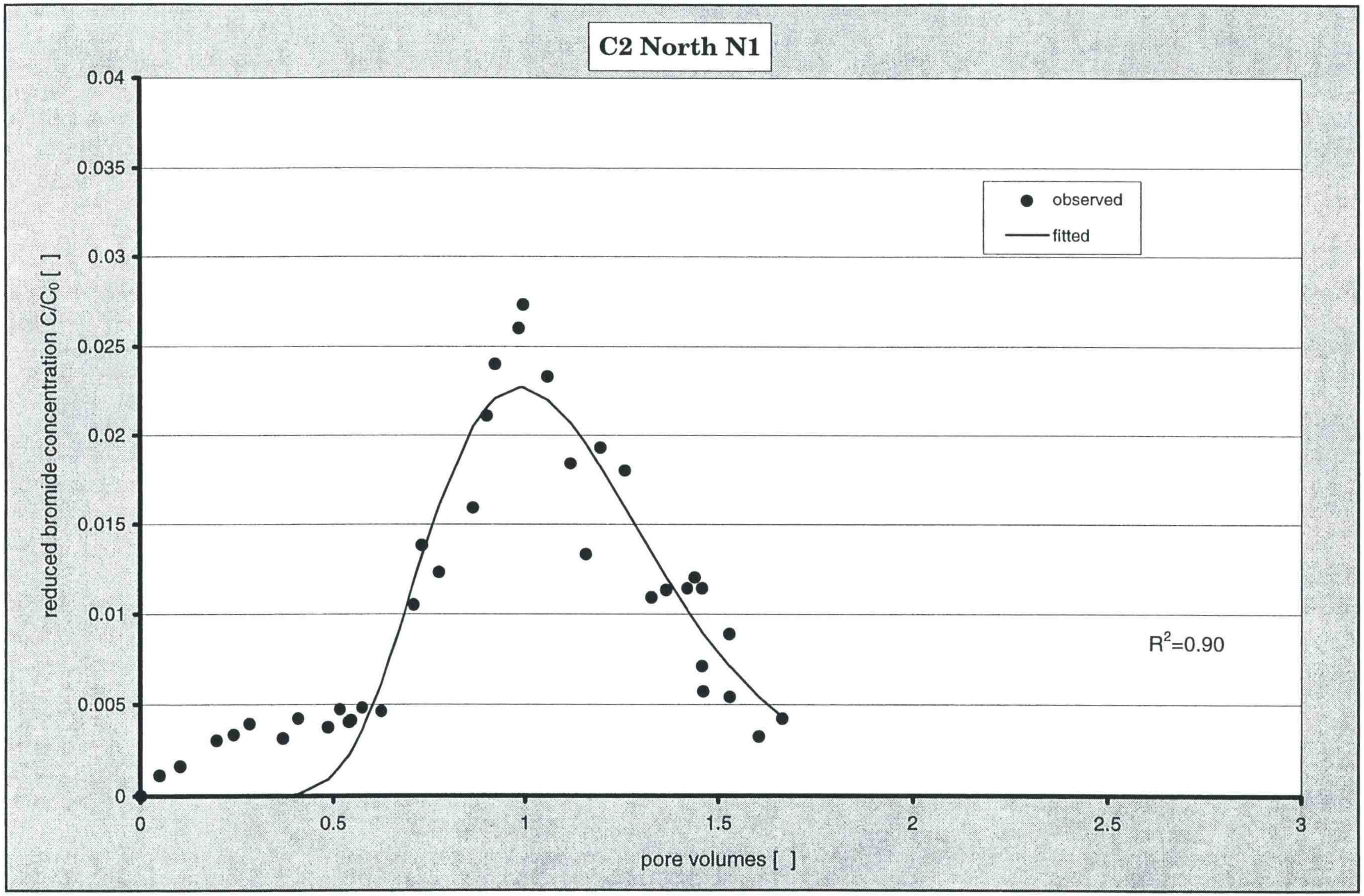

H3 North N0
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
reduced bromide concentration C/C₀ [ ]
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
—— fitted
R²=0.93

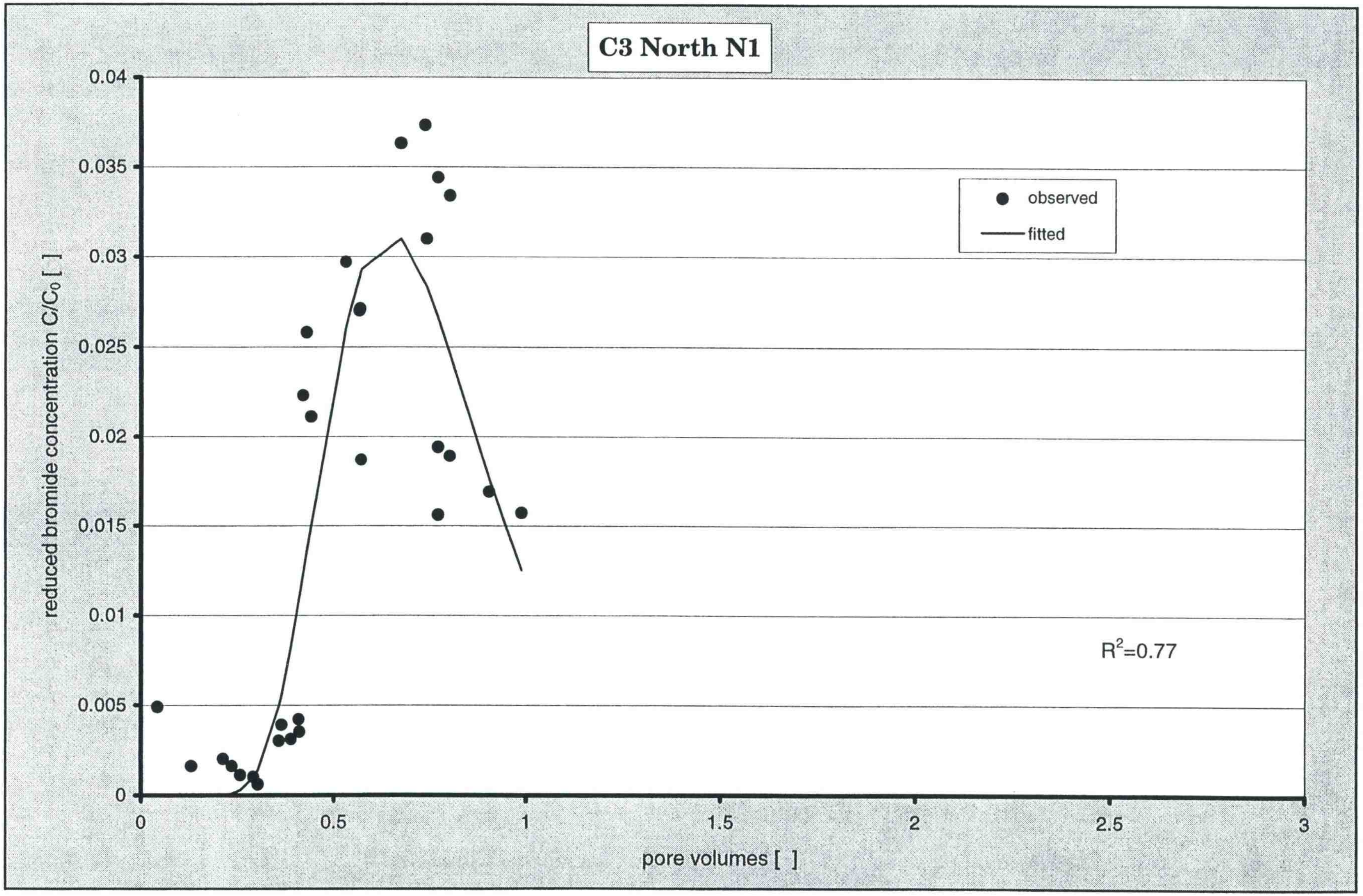

H3 South N0
reduced bromide concentration C/C0 [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
observed
fitted
R2=0.87

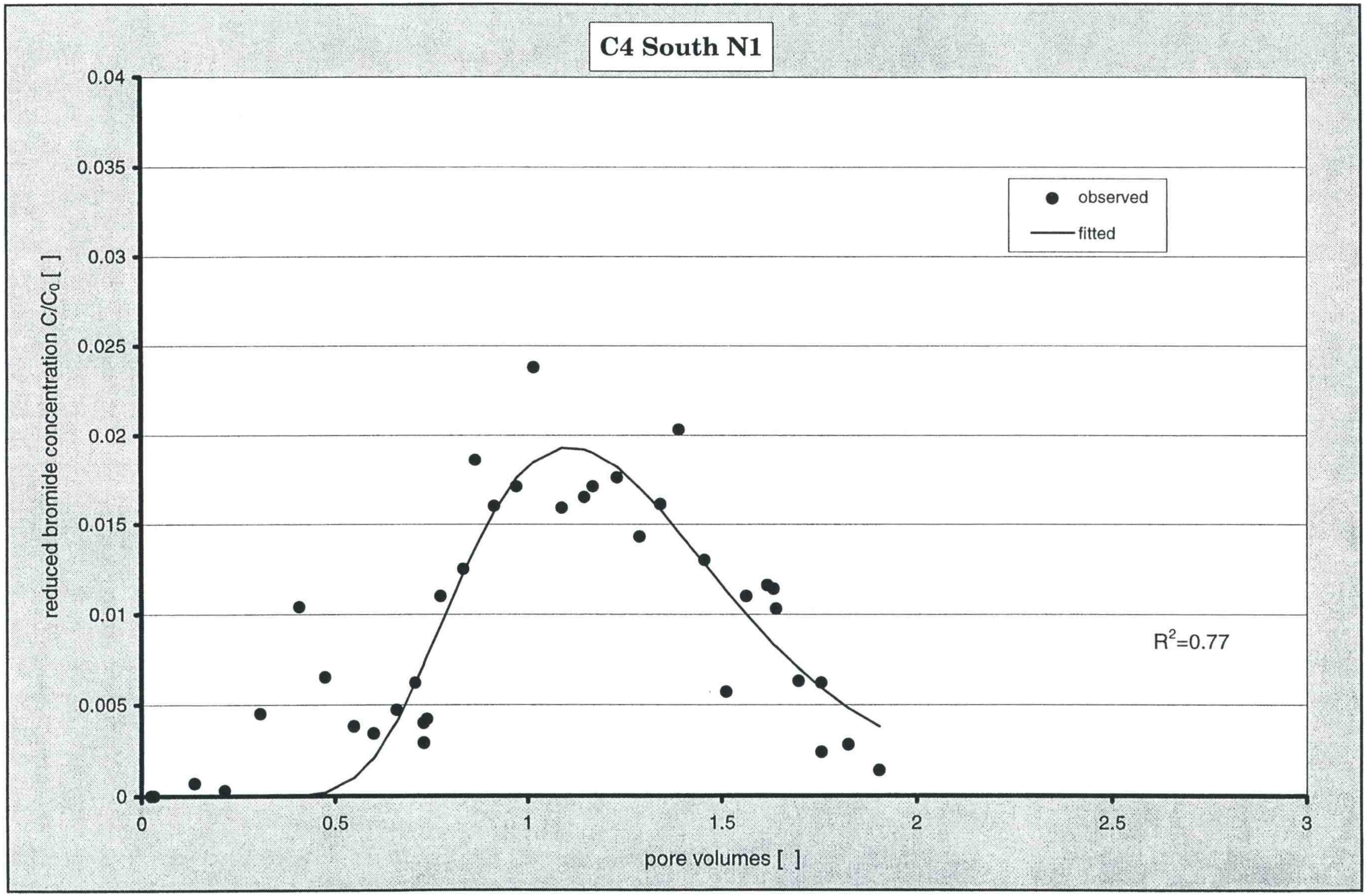

H4 North N0
observed
fitted
R²=0.81
reduced bromide concentration C/C₀ [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]

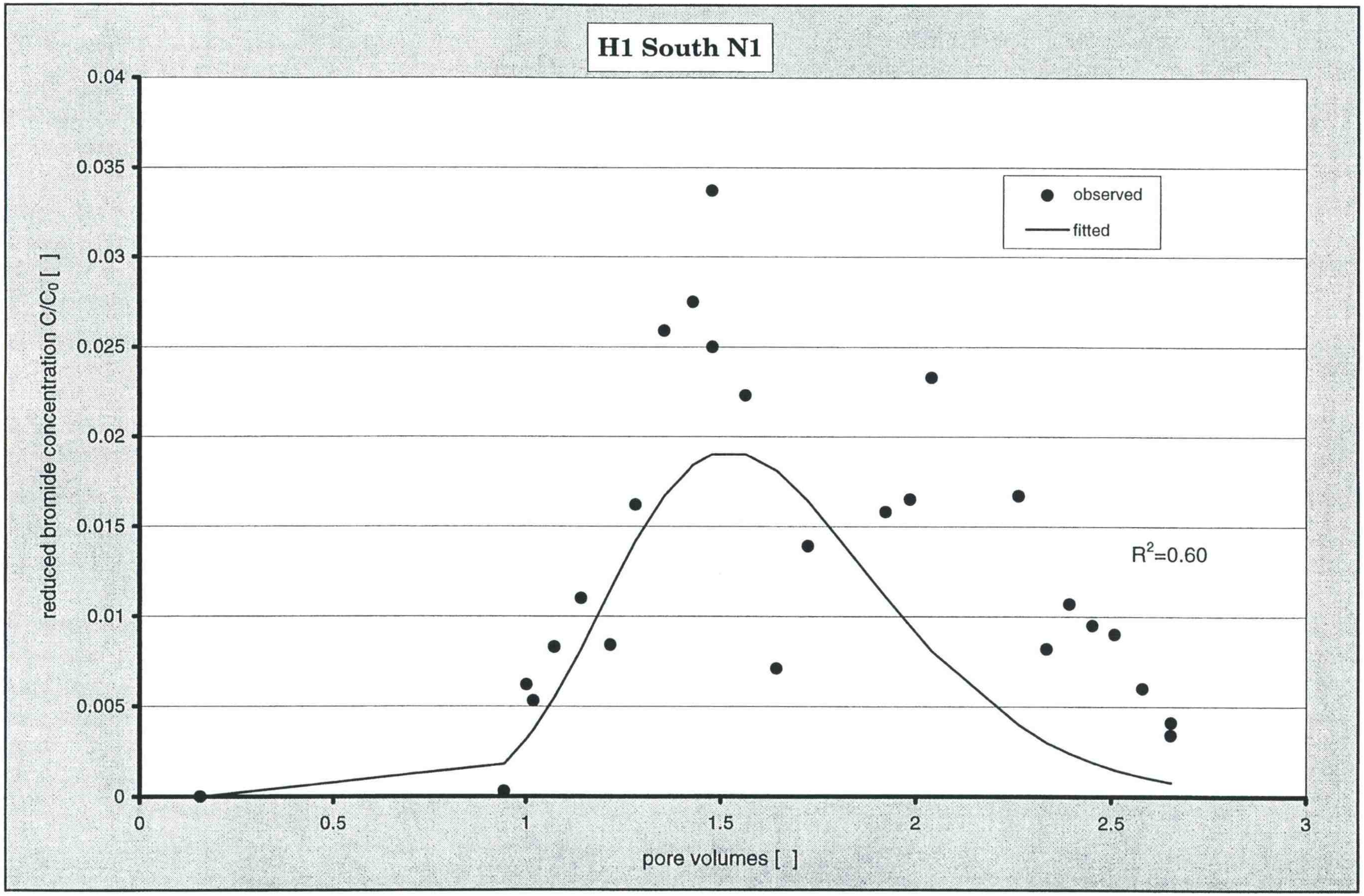

H4 South N0
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
reduced bromide concentration C/C0 [ ]
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
R2=0.87

