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Argonne NATIONAL LABORATORY

Update on the Aquifer/Wetlands Restoration Project at Utica, Nebraska, with Recommendations for Remapping of the Carbon Tetrachloride Contamination in Groundwater

Environmental Science Division

USDA United States Department of Agriculture

Work sponsored by Commodity Credit Corporation, United States Department of Agriculture

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by
Applied Geosciences and Environmental Management Section
Environmental Science Division, Argonne National Laboratory

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United States Department of Agriculture

Work sponsored by Commodity Credit Corporation,
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Contents

Figures

Figures (Cont.)

Tables

Notation

BGL	below ground level
°C	degree(s) Celsius
CCC	Commodity Credit Corporation
EPA	U.S. Environmental Protection Agency
ft	foot (feet)
gal	gallon(s)
GWEX	groundwater extraction
hr	hour(s)
in.	inch(es)
kg	kilogram(s)
µg/L	microgram(s) per liter
MW	monitoring well
NDEQ	Nebraska Department of Environmental Quality
NGPC	Nebraska Game and Parks Commission
NPDES	National Pollutant Discharge Elimination System
USDA	U.S. Department of Agriculture
VOC	volatile organic compound

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1 Introduction

1.1 Background

In 1992-1993, Argonne National Laboratory investigated potential carbon tetrachloride contamination that might be linked to the former grain storage facility operated by the Commodity Credit Corporation (CCC) of the U.S. Department of Agriculture (USDA) at Utica, Nebraska. These initial studies identified carbon tetrachloride in a plume of contaminated groundwater, extending approximately 3,500 ft southeastward from the former CCC/USDA facility, within a shallow upper aquifer that had been used previously as a municipal water source by the town (Figure 1.1). A deeper aquifer used as the current municipal water source was found to be free of carbon tetrachloride contamination. Although the shallow aquifer was no longer being used as a source of drinking water at Utica, additional studies indicated that the carbon tetrachloride could pose an unacceptable health threat to potential future residents who might install private wells along the expected downgradient migration pathway of the plume. On the basis of these findings, corrective action was recommended to decrease the carbon tetrachloride concentrations in the upper aquifer to acceptable levels (Argonne 1993a,b, 1995).

Initial discussions with the Utica village board indicated that any restoration strategies involving nonbeneficial discharge of treated groundwater in the immediate vicinity of Utica would be unacceptable to the town. To address this concern, the CCC/USDA and Argonne, in cooperation with multiple federal and state regulatory and environmental agencies (Table 1.1) proposed a treatment strategy for the Utica groundwater employing groundwater extraction coupled with the seasonal use of agricultural spray irrigation equipment to simultaneously (1) remove carbon tetrachloride from the groundwater (by volatilization to the atmosphere) and (2) discharge the treated groundwater to enhance the development of wetlands in the North Lake Basin Wildlife Management Area, just north of the town (Argonne 2000).

To develop this treatment approach, additional groundwater sampling was conducted to update the distribution of carbon tetrachloride in groundwater identified in the preliminary studies in 1992-1993. In March 1998, detailed mapping of the carbon tetrachloride plume was performed by using the Argonne cone penetrometer (CPT) vehicle to collect groundwater

samples for analyses for volatile organic compounds (VOCs) at 13 locations (PS01-PS09, PS12, PS16, PS17, PS19; Figure 1.2). The samples were collected in vertical profiles through the aquifer, at 10-ft intervals. The results of this 1998 study (Table 1.2) demonstrated that the three-dimensional distribution of carbon tetrachloride in the aquifer is complex, with multiple "hot spots" occurring in the plume at various depths and distances along its length (Argonne 2000).

In October 2002, the CCC/USDA requested that Argonne perform targeted groundwater sampling at Utica to document the migration of the carbon tetrachloride plume since the 1998 sampling event. In February 2003, vertical-profile groundwater sampling for VOCs analyses was conducted at 8 selected locations (PS01, PS04-PS07, PS12, PS19, PS20; Figure 1.2 and Table 1.3). The lateral and vertical configuration of the carbon tetrachloride plume, as identified in the 2003 study (Argonne 2003), is illustrated in Figures 1.3-1.7.

On the basis of the 2003 groundwater sampling results, a remedial system employing four extraction wells (GWEX 1-GWEX 4), with groundwater treatment by spray irrigation and conventional air stripping, was implemented at Utica, with the concurrence of the CCC/USDA and the agencies identified in Table 1.1. The principal components of the Utica system (shown in Figure 1.8) are described briefly in Section 1.2. Operation of well GWEX4 and the associated air stripper began on October 29, 2004, and routine operation of wells GWEX1-GWEX3 and the spray irrigation treatment units began on November 22, 2004.