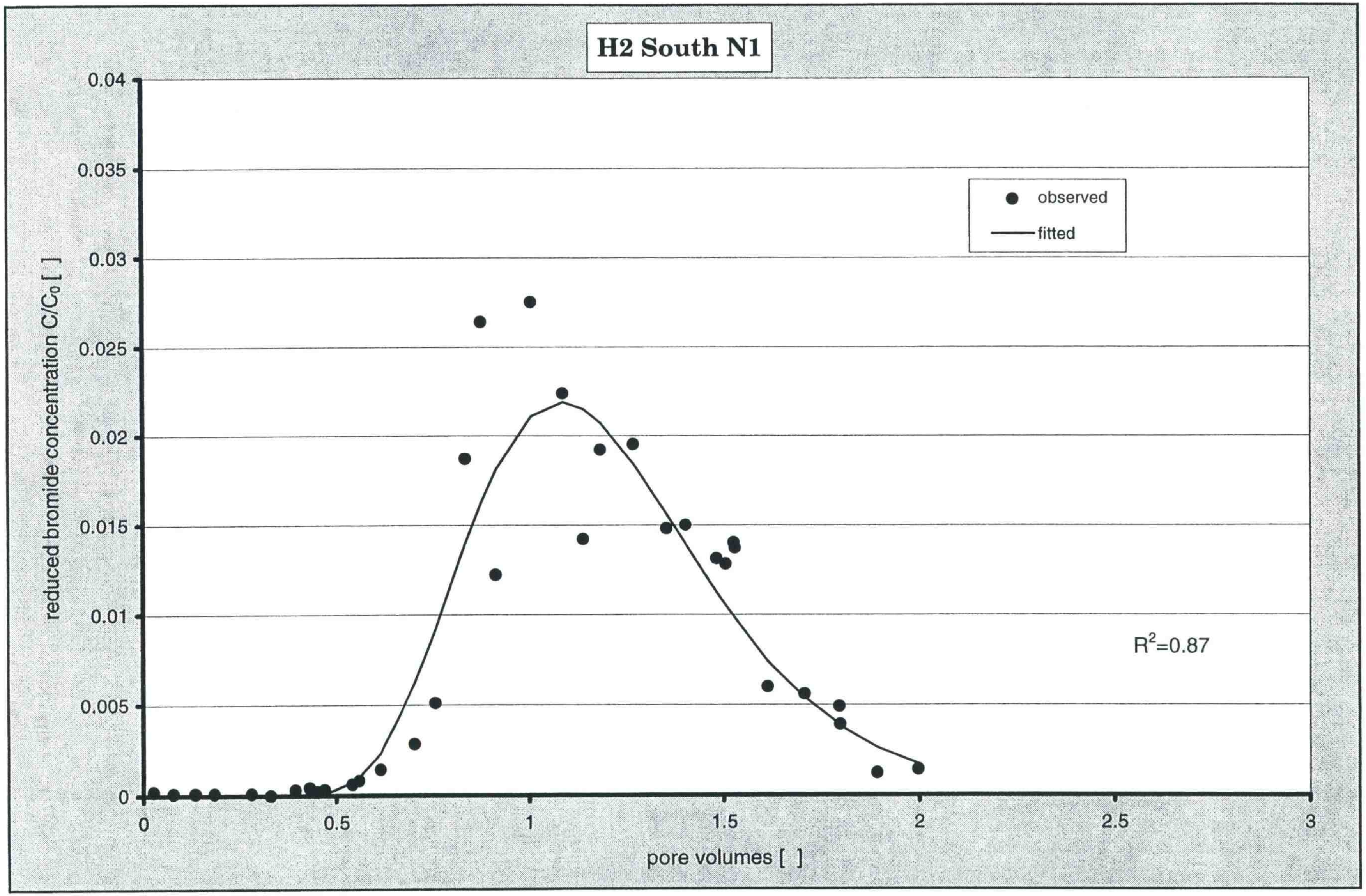

C1 South N1
Note different y-scale !
observed
fitted
R^2=0.79
reduced bromide concentration C/C$_0$ [ ]
0.06
0.05
0.04
0.03
0.02
0.01
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]

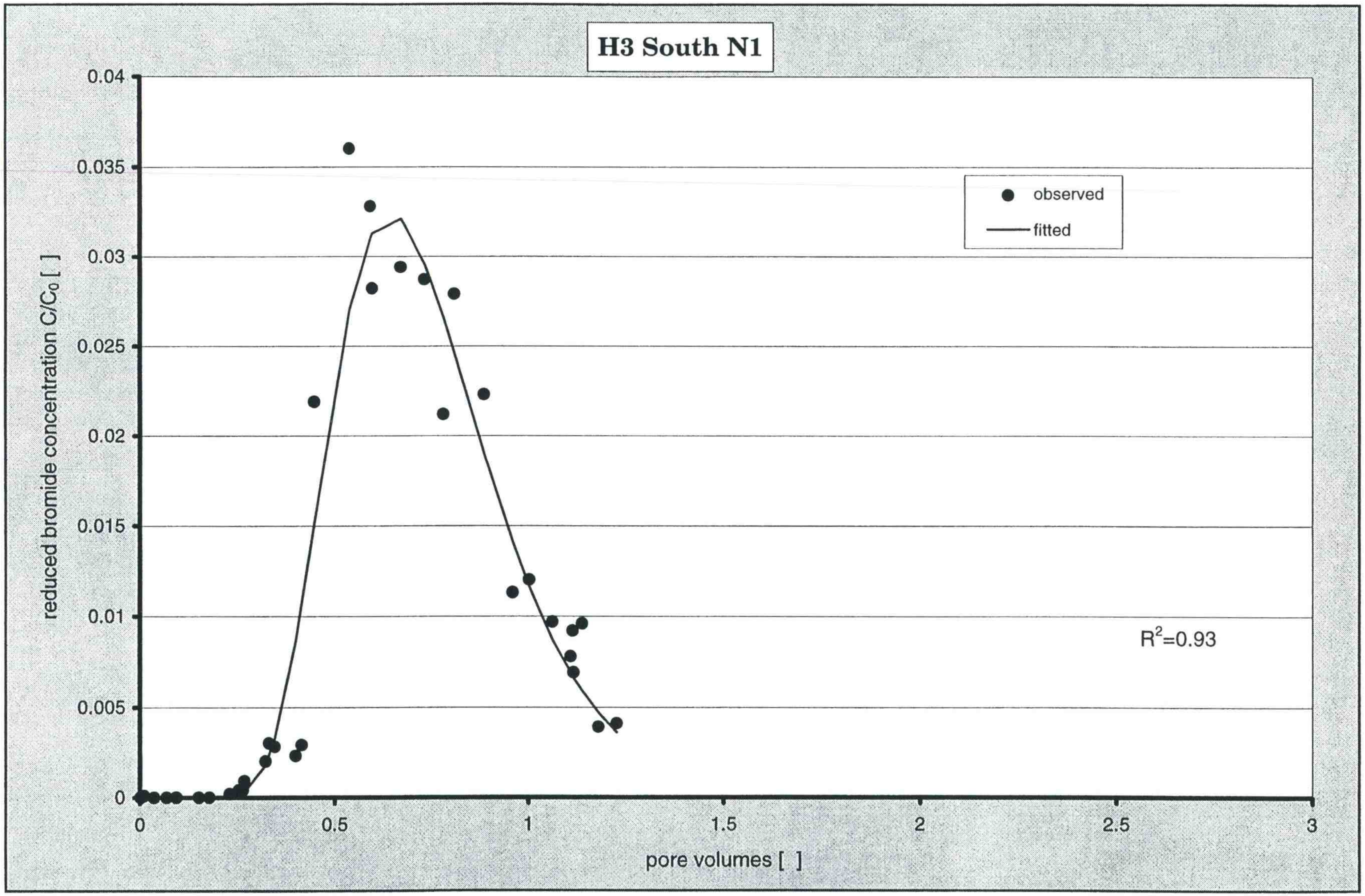

C2 North N1
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
reduced bromide concentration C/C_0 [ ]
● observed
fitted
R^2=0.90
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]

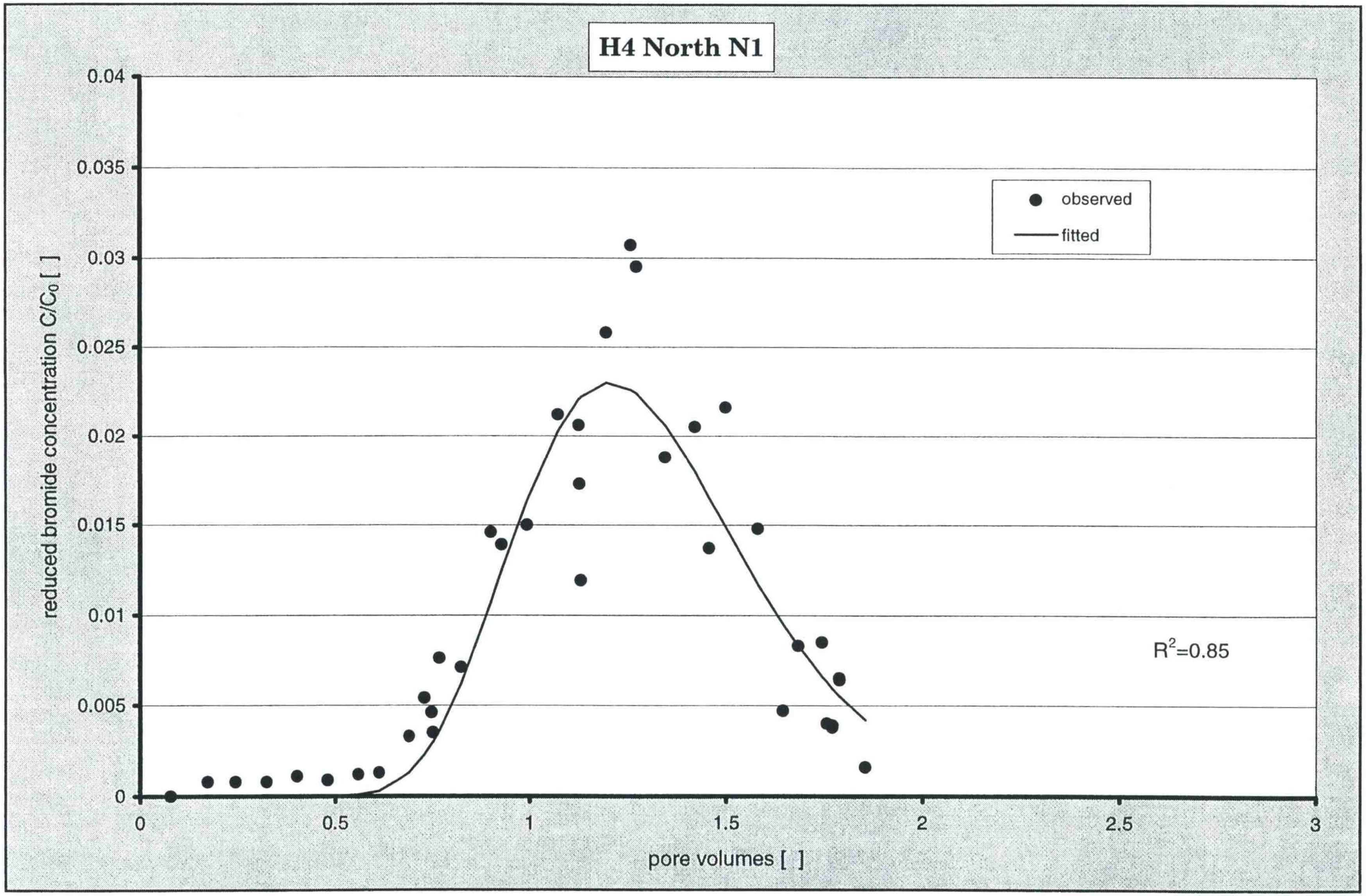

C3 North N1
reduced bromide concentration C/C₀ [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
pore volumes [ ]
0
0.5
1
1.5
2
2.5
3
● observed
fitted
R²=0.77

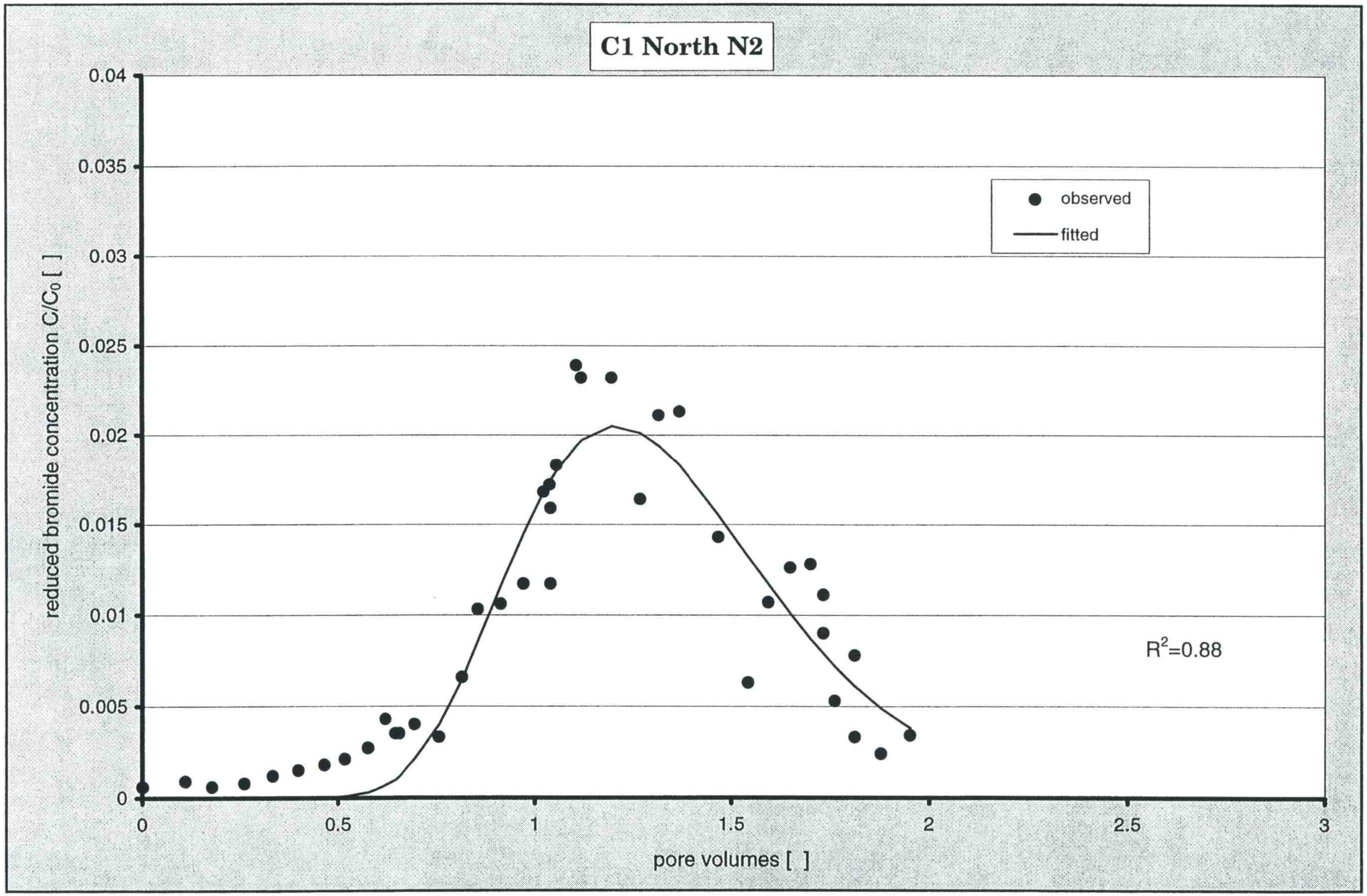

C4 South N1
reduced bromide concentration C/C0 [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
R2=0.77

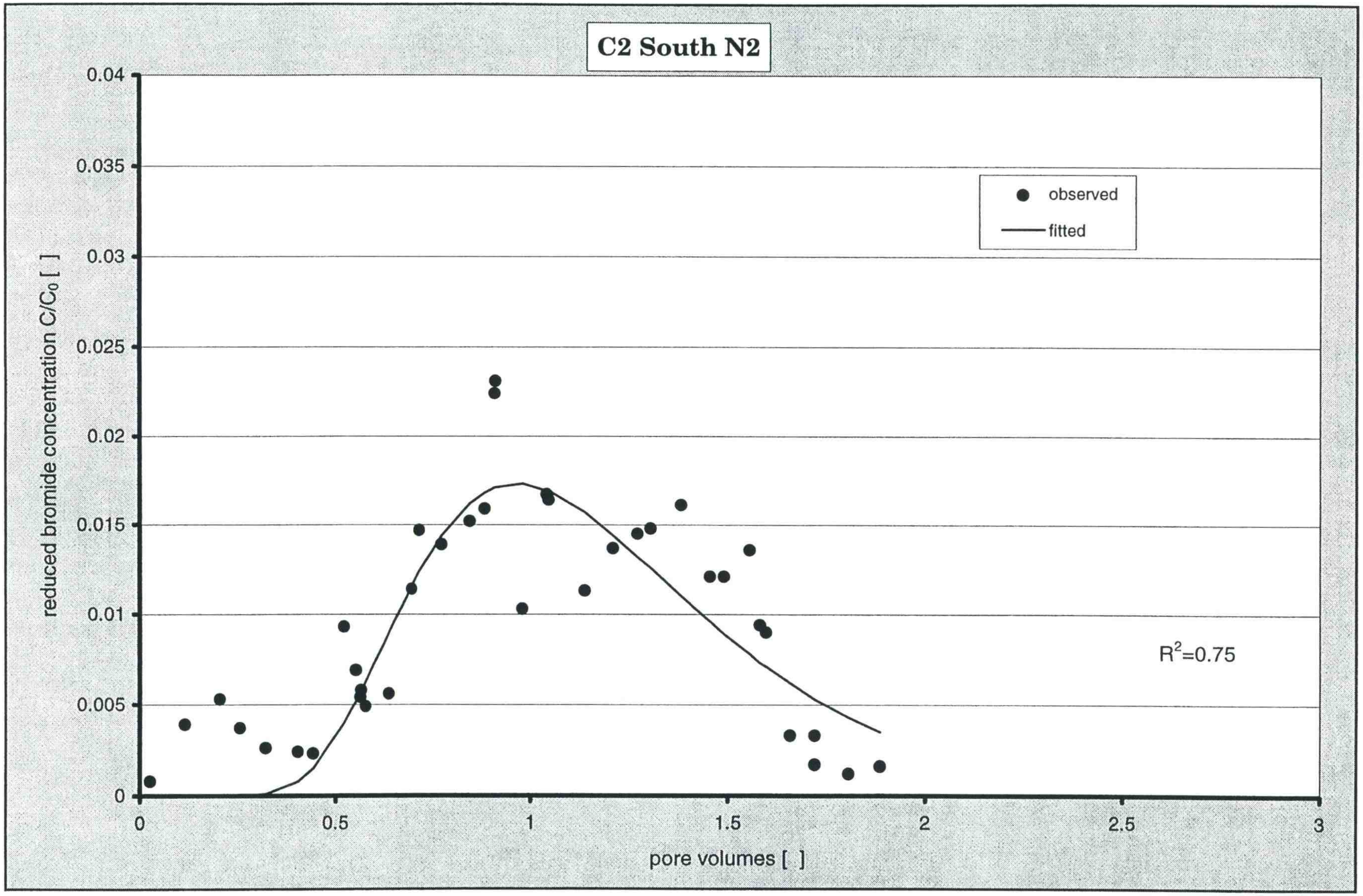

H1 South N1
observed
fitted
R²=0.60
reduced bromide concentration C/C0 [ ]
0
0.005
0.01
0.015
0.02
0.025
0.03
0.035
0.04
pore volumes [ ]
0
0.5
1
1.5
2
2.5
3

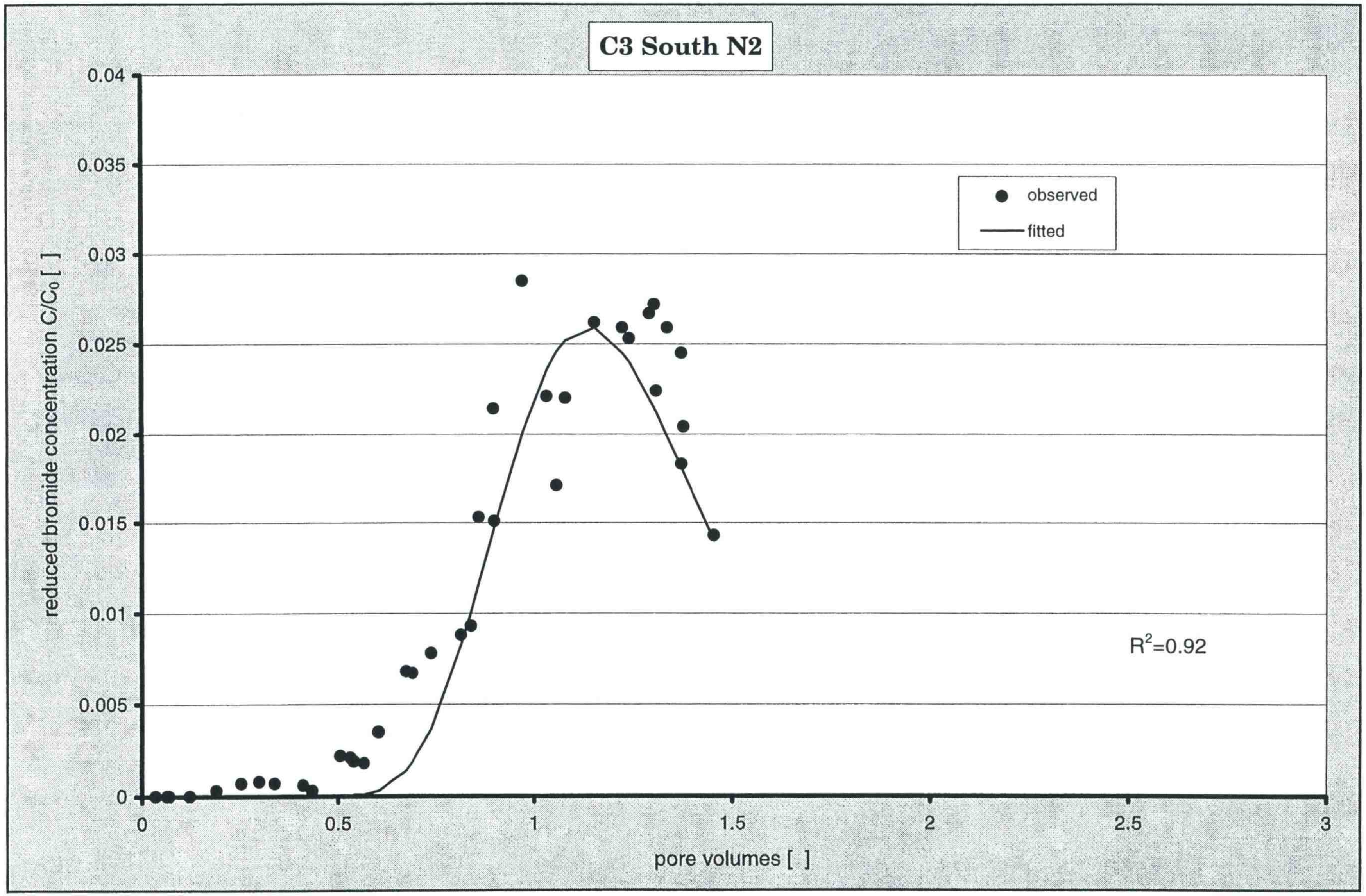

H2 South N1
reduced bromide concentration C/C_0 [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
R^2=0.87