1.2 Overview of the Aquifer Restoration Facilities at Utica

1.2.1 Wells GWEX1-GWEX3 and the Spray Irrigation Treatment Units

Extraction wells GWEX1-GWEX3, located in the northern portion of the town, are used to extract contaminated groundwater from the upgradient portion of the contaminant plume. Construction data for these wells are summarized in Table 1.4. These wells are linked by a distribution system that selectively carries untreated groundwater to either of two discharge points in the northern and southern subbasins of the North Lake Basin Wildlife Management Area (Figure 1.8). At each discharge point, the water is treated to remove carbon tetrachloride by using a custom spray irrigation treatment unit (Figure 1.9). These three extraction wells are operated simultaneously to maintain a critical operating pressure at each treatment unit.

Wells GWEX1-GWEX3 are operated intermittently during the year, subject to local weather conditions and in consultation with the Nebraska Game and Parks Commission (NGPC). NGPC owns most of the property occupied by the wetlands and has administrative and technical responsibility for management of the wildlife area.

1.2.2 Well GWEX4 and the Conventional Air Stripper

Extraction well GWEX4, located near the downgradient toe of the carbon tetrachloride plume (Figure 1.8), is operated continuously as a containment well. Construction data for GWEX4 are in Table 1.4. Groundwater produced from GWEX4 is treated by using a conventional (shallow-tray) air stripping technique, and the effluent is discharged to the surface for reinfiltration into the shallow Utica aquifer.

1.2.3 Monitoring Well Network

A network of seven permanent monitoring points has been established at Utica (Figure 1.8). Wells SB48, SB71, and SB72 were constructed during the early phases of the investigations at Utica. These wells were intended primarily for the measurement of groundwater levels; they do not penetrate the more contaminated zones of the groundwater column identified subsequently in detailed vertical-profile sampling (Argonne 2000, 2003). To improve monitoring coverage, additional wells MW1-MW4 were installed in August 2005 at strategic locations along the plume migration pathway. Construction data for the monitoring wells at Utica are in Table 1.5.

TABLE 1.1 Agencies participating with the CCC/USDA and Argonne in the Utica-North Lake Basin aquifer and wetlands restoration program.

U.S. Environmental Protection Agency Region VII
Nebraska Department of Environmental Quality
Nebraska Game and Parks Commission
U.S. Department of Agriculture, Natural Resources Conservation Service
U.S. Fish and Wildlife Service
Upper Big Blue Natural Resource District
Rainwater Basin Joint Venture
City of Utica, Nebraska

TABLE 1.2 Analytical results for groundwater samples collected at Utica in March 1998.

Location	Sampling Interval (ft BGL)	Concentration (μg/L) Carbon Tetrachloride	Chloroform	Location	Sampling Interval (ft BGL)	Concentration (μg/L) Carbon Tetrachloride	Chloroform
Cone penetrometer locations							
PS01	84-93	129	4.7	PS07	80-89	260	6.5
	94-103	282	4.1		90-99	256	< 2
	104-113	296	5.6		100-109	397	6.1
	114-123	47	< 2		110-119	294	2.9
	124-133	28	< 2		120-129	< 2	< 2
					130-136	< 2	< 2
PS02	95-104	< 2	< 2				
	105-114	4.2	< 2	PS08	80-89	< 2	< 2
	115-124	5.3	< 2		90-99	< 2	< 2
	125-134	2.8	< 2		100-109	< 2	< 2
	135-144	< 2	< 2		110-119	< 2	< 2
PS03	84-93	< 2	< 2	PS09	85-94	51	4.3
	94-103	< 2	< 2		95-104	< 2	< 2
	104-113	< 2	< 2		105-114	< 2	< 2
	114-123	< 2	< 2		115-124	< 2	< 2
	124-133	< 2	< 2				
	134-143	< 2	< 2	PS12	82-93	< 2	< 2
					93-102	6.3	< 2
PS04	80-89	433	14		103-112	< 2	< 2
	90-99	144	7.3		113-122	< 2	< 2
	100-109	< 2	< 2		123-125	< 2	< 2
	110-119	< 2	< 2				
	120-129	< 2	< 2	PS16	85-94	< 2	< 2
	130-139	< 2	< 2		95-104	< 2	< 2
					105-114	< 2	< 2
PS05	85-94	202	12		115-124	< 2	< 2
	95-104	< 2	< 2				
	105-114	< 2	< 2	PS17	86-95	< 2	< 2
	115-123	< 2	< 2				
				PS19	83-92	< 2	< 2
PS06	82-91	< 2	< 2		93-102	7.1	< 2
	92-101	30	< 2		103-112	25	< 2
	102-111	24	6.5		113-122	219	3.2
	112-121	23	3.6		123-132	159	2.3
	122-131	8.3	< 2		133-142	31	< 2
	132-141	< 2	< 2				

TABLE 1.2 (Cont.)