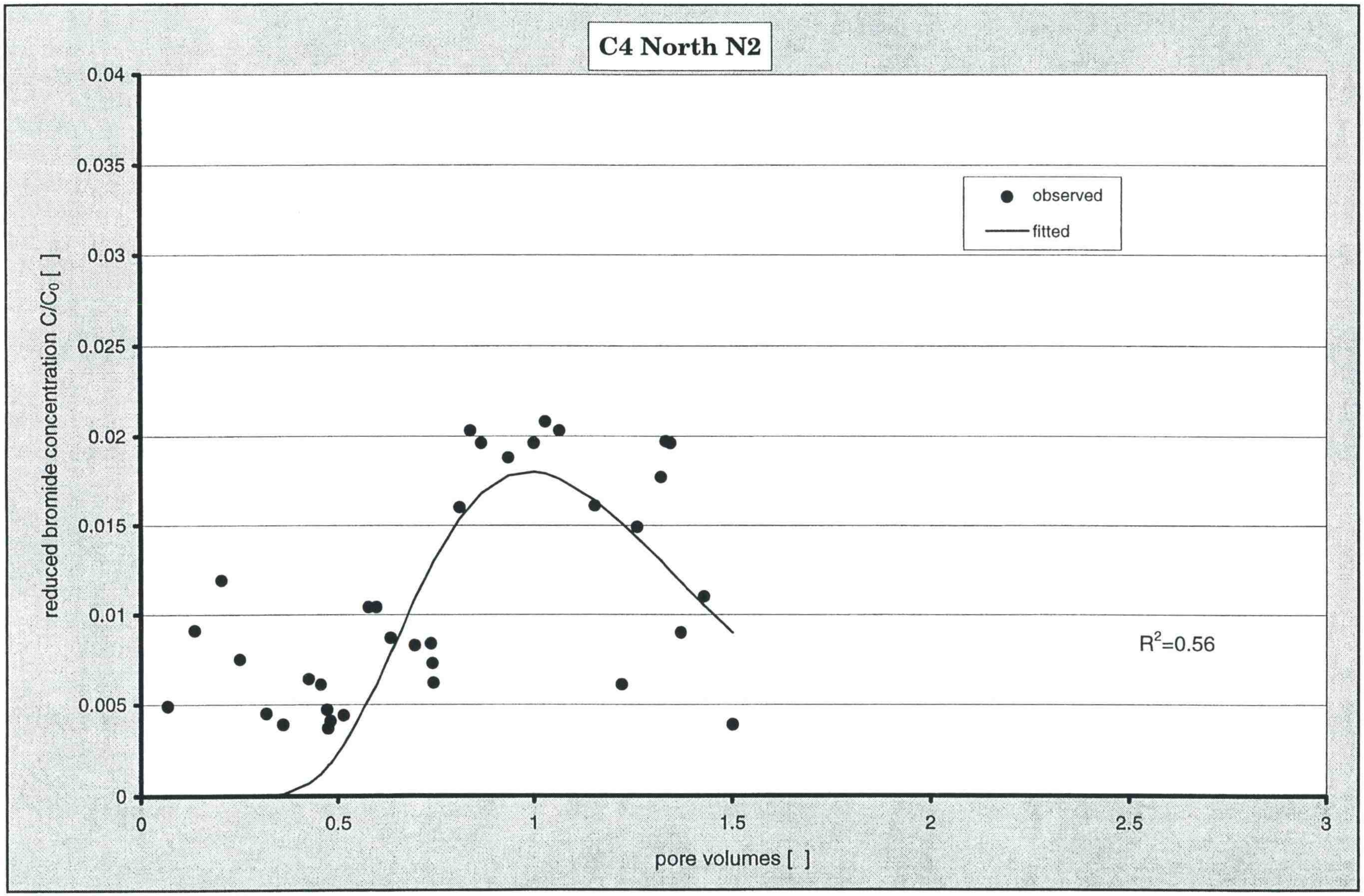

H3 South N1
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
reduced bromide concentration C/C_0 [ ]
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
R^2=0.93

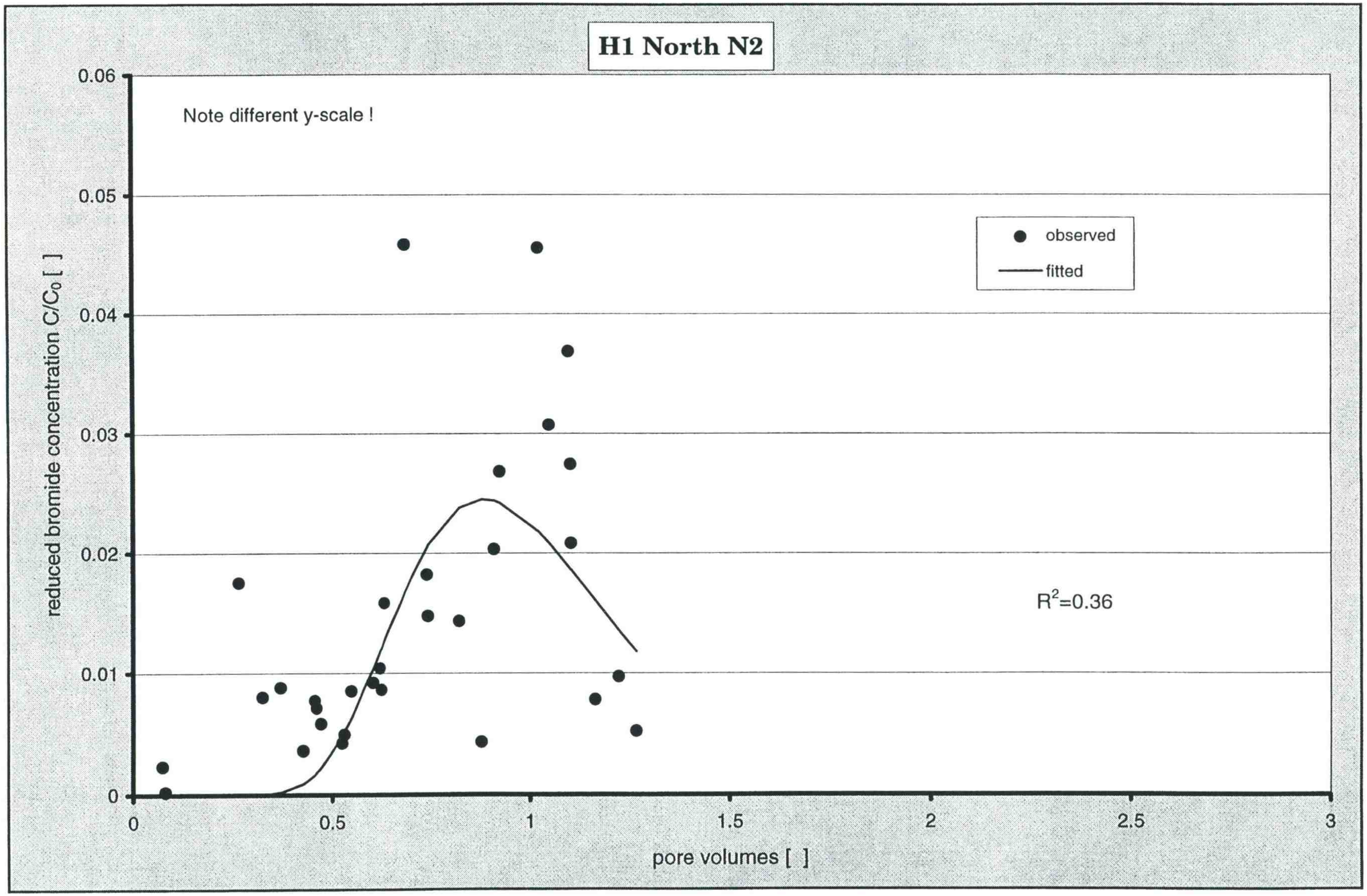

H4 North N1
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
reduced bromide concentration C/C0 [ ]
observed
fitted
R²=0.85
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]

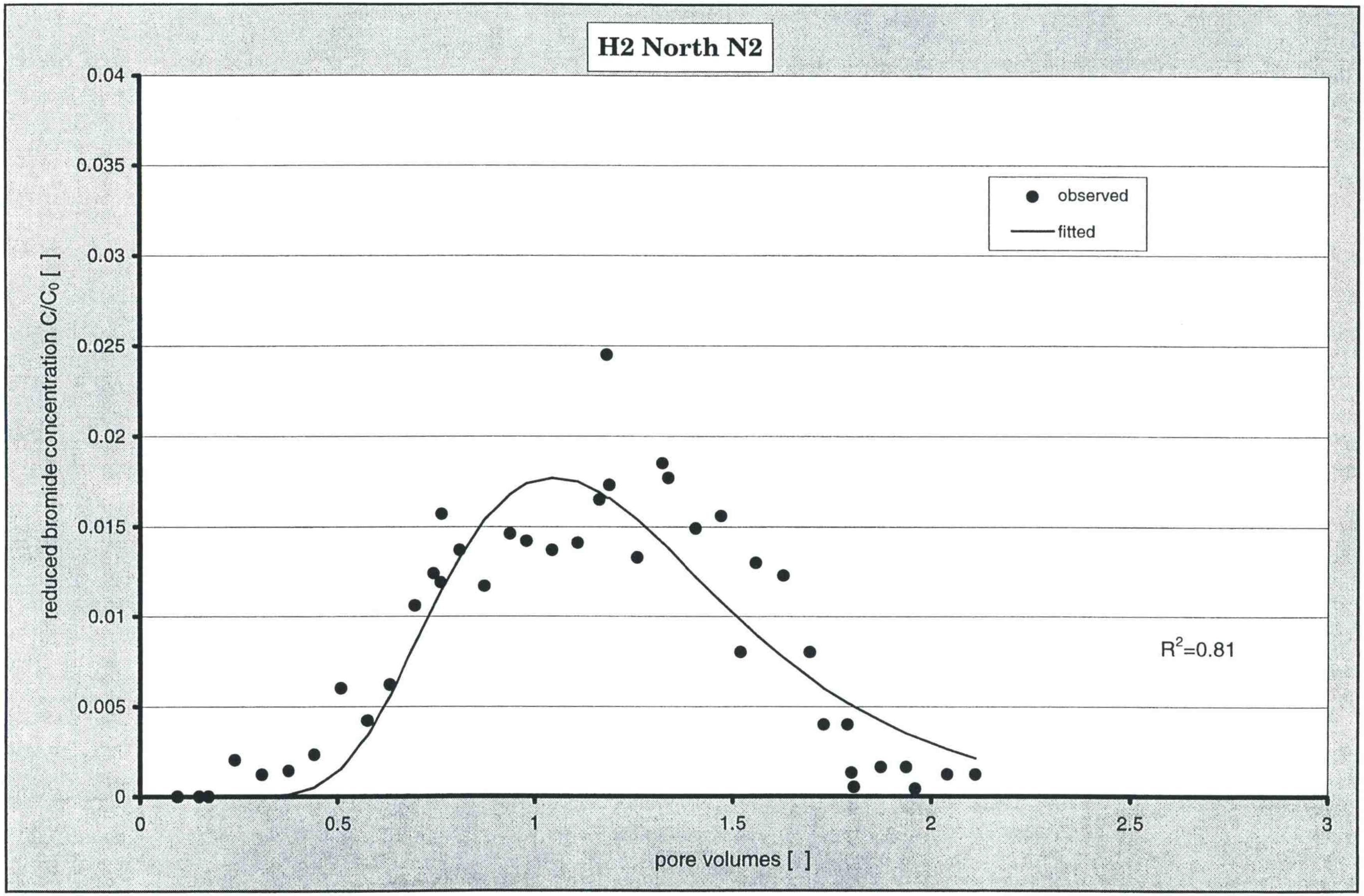

C1 North N2
observed
fitted
R^2=0.88
reduced bromide concentration C/C0 [ ]
pore volumes [ ]
0
0.005
0.01
0.015
0.02
0.025
0.03
0.035
0.04
0
0.5
1
1.5
2
2.5
3

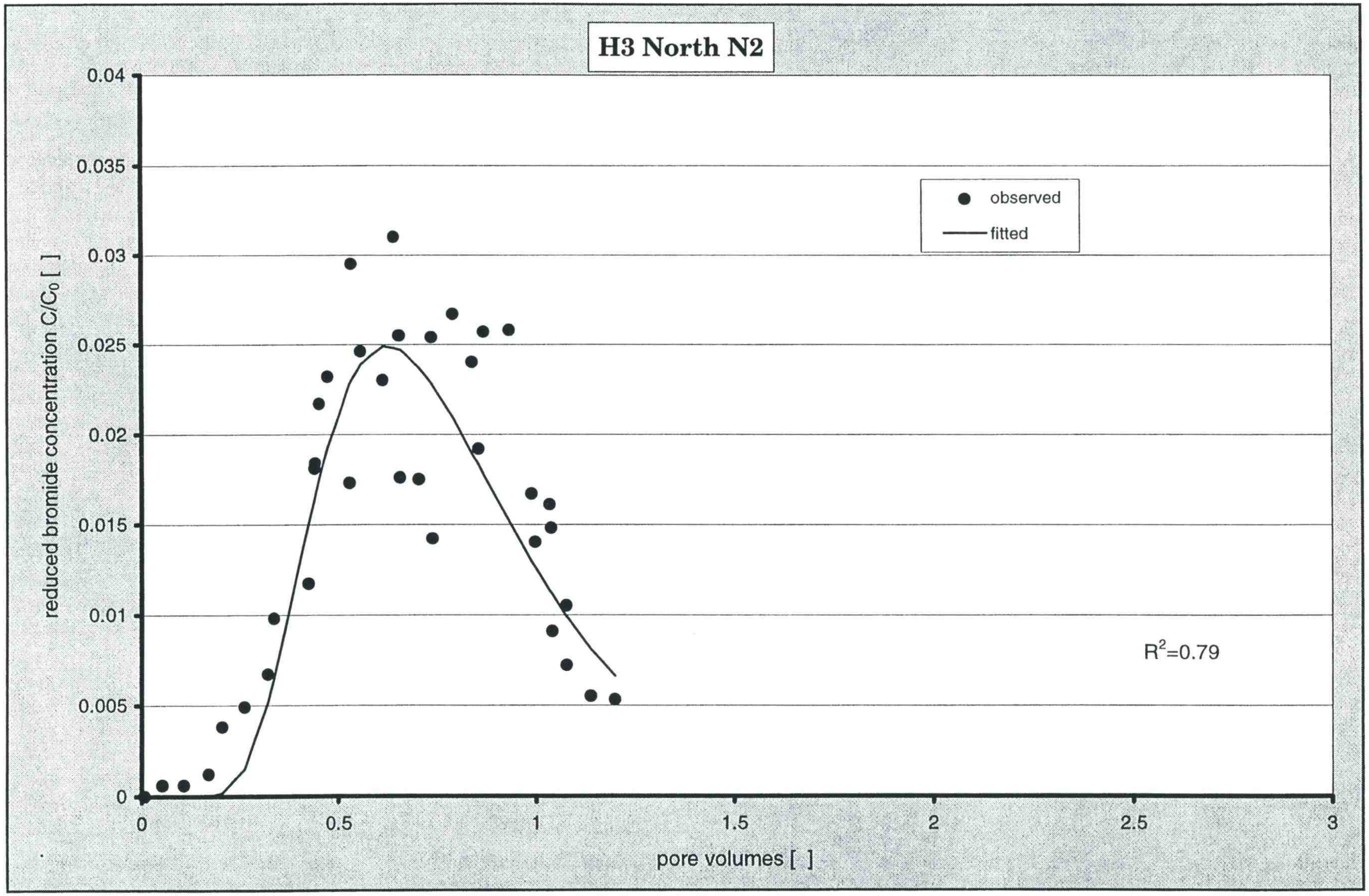

C2 South N2
reduced bromide concentration C/C0 [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
observed
fitted
R2=0.75

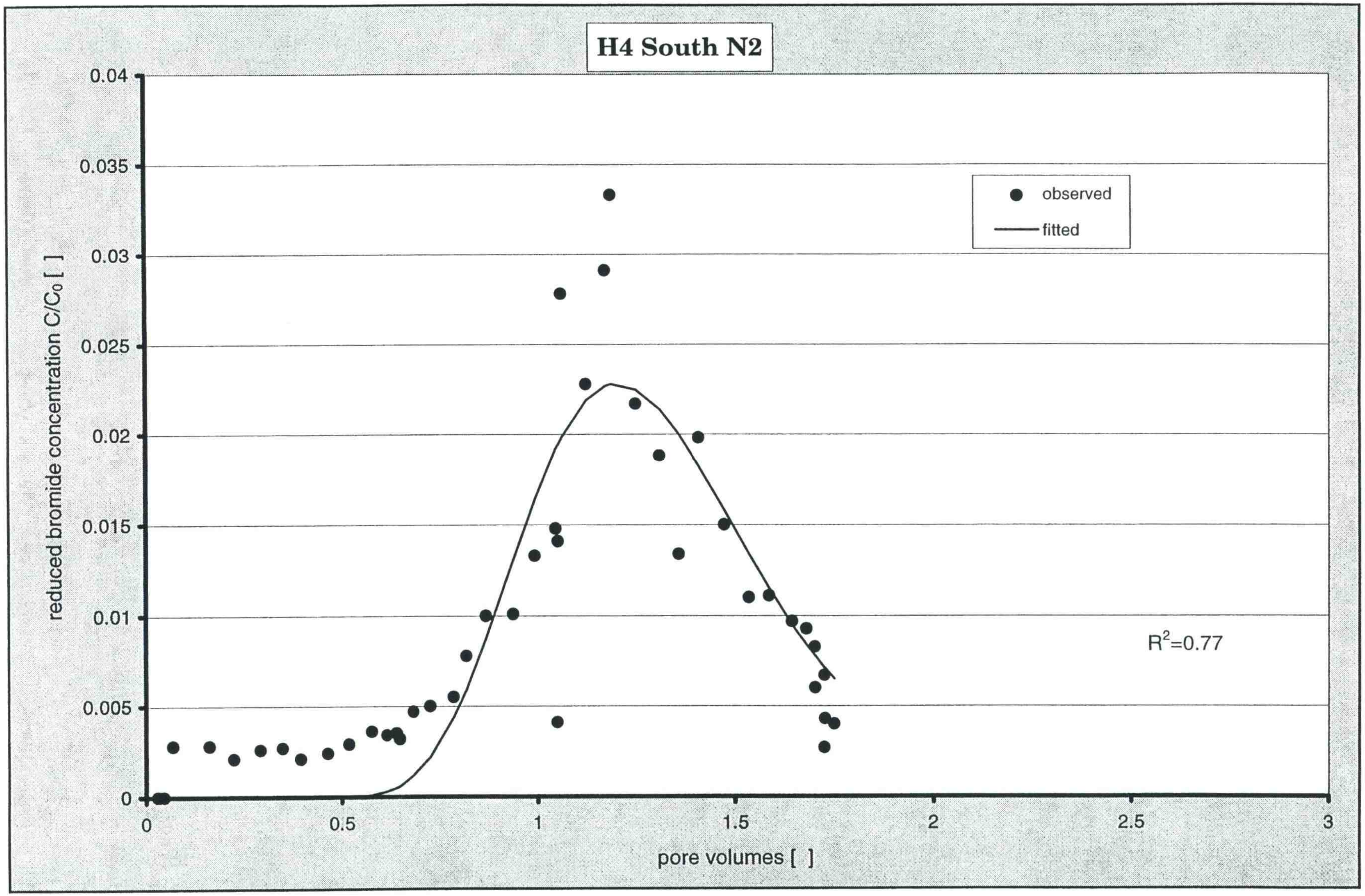

C3 South N2
reduced bromide concentration C/C₀ [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
R²=0.92


C4 North N2
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
reduced bromide concentration C/C_0 [ ]
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
observed
fitted
R^2=0.56


H1 North N2
Note different y-scale !
observed
fitted
R²=0.36
reduced bromide concentration C/C₀ [ ]
0.06
0.05
0.04
0.03
0.02
0.01
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]


H2 North N2
reduced bromide concentration C/C_0 [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
● observed
fitted
R^2=0.81


H3 North N2
observed
fitted
R²=0.79
reduced bromide concentration C/C0 [ ]
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]


H4 South N2
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
reduced bromide concentration C/C0 [ ]
0
0.5
1
1.5
2
2.5
3
pore volumes [ ]
observed
fitted
R2=0.77

Appendix E

Hydrodynamic dispersion coefficients as fitted with CXTFIT and calculated values for pore water velocity for all 32 PCAPS

# of sampler	Management	N - rate	Placement	D/vz (direct CXTFIT output) [ ]	Time of fitted peak breakthrough [days]	pore water velocity v [cm/days]	hydrodynamic dispersion coefficient D [*10^{-4} cm^2/s]
25	*C 1*	*N 0*	*North*	6.85	153	0.78	25.7
23	*C 1*	*N 0*	*South*	2.18	153	0.78	8.2
31	*C 2*	*N 0*	*North*	3.56	428	0.28	4.8
29	*C 2*	*N 0*	*South*	3.80	442	0.27	4.9
17	*C 3*	*N 0*	*North*	3.11	404	0.30	4.4
19	*C 3*	*N 0*	*South*	20.73	97	1.24	122.6
5	*C 4*	*N 0*	*North*	4.87	214	0.56	13.1
9	*C 4*	*N 0*	*South*	5.24	264	0.45	11.4
27	*H 1*	*N 0*	*North*	13.30	76	1.58	100.3
21	*H 1*	*N 0*	*South*	1.61	153	0.78	6.0
1	*H 2*	*N 0*	*North*	4.27	421	0.29	5.8
3	*H 2*	*N 0*	*South*	13.77	146	0.82	54.1
13	*H 3*	*N 0*	*North*	4.63	428	0.28	6.2
15	*H 3*	*N 0*	*South*	17.75	181	0.66	56.2
7	*H 4*	*N 0*	*North*	5.95	421	0.29	8.1
11	*H 4*	*N 0*	*South*	4.77	428	0.28	6.4
24	*C 1*	*N 1*	*South*	0.64	214	0.56	1.7
32	*C 2*	*N 1*	*North*	5.06	421	0.29	6.9
18	*C 3*	*N 1*	*North*	6.21	478	0.25	7.4
10	*C 4*	*N 1*	*South*	5.50	404	0.30	7.8
22	*H 1*	*N 1*	*South*	3.03	404	0.30	4.3
4	*H 2*	*N 1*	*South*	4.55	442	0.27	5.9
16	*H 3*	*N 1*	*South*	5.80	428	0.28	7.8
8	*H 4*	*N 1*	*North*	3.37	404	0.30	4.8
26	*C 1*	*N 2*	*North*	4.17	428	0.28	5.6
30	*C 2*	*N 2*	*South*	8.71	404	0.30	12.4
20	*C 3*	*N 2*	*South*	2.99	478	0.25	3.6
6	*C 4*	*N 2*	*North*	7.72	442	0.27	10.0
28	*H 1*	*N 2*	*North*	5.39	449	0.27	6.9
2	*H 2*	*N 2*	*North*	7.15	163	0.74	25.1
14	*H 3*	*N 2*	*North*	10.03	204	0.59	28.2
12	*H 4*	*N 2*	*South*	3.42	421	0.29	4.7
		Mean		6.25	331	0.47	18.2
		Median		4.97	404	0.30	7.2
		Max. value		20.73	478	1.58	122.6
		Min. value		0.64	76	0.25	1.7
		Std. deviation		4.49	133	0.32	27.8

Appendix F

Water flow collection as measured with PCAPS (November 1992 - November 1994)

	# of sample set				# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	# 9	# 10
	date of sample set				4-Nov-92	12-Nov-92	19-Nov-92	25-Nov-92	3-Dec-92	11-Dec-92	17-Dec-92	22-Dec-92	6-Jan-93	19-Jan-93
	# of days since Br-application				0	8	15	21	29	37	43	48	63	76
# of sampler	*Management*	*N - rate*	*Placement*		*Water flow* *[cm]*	*Water flow* *[cm]*	*Water flow* *[cm]*	*Water flow* *[cm]*	*Water flow* *[cm]*	*Water flow* *[cm]*	*Water flow* *[cm]*	*Water flow* *[cm]*	*Water flow* *[cm]*	*Water flow* *[cm]*
25	*C1*	*N0*	*North*		1.50	0.37	0.40	4.38	2.77	3.85	2.63	2.76	3.14	2.37
23	*C1*	*N0*	*South*		flooded	flooded	2.37	flooded	flooded	flooded	flooded	flooded	flooded	flooded
31	*C2*	*N0*	*North*		0.81	0.10	0.13	3.28	3.03	4.25	1.87	1.19	2.72	1.84
29	*C2*	*N0*	*South*		0.00	0.00	0.08	2.07	3.14	3.17	1.91	1.27	2.52	1.95
17	*C3*	*N0*	*North*		2.66	1.62	0.61	2.23	2.33	2.23	1.97	2.03	2.48	1.73
19	*C3*	*N0*	*South*		0.23	1.10	0.25	1.88	2.56	2.51	1.99	1.93	3.22	1.18
5	*C4*	*N0*	*North*		1.90	0.60	0.32	2.85	3.54	3.32	3.63	2.70	3.15	1.76
9	*C4*	*N0*	*South*		3.03	0.79	0.40	2.53	3.17	3.21	2.73	2.26	3.20	1.84
27	*H1*	*N0*	*North*		flooded	2.32	1.99	flooded	flooded	flooded	flooded	3.75	3.55	2.13
21	*H1*	*N0*	*South*		flooded	flooded	3.38	flooded	flooded	flooded	flooded	flooded	flooded	flooded
1	*H2*	*N0*	*North*		0.00	0.00	0.00	0.18	0.79	1.70	1.68	1.27	2.57	1.45
3	*H2*	*N0*	*South*		0.00	0.05	0.00	1.54	3.35	2.73	2.44	2.32	2.67	2.30
13	*H3*	*N0*	*North*		0.00	0.00	0.00	0.13	0.82	1.44	1.11	0.85	2.06	0.74
15	*H3*	*N0*	*South*		1.20	1.15	0.20	1.17	1.34	1.12	1.20	0.92	2.33	1.10
7	*H4*	*N0*	*North*		2.16	1.69	0.74	2.09	3.15	2.61	2.58	2.41	2.61	2.19
11	*H4*	*N0*	*South*		0.00	0.00	0.00	0.00	0.51	1.91	1.81	1.38	2.91	1.84
24	*C1*	*N1*	*South*		flooded	flooded	2.97	flooded	flooded	flooded	flooded	flooded	flooded	flooded
32	*C2*	*N1*	*North*		0.00	0.00	0.09	1.96	2.20	3.85	1.84	1.70	3.62	1.65
18	*C3*	*N1*	*North*		0.00	0.00	0.00	1.77	3.58	3.42	0.94	0.92	1.41	0.48
10	*C4*	*N1*	*South*		1.02	0.05	0.25	4.29	3.19	3.83	4.17	2.80	3.09	2.15
22	*H1*	*N1*	*South*		flooded	flooded	3.59	flooded	flooded	flooded	flooded	flooded	flooded	flooded
4	*H2*	*N1*	*South*		0.00	0.00	0.00	0.00	1.07	2.09	2.31	2.02	4.01	2.08
16	*H3*	*N1*	*South*		0.09	0.00	0.00	0.00	0.34	1.05	1.31	1.00	2.33	1.15
8	*H4*	*N1*	*North*		3.18	0.00	0.00	3.85	2.95	3.32	3.26	3.29	3.28	2.22
26	*C1*	*N2*	*North*		0.00	0.00	0.05	4.38	2.82	3.42	3.04	2.73	2.76	2.19
30	*C2*	*N2*	*South*		0.00	0.00	0.00	1.06	3.65	3.68	2.15	2.73	3.43	1.60
20	*C3*	*N2*	*South*		1.43	1.16	0.24	2.19	2.76	2.63	1.89	1.63	3.05	0.96
6	*C4*	*N2*	*North*		0.00	0.00	0.00	0.00	2.77	2.80	2.77	1.94	2.78	1.77
28	*H1*	*N2*	*North*		flooded	2.55	0.27	flooded	flooded	flooded	flooded	2.91	2.49	1.90
2	*H2*	*N2*	*North*		3.87	2.22	0.96	2.76	2.83	2.82	2.72	2.81	2.81	2.35
14	*H3*	*N2*	*North*		0.28	0.00	0.00	1.84	2.22	2.59	1.44	2.35	2.45	0.63
12	*H4*	*N2*	*South*		1.25	0.60	0.97	3.79	2.59	2.81	2.37	1.89	2.89	2.29

Note: "Flooded" means that no reliable amount of percolation could be measured, for which there are two reasons: either irrigation box was inaccessible due to surface ponding or PCAPS overflowed (i.e., collected more than 3780 ml).