Location	Sampling Interval (ft BGL)	Concentration (μg/L) Carbon Tetrachloride	Chloroform
Monitoring wells			
SB48	83.5-93.5	2.4	< 2
SB71	84-94	< 2	< 2
SB72	82.5-112.5	13	< 2

TABLE 1.3 Analytical results for groundwater samples collected at Utica in February 2003.

Location	Sampling Interval (ft BGL)	Concentration (μg/L) Carbon Tetrachloride	Chloroform	Location	Sampling Interval (ft BGL)	Concentration (μg/L) Carbon Tetrachloride	Chloroform
Cone penetrometer locations							
PS01	84-93	ND[a]	ND	PS12	82-93	ND	ND
	94-103	145[a]	3.7		93-102	0.7 J	ND
	104-113	184	9.6		103-112	0.7 J	ND
	114-123	42	10		113-122	ND	ND
	124-133	14	1.5		123-132	ND	ND
	134-143	ND	ND				
				PS19	83-92	6.2	1.6
PS04	80-89	173	10		93-102	ND	1.9
	90-99	87	6.7		103-112	1.8	1.6
	100-109	5.6	ND		113-122	9.3	ND
	110-119	ND	ND		123-132	4.9	ND
					133-142	0.6 J	ND
PS05	85-94	759	31				
	95-104	0.5 J[b]	ND	PS20	83-92	6.0	0.4 J
					93-102	11	ND
PS06	82-91	ND	ND		103-112	89	2.8
	92-101	2.0	ND		113-122	30	1.0
	102-111	94	5.4		123-132	4.3	ND
	112-121	100	3.3		133-142	ND	ND
	122-131	41	0.8 J				
PS07	80-89	57	2.1				
	90-99	22	1.6				
	100-109	21	1.7				
	110-119	28	ND				
	120-129	34	8.2				
Monitoring wells							
SB48	83.5-93.5	0.9 J	ND				
SB71	84-94	19	ND				
SB72	82.5-112.5	4.8	ND				

[a] ND, contaminant not detected.

[b] Qualifier J indicates an estimated concentration below the quantitation limit of 1.0 μg/L for purge-and-trap analysis.

TABLE 1.4 Summary of construction details for GWEX wells at Utica.

	Depth (ft BGL)			
Well	Total Depth	Screen Interval	Gravel Pack Interval	Casing Diameter (in.)
GWEX1	132	106-126	97-132	8
GWEX2	148	110-145	106-148	8
GWEX3	146	105-140	101-146	8
GWEX4	150	115-145	110-150	6

TABLE 1.5 Summary of construction details for monitoring wells at Utica.

	Depth (ft BGL)			
Well	Total Depth	Screen Interval	Gravel Pack Interval	Casing Diameter (in.)
MW1	108	85-105	83-108	2
MW2	117	90-115	88-117	2
MW3	128	100-125	98-128	2
MW4	128	100-125	98-128	2
SB48	98.5	83.5-93.5	78.4-98.5	2
SB71	94.2	84-94	84-94	2
SB72	128	82.6-112.6	78-128	4