	# of sample set				# 11	# 12	# 13	# 14	# 15	# 16	# 17	# 18	# 19	# 20
	date of sample set				27-Jan-93	2-Feb-93	9-Feb-93	23-Feb-93	9-Mar-93	19-Mar-93	30-Mar-93	6-Apr-93	16-Apr-93	4-May-93
	# of days since Br-application				84	90	97	111	125	135	146	153	163	181
# of sampler	*Management*	*N - rate*	*Placement*		*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*
25	*C1*	*N0*	*North*		2.70	2.00	0.99	0.24	1.62	2.73	2.65	1.84	2.70	2.68
23	*C1*	*N0*	*South*		flooded	2.84	1.46	0.28	1.01	2.05	2.57	1.13	2.15	2.55
31	*C2*	*N0*	*North*		2.79	1.16	0.69	0.37	0.67	1.31	3.02	0.95	2.02	3.09
29	*C2*	*N0*	*South*		2.45	1.31	0.70	0.45	0.56	1.33	2.45	0.98	1.63	2.47
17	*C3*	*N0*	*North*		2.31	1.18	0.52	0.13	0.50	1.34	2.23	0.76	1.65	2.28
19	*C3*	*N0*	*South*		3.16	1.04	0.44	0.14	1.89	2.13	2.80	1.19	2.66	3.22
5	*C4*	*N0*	*North*		3.50	1.36	0.68	0.08	0.36	1.89	3.42	0.87	1.94	3.28
9	*C4*	*N0*	*South*		3.08	1.52	0.63	0.10	0.63	1.96	3.02	1.21	2.31	2.47
27	*H1*	*N0*	*North*		2.34	2.31	1.59	0.42	2.36	2.40	2.29	2.37	2.36	2.47
21	*H1*	*N0*	*South*		flooded	3.29	2.49	1.07	2.59	3.30	3.78	3.18	3.18	3.19
1	*H2*	*N0*	*North*		2.19	1.14	0.42	0.02	0.45	1.39	2.76	0.52	1.97	2.66
3	*H2*	*N0*	*South*		2.45	1.84	0.94	0.30	2.00	2.49	2.45	1.66	2.39	2.40
13	*H3*	*N0*	*North*		1.86	0.60	0.16	0.00	0.00	0.21	1.73	0.15	0.98	3.37
15	*H3*	*N0*	*South*		3.66	0.90	0.33	0.38	0.66	1.92	3.15	0.90	2.47	3.28
7	*H4*	*N0*	*North*		2.59	1.57	0.69	0.10	1.11	2.01	2.45	1.50	2.37	2.43
11	*H4*	*N0*	*South*		2.07	1.27	0.77	0.37	0.72	1.19	2.60	0.74	1.73	3.09
24	*C1*	*N1*	*South*		flooded	3.81	2.11	0.69	1.37	2.36	3.70	1.61	2.29	3.04
32	*C2*	*N1*	*North*		3.20	1.32	0.95	0.24	1.21	2.05	3.59	0.89	1.80	3.61
18	*C3*	*N1*	*North*		2.28	0.27	0.00	0.00	0.00	0.00	1.03	0.00	0.00	0.84
10	*C4*	*N1*	*South*		2.47	2.09	0.88	0.05	0.33	1.45	2.39	1.28	1.99	2.33
22	*H1*	*N1*	*South*		flooded	2.93	2.36	0.73	2.20	2.78	3.13	2.69	3.03	3.07
4	*H2*	*N1*	*South*		2.65	1.53	0.52	0.00	0.33	0.77	3.00	0.73	2.31	3.71
16	*H3*	*N1*	*South*		2.16	0.99	0.42	0.00	0.00	0.18	2.23	0.39	0.60	2.23
8	*H4*	*N1*	*North*		3.27	1.62	0.74	0.16	0.65	2.28	3.15	1.13	2.64	3.21
26	*C1*	*N2*	*North*		2.47	1.86	1.06	0.44	1.67	2.50	2.37	1.66	2.37	2.35
30	*C2*	*N2*	*South*		3.29	1.24	0.48	0.08	0.47	2.45	2.42	0.84	2.34	2.97
20	*C3*	*N2*	*South*		2.98	1.06	0.36	0.00	1.08	1.51	2.92	0.73	1.99	3.15
6	*C4*	*N2*	*North*		2.74	1.26	0.67	0.10	0.26	1.39	2.65	0.81	1.53	2.66
28	*H1*	*N2*	*North*		2.33	1.20	0.20	0.00	0.00	0.47	2.23	0.24	0.73	2.29
2	*H2*	*N2*	*North*		2.72	1.92	0.75	0.12	1.86	2.58	2.64	1.69	2.66	2.66
14	*H3*	*N2*	*North*		3.66	0.63	0.08	0.00	0.42	0.90	2.31	0.20	0.96	2.34
12	*H4*	*N2*	*South*		2.41	1.63	0.97	0.36	1.46	1.77	2.45	1.31	2.07	2.85

	# of sample set				**# 21**	**# 22**	**# 23**	**# 24**	**# 25**	**# 26**	**# 27**	**# 28**	**# 29**	**# 30**
	date of sample set				**27-May-93**	**6-Jun-93**	**26-Jul-93**	**26-Aug-93**	**8-Oct-93**	**8-Nov-93**	**2-Dec-93**	**13-Dec-93**	**23-Dec-93**	**30-Dec-93**
	# of days since Br-application				**204**	**214**	**264**	**295**	**338**	**369**	**393**	**404**	**414**	**421**
# of sampler	*Management*	*N - rate*	*Placement*		*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*
25	*C1*	*N0*	*North*		2.28	0.00	0.00	0.00	0.00	0.00	0.00	1.18	2.53	0.55
23	*C1*	*N0*	*South*		2.08	0.58	0.05	0.19	0.00	0.00	0.00	flooded	2.72	1.57
31	*C2*	*N0*	*North*		2.34	0.00	0.02	0.00	0.00	0.00	0.00	2.57	2.58	0.69
29	*C2*	*N0*	*South*		2.21	0.48	0.12	0.16	0.00	0.00	0.00	1.79	1.04	0.80
17	*C3*	*N0*	*North*		1.79	0.00	0.02	0.00	0.00	0.00	0.00	0.53	1.24	0.38
19	*C3*	*N0*	*South*		1.87	0.76	0.00	0.00	0.00	0.00	0.00	1.59	1.71	0.14
5	*C4*	*N0*	*North*		1.57	0.00	0.00	0.02	0.00	0.00	0.00	3.48	1.08	1.26
9	*C4*	*N0*	*South*		2.14	0.29	0.12	0.00	0.00	0.00	0.00	2.54	2.46	0.80
27	*H1*	*N0*	*North*		1.79	2.18	1.28	1.94	0.00	0.00	0.00	2.66	2.34	0.67
21	*H1*	*N0*	*South*		2.22	0.13	0.00	1.10	0.61	0.03	0.00	flooded	3.48	2.54
1	*H2*	*N0*	*North*		1.89	0.00	0.02	0.00	0.00	0.00	0.00	2.82	2.37	0.33
3	*H2*	*N0*	*South*		2.24	0.57	0.00	3.05	0.55	0.00	0.00	2.24	1.92	1.47
13	*H3*	*N0*	*North*		0.58	0.00	0.00	0.00	0.00	0.00	0.00	3.92	1.62	0.06
15	*H3*	*N0*	*South*		2.75	0.00	3.69	0.75	0.00	0.00	0.56	3.72	2.06	0.26
7	*H4*	*N0*	*North*		2.07	0.20	0.07	0.00	0.00	0.00	0.00	2.69	2.37	0.71
11	*H4*	*N0*	*South*		2.23	1.27	0.30	0.13	0.23	0.02	0.00	0.22	1.95	0.57
24	*C1*	*N1*	*South*		2.16	1.04	0.00	0.56	0.00	0.00	0.00	flooded	3.75	2.17
32	*C2*	*N1*	*North*		1.48	0.00	0.00	0.00	0.00	0.00	0.00	0.88	2.49	0.45
18	*C3*	*N1*	*North*		0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.36	0.38	0.48
10	*C4*	*N1*	*South*		1.85	0.00	0.00	0.00	0.00	0.00	0.00	2.95	2.38	0.93
22	*H1*	*N1*	*South*		2.02	0.00	0.00	0.05	0.00	0.00	0.00	flooded	flooded	3.31
4	*H2*	*N1*	*South*		2.21	0.00	0.00	0.00	0.00	0.00	0.00	3.19	1.69	1.52
16	*H3*	*N1*	*South*		0.66	0.00	0.00	0.00	0.00	0.00	1.33	3.76	2.24	0.23
8	*H4*	*N1*	*North*		2.17	0.00	0.08	0.17	0.00	0.00	0.00	2.63	2.60	0.60
26	*C1*	*N2*	*North*		2.10	0.00	0.63	0.09	0.02	0.00	0.00	0.61	2.07	0.51
30	*C2*	*N2*	*South*		1.56	1.07	0.08	0.00	0.00	0.00	0.00	2.84	2.55	0.21
20	*C3*	*N2*	*South*		1.03	0.00	0.00	0.00	0.00	0.00	0.00	0.83	1.54	0.07
6	*C4*	*N2*	*North*		1.66	0.16	0.12	0.00	0.00	0.00	0.00	2.72	1.11	1.14
28	*H1*	*N2*	*North*		0.73	0.00	0.15	0.29	0.00	0.00	0.00	2.19	2.33	0.10
2	*H2*	*N2*	*North*		2.29	0.79	0.23	0.00	0.00	0.00	0.00	2.88	2.63	0.60
14	*H3*	*N2*	*North*		1.16	0.53	0.08	0.00	0.00	0.00	0.00	2.08	1.30	0.06
12	*H4*	*N2*	*South*		2.24	2.16	0.20	0.03	0.38	0.00	0.00	2.60	2.05	0.61

	# of sample set				**# 31**	**# 32**	**# 33**	**# 34**	**# 35**	**# 36**	**# 37**	**# 38**	**# 39**	**# 40**
	date of sample set				**6-Jan-94**	**20-Jan-94**	**27-Jan-94**	**17-Feb-94**	**25-Feb-94**	**7-Mar-94**	**21-Mar-94**	**5-Apr-94**	**14-Apr-94**	**28-Apr-94**
	# of days since Br-application				**428**	**442**	**449**	**470**	**478**	**488**	**502**	**517**	**526**	**540**
# of sampler	*Management*	*N - rate*	*Placement*		*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*
25	*C1*	*N0*	*North*		2.77	2.68	2.42	2.34	2.82	2.72	2.12	2.47	1.41	0.93
23	*C1*	*N0*	*South*		flooded	2.57	1.97	flooded	flooded	flooded	2.58	2.42	1.01	0.91
31	*C2*	*N0*	*North*		3.67	2.93	1.31	1.91	3.30	3.13	1.56	2.67	0.85	0.87
29	*C2*	*N0*	*South*		2.59	2.42	1.34	1.67	2.56	2.48	1.53	2.32	0.79	0.78
17	*C3*	*N0*	*North*		2.47	2.27	0.84	1.11	2.38	2.33	1.21	1.96	0.18	0.14
19	*C3*	*N0*	*South*		2.90	2.58	1.49	1.01	3.22	3.10	1.01	2.28	1.16	0.28
5	*C4*	*N0*	*North*		3.96	3.02	1.05	1.23	flooded	2.85	2.00	2.08	0.81	0.66
9	*C4*	*N0*	*South*		2.62	2.50	2.62	1.61	flooded	2.48	2.49	2.38	2.07	0.85
27	*H1*	*N0*	*North*		3.04	2.25	2.40	2.09	flooded	2.49	2.42	2.14	2.04	0.27
21	*H1*	*N0*	*South*		flooded	2.65	2.68	2.31	flooded	flooded	2.67	2.51	2.47	1.70
1	*H2*	*N0*	*North*		2.72	2.64	1.57	1.46	2.78	2.74	1.29	2.57	1.26	0.62
3	*H2*	*N0*	*South*		2.64	2.50	2.02	2.23	2.68	2.56	2.04	2.45	1.90	1.26
13	*H3*	*N0*	*North*		4.31	2.10	0.44	0.36	3.23	2.98	0.29	1.89	0.31	0.06
15	*H3*	*N0*	*South*		3.30	2.56	1.30	1.04	3.33	3.25	1.00	2.45	1.44	0.36
7	*H4*	*N0*	*North*		2.59	2.45	1.77	1.94	2.65	2.57	1.98	2.33	1.18	0.64
11	*H4*	*N0*	*South*		2.56	2.40	1.31	1.86	2.63	2.47	1.73	2.10	1.01	0.89
24	*C1*	*N1*	*South*		flooded	3.74	2.39	flooded	flooded	flooded	2.98	2.33	1.53	1.43
32	*C2*	*N1*	*North*		2.56	2.46	1.67	1.54	2.60	2.87	1.57	2.28	0.82	0.77
18	*C3*	*N1*	*North*		3.73	1.41	0.10	0.14	4.19	2.68	0.17	1.19	0.03	0.03
10	*C4*	*N1*	*South*		2.55	2.40	2.17	1.97	flooded	2.34	2.12	2.23	0.65	0.25
22	*H1*	*N1*	*South*		flooded	3.47	2.54	2.27	flooded	flooded	2.94	2.39	2.46	2.35
4	*H2*	*N1*	*South*		3.78	3.33	2.16	1.82	3.55	3.49	2.01	3.27	0.99	0.86
16	*H3*	*N1*	*South*		3.04	2.62	1.97	1.17	3.13	3.04	1.73	2.43	1.93	0.21
8	*H4*	*N1*	*North*		3.00	3.15	1.51	1.75	flooded	2.69	1.56	2.47	0.55	0.56
26	*C1*	*N2*	*North*		3.17	3.00	1.94	2.18	4.15	3.08	2.09	2.30	2.12	1.31
30	*C2*	*N2*	*South*		3.78	2.95	2.56	1.37	3.17	3.06	1.48	2.67	1.08	0.63
20	*C3*	*N2*	*South*		2.97	2.50	1.02	0.94	3.01	2.91	0.71	2.10	0.51	0.19
6	*C4*	*N2*	*North*		2.81	2.66	1.17	1.47	3.70	2.76	1.59	2.50	0.51	0.46
28	*H1*	*N2*	*North*		3.23	2.31	1.26	0.58	flooded	2.50	1.09	2.01	0.20	0.04
2	*H2*	*N2*	*North*		2.90	2.67	2.00	1.60	2.85	2.72	1.47	2.49	0.41	0.27
14	*H3*	*N2*	*North*		2.12	1.97	0.66	0.55	2.67	2.27	0.37	1.52	0.16	0.04
12	*H4*	*N2*	*South*		2.56	2.48	1.99	2.14	2.67	2.54	2.09	2.37	1.49	0.87

	# of sample set				**# 41**	**# 42**	**# 43**	**# 44**	**# 45**	**# 46**	**# 47**			
	date of sample set				**22-May-94**	**29-Jun-94**	**22-Jul-94**	**9-Sep-94**	**5-Oct-94**	**28-Oct-94**	**1-Nov-94**			
	# of days since Br-application				**564**	**602**	**625**	**674**	**700**	**723**	**727**			
# of sampler	*Management*	*N - rate*	*Placement*		*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*	*Water flow [cm]*			
25	*C1*	*N0*	*North*		0.01	2.73	2.68	1.53	0.02	2.80	2.76			
23	*C1*	*N0*	*South*		0.00	0.04	0.54	0.00	0.00	flooded	flooded			
31	*C2*	*N0*	*North*		0.02	3.30	3.23	3.03	0.14	3.56	3.21			
29	*C2*	*N0*	*South*		0.01	2.62	2.21	1.22	0.00	3.19	2.73			
17	*C3*	*N0*	*North*		0.02	0.00	1.48	0.00	0.00	2.45	2.40			
19	*C3*	*N0*	*South*		0.00	0.51	1.67	0.00	0.00	0.50	2.51			
5	*C4*	*N0*	*North*		0.13	1.88	3.20	0.15	0.04	3.17	flooded			
9	*C4*	*N0*	*South*		0.00	2.58	2.26	0.15	0.00	2.93	flooded			
27	*H1*	*N0*	*North*		0.00	2.44	2.36	1.79	0.00	flooded	flooded			
21	*H1*	*N0*	*South*		0.00	2.66	2.15	0.00	0.00	flooded	flooded			
1	*H2*	*N0*	*North*		0.02	2.78	2.28	0.96	0.00	2.85	2.96			
3	*H2*	*N0*	*South*		0.01	3.31	2.45	2.03	0.00	2.63	2.70			
13	*H3*	*N0*	*North*		0.00	2.00	2.00	0.04	0.00	3.34	3.33			
15	*H3*	*N0*	*South*		0.00	0.25	3.22	0.71	0.00	2.58	3.28			
7	*H4*	*N0*	*North*		0.00	2.60	2.43	1.94	0.00	2.57	flooded			
11	*H4*	*N0*	*South*		0.00	0.00	0.00	0.00	0.00	0.00	1.18			
24	*C1*	*N1*	*South*		0.00	0.00	0.98	0.00	0.00	flooded	flooded			
32	*C2*	*N1*	*North*		0.01	0.13	2.80	0.05	0.00	3.08	2.50			
18	*C3*	*N1*	*North*		0.00	0.00	1.21	0.00	0.02	4.22	3.47			
10	*C4*	*N1*	*South*		0.00	2.39	2.38	0.01	0.00	2.88	3.25			
22	*H1*	*N1*	*South*		0.00	2.98	2.99	0.03	0.00	flooded	flooded			
4	*H2*	*N1*	*South*		0.13	3.50	3.80	3.64	0.09	3.91	4.35			
16	*H3*	*N1*	*South*		0.00	0.09	0.91	0.00	0.00	1.71	1.95			
8	*H4*	*N1*	*North*		0.02	0.00	0.69	0.04	0.00	2.73	flooded			
26	*C1*	*N2*	*North*		0.02	1.19	2.08	0.02	0.00	2.73	3.05			
30	*C2*	*N2*	*South*		0.00	2.52	2.57	0.02	0.00	3.56	3.26			
20	*C3*	*N2*	*South*		0.00	1.16	1.44	0.02	0.00	0.21	3.20			
6	*C4*	*N2*	*North*		0.00	1.10	2.46	0.00	0.00	3.00	flooded			
28	*H1*	*N2*	*North*		0.00	2.50	2.45	1.82	0.00	flooded	flooded			
2	*H2*	*N2*	*North*		0.00	2.80	2.61	0.95	0.00	3.34	2.93			
14	*H3*	*N2*	*North*		0.00	0.08	1.46	0.05	0.00	2.50	2.52			
12	*H4*	*N2*	*South*		0.03	0.00	0.98	0.02	0.00	0.05	0.99			

Appendix G

Flow-weighted nitrate-N concentrations as measured with PCAPS (November 1992 - November 1994)

	# of sample set				# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	# 9	# 10
	date of sample set				4-Nov-92	12-Nov-92	19-Nov-92	25-Nov-92	3-Dec-92	11-Dec-92	17-Dec-92	22-Dec-92	6-Jan-93	19-Jan-93
	# of days since Br-application				0	8	15	21	29	37	43	48	63	76
# of sampler	*Management*	*N - rate*	*Placement*		*Concentration*	*Concentration*	*Concentration*	*Concentration*	*Concentration*	*Concentration*	*Concentration*	*Concentration*	*Concentration*	*Concentration*
					[mg/l]	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*
25	*C1*	*N0*	*North*		0.91	5.35	2.54	4.61	4.63	5.90	7.12	7.19	7.82	8.17
23	*C1*	*N0*	*South*		flooded	8.01	4.49	flooded	flooded	flooded	flooded	flooded	flooded	flooded
31	*C2*	*N0*	*North*		1.60	2.51	0.68	2.85	2.67	2.89	2.91	2.91	3.16	3.17
29	*C2*	*N0*	*South*		empty	empty	0.66	3.37	3.90	3.80	4.28	3.77	4.07	4.66
17	*C3*	*N0*	*North*		4.88	3.16	2.64	4.83	6.55	8.22	9.33	10.23	10.72	11.13
19	*C3*	*N0*	*South*		5.76	3.98	6.20	8.82	9.14	9.64	9.60	9.07	8.53	8.25
5	*C4*	*N0*	*North*		2.74	2.62	3.06	3.42	4.25	3.56	2.80	2.74	3.37	3.46
9	*C4*	*N0*	*South*		4.64	3.39	2.86	4.73	3.29	3.78	3.83	4.04	4.33	4.54
27	*H1*	*N0*	*North*		flooded	1.46	0.27	flooded	flooded	flooded	flooded	1.68	1.49	1.35
21	*H1*	*N0*	*South*		flooded	flooded	3.86	flooded	flooded	flooded	flooded	flooded	flooded	flooded
1	*H2*	*N0*	*North*		empty	empty	empty	7.53	4.93	3.40	2.56	2.37	2.54	2.78
3	*H2*	*N0*	*South*		empty	0.85	empty	4.32	4.26	5.25	5.95	5.78	5.86	6.52
13	*H3*	*N0*	*North*		empty	empty	empty	7.65	7.99	6.13	5.31	5.18	4.89	4.20
15	*H3*	*N0*	*South*		3.76	2.98	2.95	2.41	2.77	2.54	2.36	2.33	2.23	2.20
7	*H4*	*N0*	*North*		2.43	2.34	3.26	3.08	2.23	2.57	2.49	2.67	2.67	2.83
11	*H4*	*N0*	*South*		empty	empty	empty	empty	2.73	3.85	3.74	3.52	3.75	3.01
24	*C1*	*N1*	*South*		flooded	2.30	6.61	flooded	flooded	flooded	flooded	flooded	flooded	flooded
32	*C2*	*N1*	*North*		empty	empty	4.52	15.85	15.36	14.14	13.55	13.62	13.11	13.32
18	*C3*	*N1*	*North*		empty	empty	empty	3.00	3.53	3.17	3.43	3.85	3.41	3.35
10	*C4*	*N1*	*South*		2.16	3.57	6.60	4.12	4.06	5.90	6.81	6.44	5.42	5.72
22	*H1*	*N1*	*South*		flooded	flooded	4.46	flooded	flooded	flooded	flooded	flooded	flooded	flooded
4	*H2*	*N1*	*South*		empty	empty	empty	empty	7.01	7.52	7.37	7.38	7.04	6.44
16	*H3*	*N1*	*South*		0.00	empty	empty	empty	8.57	8.51	7.48	7.55	6.01	6.44
8	*H4*	*N1*	*North*		1.07	empty	empty	1.45	1.76	2.73	2.66	1.71	2.35	2.47
26	*C1*	*N2*	*North*		empty	empty	1.65	8.59	10.05	8.89	7.42	8.53	9.29	10.11
30	*C2*	*N2*	*South*		empty	empty	empty	13.43	12.26	10.71	10.07	10.51	10.29	9.83
20	*C3*	*N2*	*South*		16.78	8.22	14.95	19.61	20.98	21.61	21.09	20.58	20.04	18.49
6	*C4*	*N2*	*North*		empty	empty	empty	empty	8.38	11.67	11.18	12.10	13.64	12.14
28	*H1*	*N2*	*North*		flooded	1.67	0.56	flooded	flooded	flooded	flooded	1.65	3.19	3.23
2	*H2*	*N2*	*North*		25.86	18.60	13.15	16.76	17.17	15.77	14.67	11.37	13.43	12.46
14	*H3*	*N2*	*North*		10.92	empty	empty	11.00	12.79	13.49	14.87	15.84	15.70	14.71
12	*H4*	*N2*	*South*		6.62	3.88	3.79	1.48	1.91	1.99	2.00	2.23	1.94	2.04

Note: "empty" means that PCAPS did not collect any water;
"flooded" means that irrigation box was inaccessible due to surface ponding.

	# of sample set				# 11	# 12	# 13	# 14	# 15	# 16	# 17	# 18	# 19	# 20
	date of sample set				27-Jan-93	2-Feb-93	9-Feb-93	23-Feb-93	9-Mar-93	19-Mar-93	30-Mar-93	6-Apr-93	16-Apr-93	4-May-93
	# of days since Br-application				84	90	97	111	125	135	146	153	163	181
# of sampler	*Management*	*N - rate*	*Placement*		*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*
25	*C1*	*N0*	*North*		8.70	9.03	7.62	8.32	7.55	6.80	8.04	8.05	8.51	7.84
23	*C1*	*N0*	*South*		flooded	4.92	3.45	3.40	3.20	2.47	2.77	3.18	3.49	3.19
31	*C2*	*N0*	*North*		3.92	4.11	4.13	4.65	4.59	5.01	5.97	6.55	8.06	9.78
29	*C2*	*N0*	*South*		6.13	7.04	6.70	7.07	6.63	6.36	7.22	8.69	11.16	12.38
17	*C3*	*N0*	*North*		13.48	12.81	11.77	11.28	10.41	9.69	12.54	10.79	10.75	11.29
19	*C3*	*N0*	*South*		8.00	7.91	7.04	7.02	7.37	6.21	6.29	7.32	7.18	7.48
5	*C4*	*N0*	*North*		4.63	4.70	4.58	4.70	5.03	5.37	6.01	6.35	6.88	7.65
9	*C4*	*N0*	*South*		6.19	5.73	5.18	4.72	5.41	5.64	7.21	7.65	9.25	8.44
27	*H1*	*N0*	*North*		1.48	1.49	1.28	1.17	1.35	1.32	1.58	1.80	2.12	2.28
21	*H1*	*N0*	*South*		flooded	3.86	2.32	2.80	3.09	2.49	1.85	2.52	3.01	3.28
1	*H2*	*N0*	*North*		3.18	4.21	3.43	4.22	2.18	2.11	1.48	0.13	0.03	0.00
3	*H2*	*N0*	*South*		5.37	4.33	2.13	0.58	0.41	0.24	0.18	0.01	0.03	0.01
13	*H3*	*N0*	*North*		4.11	3.65	3.39	empty	empty	2.72	2.64	2.24	0.86	0.09
15	*H3*	*N0*	*South*		2.72	2.49	2.32	2.54	2.51	2.62	2.46	2.58	2.78	2.03
7	*H4*	*N0*	*North*		3.20	3.17	3.19	3.02	3.17	2.86	3.53	3.60	3.77	3.30
11	*H4*	*N0*	*South*		3.12	3.06	3.08	2.86	2.72	2.49	3.81	2.80	2.96	3.17
24	*C1*	*N1*	*South*		flooded	3.47	2.84	2.94	3.00	2.92	3.21	4.02	4.90	4.98
32	*C2*	*N1*	*North*		15.41	15.60	15.67	15.31	15.47	12.67	15.50	17.01	17.82	18.22
18	*C3*	*N1*	*North*		4.34	3.66	empty	empty	empty	empty	3.86	empty	empty	4.42
10	*C4*	*N1*	*South*		6.07	7.16	5.09	3.26	5.18	6.80	6.94	8.66	8.18	8.05
22	*H1*	*N1*	*South*		flooded	4.43	5.05	5.29	6.09	5.73	5.34	6.40	7.07	6.58
4	*H2*	*N1*	*South*		6.71	6.42	6.00	empty	5.65	5.56	5.10	3.18	3.19	1.85
16	*H3*	*N1*	*South*		5.55	6.34	5.92	empty	empty	5.25	5.43	6.23	6.52	6.05
8	*H4*	*N1*	*North*		2.34	3.75	3.71	3.32	4.59	4.22	3.53	2.13	2.44	1.70
26	*C1*	*N2*	*North*		10.23	11.43	11.36	11.83	11.57	7.95	10.72	12.44	12.54	11.94
30	*C2*	*N2*	*South*		13.28	12.44	11.61	11.84	10.88	9.87	12.67	14.51	14.29	15.54
20	*C3*	*N2*	*South*		21.53	21.00	20.75	empty	20.09	19.10	18.79	20.56	20.91	20.83
6	*C4*	*N2*	*North*		14.77	13.26	11.94	10.41	11.29	11.38	15.17	14.38	12.35	11.46
28	*H1*	*N2*	*North*		1.40	3.13	3.62	empty	empty	3.84	3.15	3.27	4.68	5.24
2	*H2*	*N2*	*North*		8.80	11.68	11.50	6.15	6.72	3.02	1.92	0.38	0.31	0.06
14	*H3*	*N2*	*North*		16.04	16.82	14.81	empty	15.93	14.99	14.93	16.31	15.10	15.53
12	*H4*	*N2*	*South*		2.76	2.89	3.10	2.89	3.62	3.78	4.79	5.99	6.77	6.69