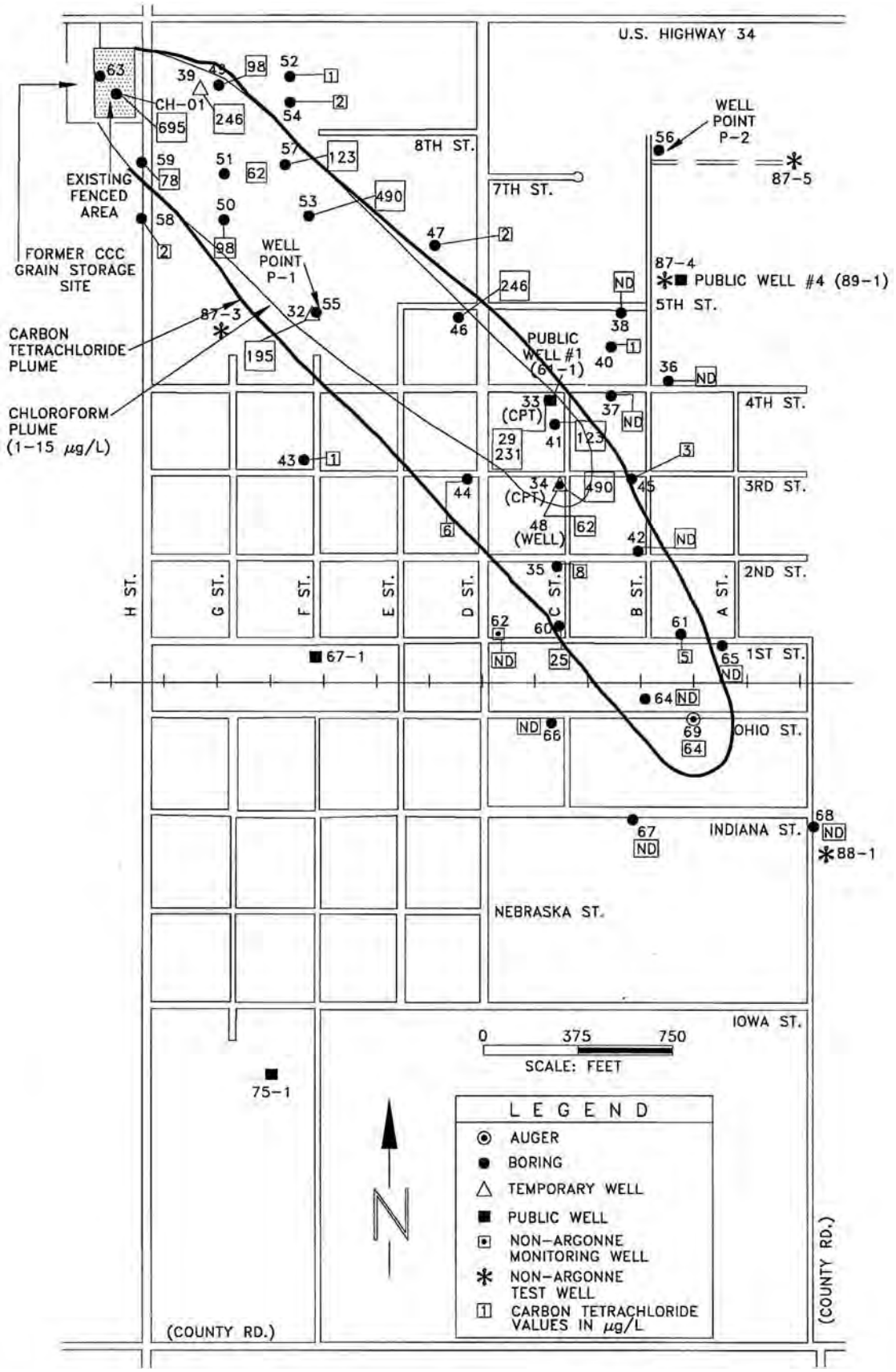

FIGURE 1.1 Distribution of carbon tetrachloride (µg/L) in the Utica shallow aquifer, as identified in 1992-1993.

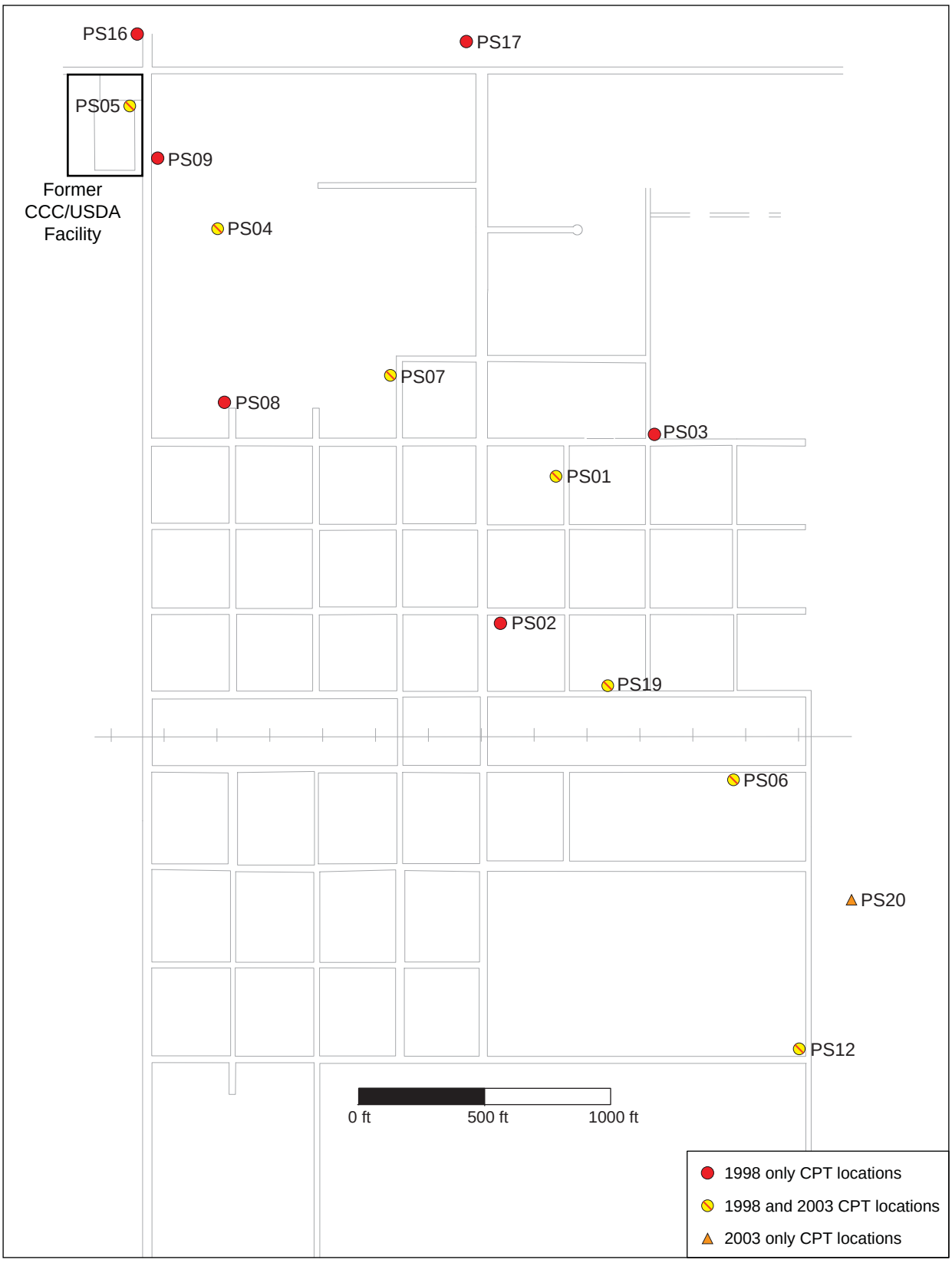

FIGURE 1.2 Locations of vertical-profile groundwater sampling with the Argonne cone penetrometer vehicle in 1998 and 2003.