	# of sample set				**# 21**	**# 22**	**# 23**	**# 24**	**# 25**	**# 26**	**# 27**	**# 28**	**# 29**	**# 30**
	date of sample set				**27-May-93**	**6-Jun-93**	**26-Jul-93**	**26-Aug-93**	**8-Oct-93**	**8-Nov-93**	**2-Dec-93**	**13-Dec-93**	**23-Dec-93**	**30-Dec-93**
	# of days since Br-application				**204**	**214**	**264**	**295**	**338**	**369**	**393**	**404**	**414**	**421**
# of sampler	*Management*	*N - rate*	*Placement*		*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*
25	*C1*	*N0*	*North*		6.45	empty	empty	empty	empty	empty	empty	6.07	3.86	3.74
23	*C1*	*N0*	*South*		3.43	3.65	4.01	3.96	empty	empty	empty	5.87	3.45	4.55
31	*C2*	*N0*	*North*		10.18	empty	8.44	empty	empty	empty	empty	5.86	4.56	4.69
29	*C2*	*N0*	*South*		12.51	12.28	7.18	15.67	empty	empty	empty	6.98	4.72	4.35
17	*C3*	*N0*	*North*		7.76	empty	4.01	empty	empty	empty	empty	5.49	5.56	5.22
19	*C3*	*N0*	*South*		6.52	7.62	empty	empty	empty	empty	empty	10.18	7.25	6.02
5	*C4*	*N0*	*North*		7.08	empty	empty	5.23	empty	empty	empty	8.36	6.34	6.97
9	*C4*	*N0*	*South*		7.65	8.77	7.03	empty	empty	empty	empty	6.28	4.72	5.33
27	*H1*	*N0*	*North*		2.62	2.63	3.61	6.26	empty	empty	empty	5.68	3.10	3.33
21	*H1*	*N0*	*South*		3.78	3.43	empty	5.79	5.76	1.58	empty	9.77	10.37	7.28
1	*H2*	*N0*	*North*		0.00	empty	0.00	empty	empty	empty	empty	2.18	3.14	2.45
3	*H2*	*N0*	*South*		0.01	2.06	empty	4.59	3.60	empty	empty	2.37	3.01	2.71
13	*H3*	*N0*	*North*		0.01	empty	empty	empty	empty	empty	empty	1.84	2.04	1.57
15	*H3*	*N0*	*South*		0.02	empty	3.57	4.13	empty	empty	3.95	3.23	2.31	2.20
7	*H4*	*N0*	*North*		2.26	2.72	2.04	empty	empty	empty	empty	3.02	2.29	2.33
11	*H4*	*N0*	*South*		1.69	2.61	3.53	2.84	0.61	0.12	empty	3.39	2.00	2.02
24	*C1*	*N1*	*South*		4.71	5.42	empty	5.67	empty	empty	empty	2.91	2.13	6.36
32	*C2*	*N1*	*North*		16.67	empty	empty	empty	empty	empty	empty	18.97	15.80	15.45
18	*C3*	*N1*	*North*		3.06	empty	empty	empty	empty	empty	empty	6.63	4.06	4.41
10	*C4*	*N1*	*South*		8.11	empty	empty	empty	empty	empty	empty	8.93	10.43	8.43
22	*H1*	*N1*	*South*		5.40	empty	empty	5.24	empty	empty	empty	4.77	3.61	5.50
4	*H2*	*N1*	*South*		2.03	empty	empty	empty	empty	empty	empty	6.35	5.98	4.06
16	*H3*	*N1*	*South*		4.17	empty	empty	empty	empty	empty	3.46	5.06	4.13	3.84
8	*H4*	*N1*	*North*		1.07	empty	2.04	2.92	empty	empty	empty	4.90	3.42	3.17
26	*C1*	*N2*	*North*		11.42	empty	10.22	9.15	6.48	empty	empty	16.55	13.60	12.43
30	*C2*	*N2*	*South*		15.40	19.31	18.81	empty	empty	empty	empty	19.19	19.25	15.01
20	*C3*	*N2*	*South*		19.88	empty	empty	empty	empty	empty	empty	23.71	25.13	16.67
6	*C4*	*N2*	*North*		9.81	10.38	8.81	empty	empty	empty	empty	28.52	45.15	29.47
28	*H1*	*N2*	*North*		5.10	empty	3.97	5.23	empty	empty	empty	7.90	4.73	3.89
2	*H2*	*N2*	*North*		0.15	1.61	3.17	empty	empty	empty	empty	9.77	5.89	4.69
14	*H3*	*N2*	*North*		14.53	14.53	9.03	empty	empty	empty	empty	14.94	16.51	7.44
12	*H4*	*N2*	*South*		6.73	8.81	3.38	4.15	9.39	empty	empty	11.21	8.93	9.32

	# of sample set				# 31	# 32	# 33	# 34	# 35	# 36	# 37	# 38	# 39	# 40
	date of sample set				6-Jan-94	20-Jan-94	27-Jan-94	17-Feb-94	25-Feb-94	7-Mar-94	21-Mar-94	5-Apr-94	14-Apr-94	28-Apr-94
	# of days since Br-application				428	442	449	470	478	488	502	517	526	540
# of sampler	*Management*	*N - rate*	*Placement*		*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*
25	*C1*	*N0*	*North*		5.10	5.33	5.84	5.64	6.77	8.24	8.09	7.62	7.83	8.20
23	*C1*	*N0*	*South*		flooded	4.04	5.94	flooded	flooded	4.52	4.28	4.15	4.73	5.21
31	*C2*	*N0*	*North*		4.46	4.90	4.36	5.64	5.94	6.78	7.19	7.02	7.19	7.65
29	*C2*	*N0*	*South*		4.73	5.21	4.92	5.27	5.47	6.72	6.81	7.40	6.98	7.98
17	*C3*	*N0*	*North*		4.88	4.10	4.33	4.71	5.95	8.45	9.24	9.30	8.04	8.37
19	*C3*	*N0*	*South*		7.59	7.18	8.94	7.20	6.94	5.74	5.46	5.20	4.91	5.12
5	*C4*	*N0*	*North*		6.62	6.26	5.70	6.43	6.88	5.38	5.36	7.51	5.82	5.01
9	*C4*	*N0*	*South*		3.71	4.30	4.23	4.05	2.72	1.39	3.11	2.81	3.15	3.40
27	*H1*	*N0*	*North*		2.87	1.20	5.00	4.18	flooded	3.47	3.30	3.56	3.12	2.54
21	*H1*	*N0*	*South*		flooded	6.22	7.34	7.09	flooded	6.36	5.75	6.75	6.61	6.87
1	*H2*	*N0*	*North*		3.95	3.76	2.03	1.12	0.86	0.22	0.03	0.00	0.00	0.00
3	*H2*	*N0*	*South*		4.33	3.70	2.20	2.71	2.26	1.03	0.71	0.44	0.13	0.03
13	*H3*	*N0*	*North*		3.80	3.78	2.24	3.25	3.11	2.48	1.77	1.29	0.54	0.38
15	*H3*	*N0*	*South*		2.27	2.18	2.09	2.07	1.80	1.23	1.02	1.01	0.45	0.21
7	*H4*	*N0*	*North*		2.51	2.31	1.83	2.46	2.48	1.71	1.88	2.03	1.12	0.60
11	*H4*	*N0*	*South*		2.28	2.26	1.61	1.75	2.51	2.55	2.51	2.46	2.04	1.43
24	*C1*	*N1*	*South*		flooded	4.52	7.36	flooded	flooded	6.25	6.27	5.37	5.87	6.53
32	*C2*	*N1*	*North*		23.74	23.23	13.58	17.78	21.60	22.41	21.36	24.63	24.01	23.80
18	*C3*	*N1*	*North*		4.37	4.17	5.47	3.11	7.97	10.76	8.75	9.57	4.37	4.43
10	*C4*	*N1*	*South*		10.67	14.24	14.67	11.31	12.13	10.15	14.71	13.93	13.86	13.13
22	*H1*	*N1*	*South*		flooded	3.56	4.45	4.18	flooded	3.84	3.02	3.03	2.06	3.42
4	*H2*	*N1*	*South*		9.16	7.28	6.15	6.54	5.80	5.05	4.79	3.65	3.89	4.74
16	*H3*	*N1*	*South*		3.68	3.42	2.67	2.84	1.85	0.77	0.92	0.64	0.37	0.30
8	*H4*	*N1*	*North*		6.78	6.46	5.24	5.98	5.43	3.55	2.64	2.03	0.63	0.19
26	*C1*	*N2*	*North*		16.42	17.82	19.37	15.93	18.99	18.92	21.74	23.06	23.89	23.60
30	*C2*	*N2*	*South*		14.02	15.04	17.24	14.29	14.47	13.30	15.48	15.10	12.97	14.41
20	*C3*	*N2*	*South*		26.11	25.73	17.30	18.62	18.64	18.04	17.52	19.41	18.76	17.23
6	*C4*	*N2*	*North*		84.82	37.32	24.69	17.63	20.77	21.07	24.65	24.88	25.84	25.65
28	*H1*	*N2*	*North*		3.78	1.57	5.28	5.59	flooded	6.62	6.23	6.53	6.29	5.14
2	*H2*	*N2*	*North*		8.86	7.11	4.82	8.13	6.45	4.24	3.00	2.26	0.56	0.08
14	*H3*	*N2*	*North*		15.94	21.43	18.75	17.88	18.24	21.00	19.85	20.62	17.94	12.24
12	*H4*	*N2*	*South*		7.92	7.55	7.70	9.55	9.15	11.02	12.70	11.03	11.46	10.86

	# of sample set			**# 41**	**# 42**	**# 43**	**# 44**	**# 45**	**# 46**	**# 47**
	date of sample set			**22-May-94**	**29-Jun-94**	**22-Jul-94**	**9-Sep-94**	**5-Oct-94**	**28-Oct-94**	**1-Nov-94**
	# of days since Br-application			**564**	**602**	**625**	**674**	**700**	**723**	**727**
# of sampler	*Management*	*N - rate*	*Placement*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*	*Concentration [mg/l]*
25	*C1*	*N0*	*North*	5.02	4.98	9.94	7.96	5.99	6.35	6.71
23	*C1*	*N0*	*South*	empty	6.19	5.67	empty	empty	flooded	flooded
31	*C2*	*N0*	*North*	3.90	4.73	3.14	2.24	1.74	4.86	5.95
29	*C2*	*N0*	*South*	3.38	6.51	6.77	6.08	empty	2.17	2.42
17	*C3*	*N0*	*North*	5.10	empty	10.20	empty	empty	6.42	6.42
19	*C3*	*N0*	*South*	empty	2.49	5.77	empty	empty	9.33	10.34
5	*C4*	*N0*	*North*	0.39	5.75	5.46	3.71	6.95	8.76	flooded
9	*C4*	*N0*	*South*	empty	3.38	3.90	2.82	empty	8.70	flooded
27	*H1*	*N0*	*North*	empty	1.77	2.55	2.26	empty	flooded	flooded
21	*H1*	*N0*	*South*	empty	3.92	4.40	empty	empty	flooded	flooded
1	*H2*	*N0*	*North*	0.04	0.93	2.20	3.57	empty	5.98	7.71
3	*H2*	*N0*	*South*	0.04	2.82	5.81	3.52	empty	7.66	11.71
13	*H3*	*N0*	*North*	empty	0.82	2.01	1.28	empty	2.32	2.16
15	*H3*	*N0*	*South*	empty	1.14	1.48	1.12	empty	5.96	4.61
7	*H4*	*N0*	*North*	empty	1.04	1.60	1.47	empty	1.97	flooded
11	*H4*	*N0*	*South*	empty	empty	empty	empty	empty	empty	2.58
24	*C1*	*N1*	*South*	empty	empty	6.67	empty	empty	flooded	flooded
32	*C2*	*N1*	*North*	16.48	13.39	25.35	16.31	empty	20.55	20.76
18	*C3*	*N1*	*North*	empty	empty	10.68	empty	6.43	12.03	9.50
10	*C4*	*N1*	*South*	empty	9.75	12.97	4.46	empty	14.36	13.75
22	*H1*	*N1*	*South*	empty	3.08	2.75	3.06	empty	flooded	flooded
4	*H2*	*N1*	*South*	4.19	3.13	4.52	3.14	3.12	7.71	10.95
16	*H3*	*N1*	*South*	empty	1.07	1.02	empty	empty	4.52	5.40
8	*H4*	*N1*	*North*	0.24	empty	1.51	6.82	empty	8.30	flooded
26	*C1*	*N2*	*North*	21.90	11.84	21.80	9.80	empty	30.82	28.98
30	*C2*	*N2*	*South*	empty	5.71	9.30	5.78	empty	15.50	19.38
20	*C3*	*N2*	*South*	empty	18.66	19.20	18.83	empty	22.51	20.68
6	*C4*	*N2*	*North*	empty	25.95	30.37	empty	empty	23.53	flooded
28	*H1*	*N2*	*North*	empty	4.45	6.56	4.73	empty	flooded	flooded
2	*H2*	*N2*	*North*	empty	5.04	5.90	3.84	empty	25.63	17.66
14	*H3*	*N2*	*North*	empty	10.98	13.12	8.85	empty	15.50	16.07
12	*H4*	*N2*	*South*	5.93	empty	8.39	4.52	empty	8.41	8.18