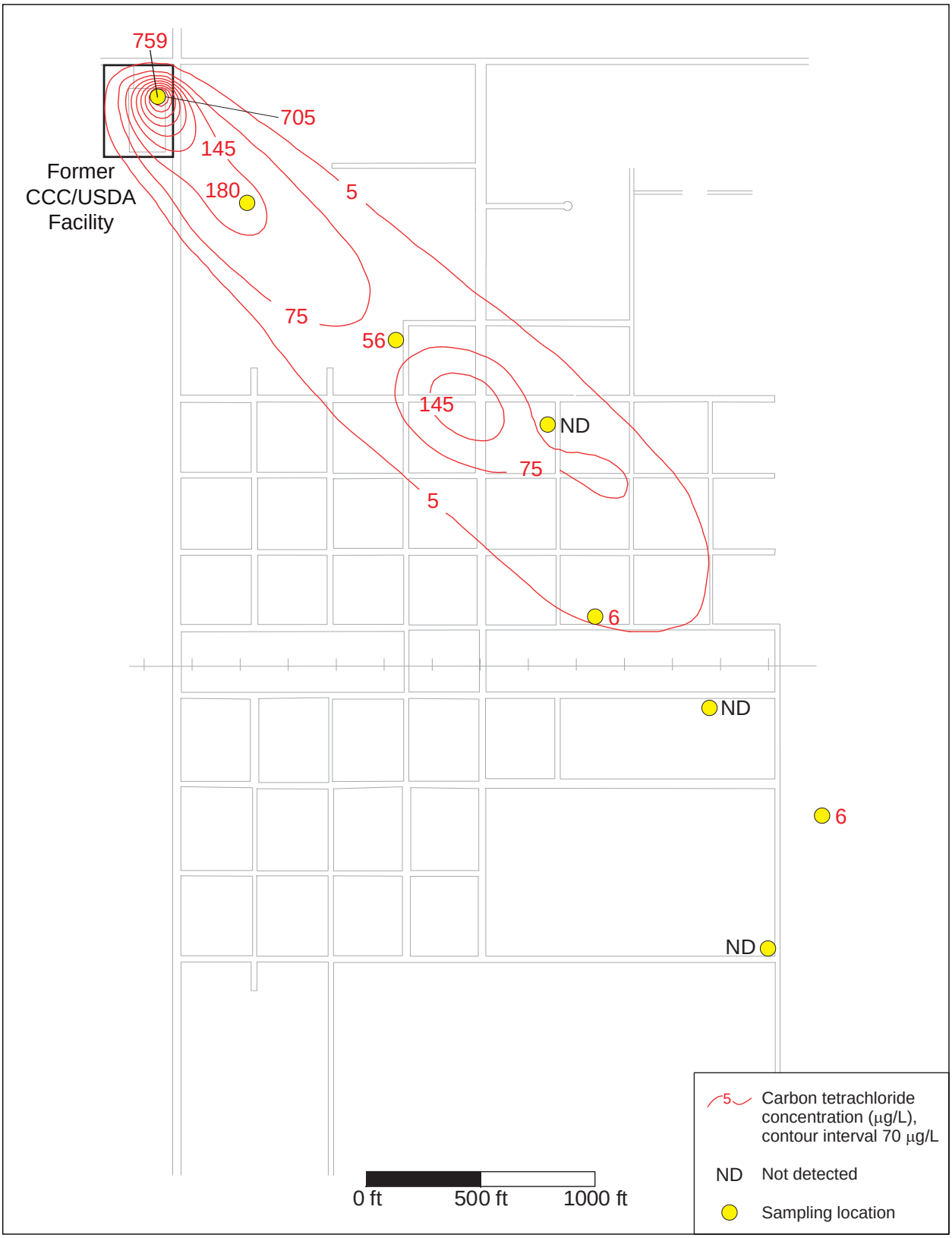

FIGURE 1.3 Carbon tetrachloride concentrations (µg/L) in groundwater at Utica in February 2003, at the depth interval 80-90 ft BGL.

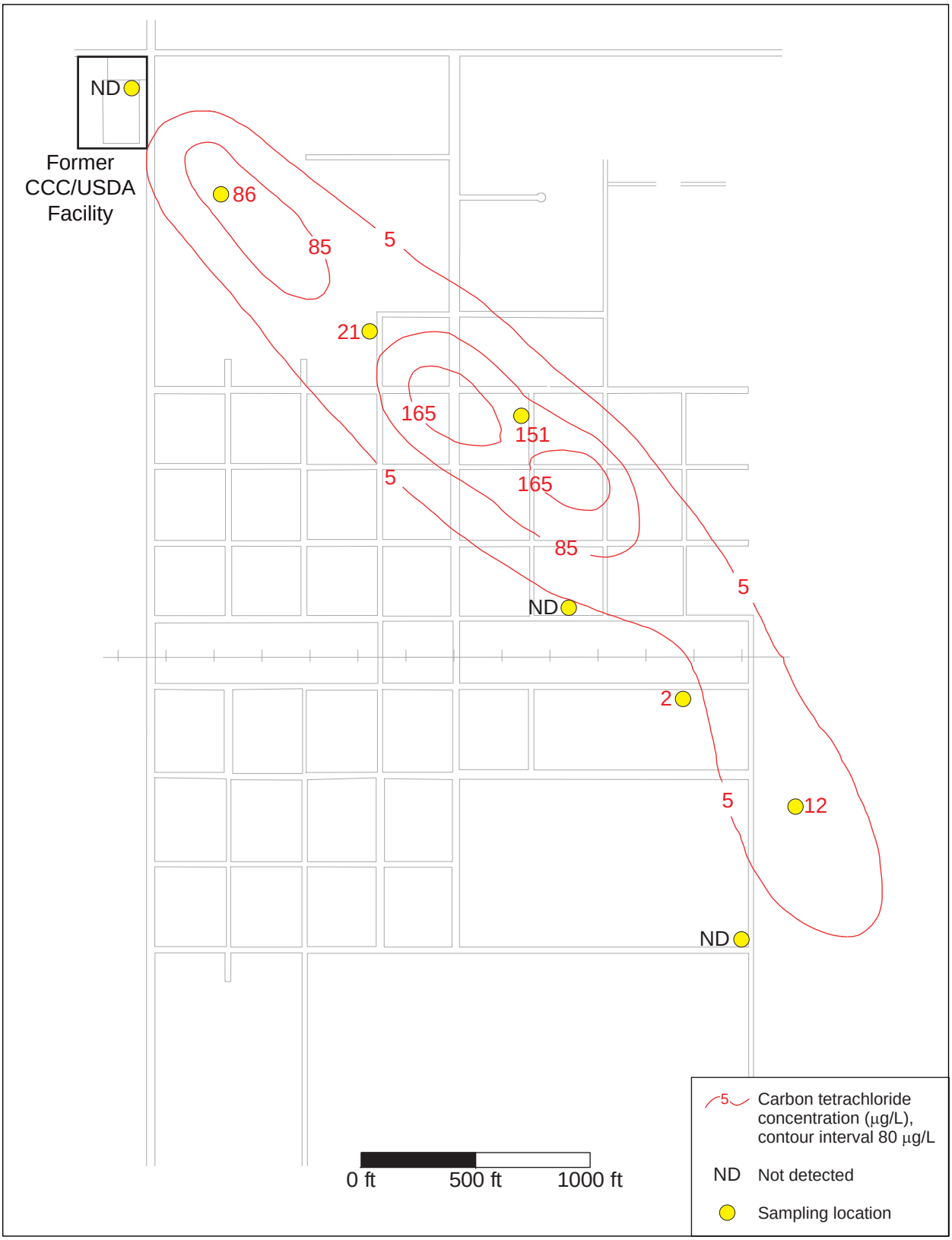

FIGURE 1.4 Carbon tetrachloride concentrations (µg/L) in groundwater at Utica in February 2003, at the depth interval 90-100 ft BGL.

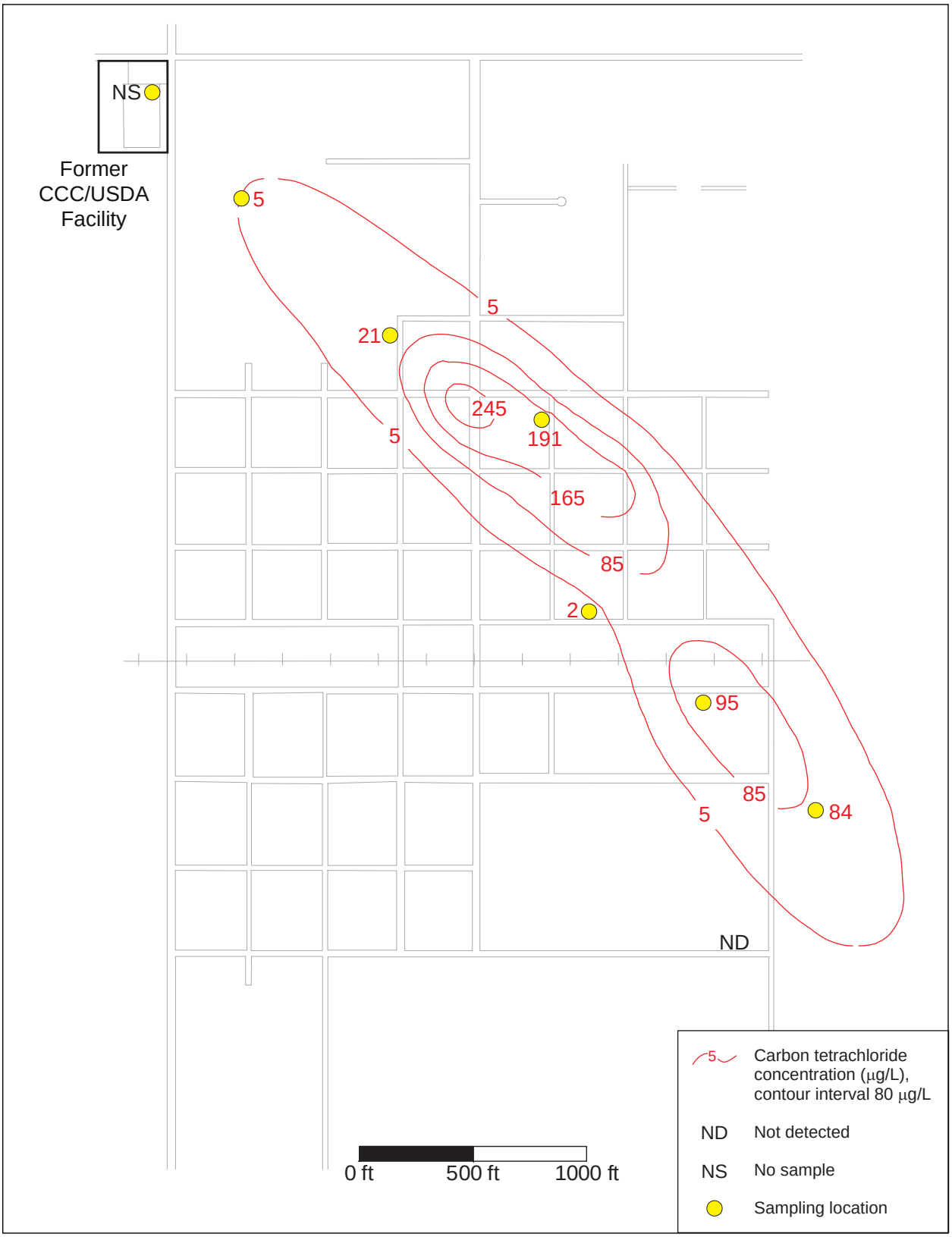

FIGURE 1.5 Carbon tetrachloride concentrations (µg/L) in groundwater at Utica in February 2003, at the depth interval 100-110 ft BGL.

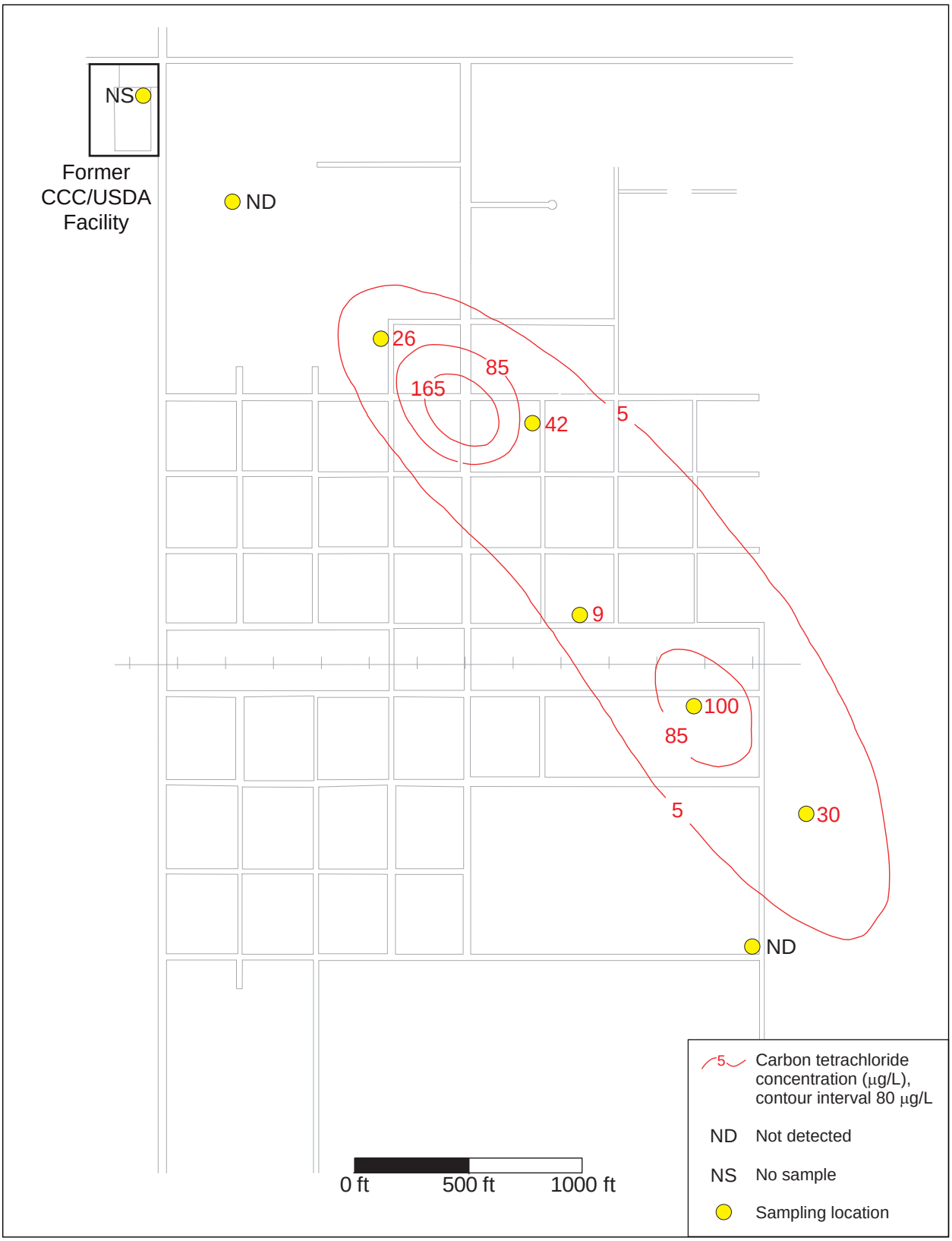

FIGURE 1.6 Carbon tetrachloride concentrations (µg/L) in groundwater at Utica in February 2003, at the depth interval 110-120 ft BGL.

FIGURE 1.7 Carbon tetrachloride concentrations (µg/L) in groundwater at Utica in February 2003, at the depth interval 120-130 ft BGL.

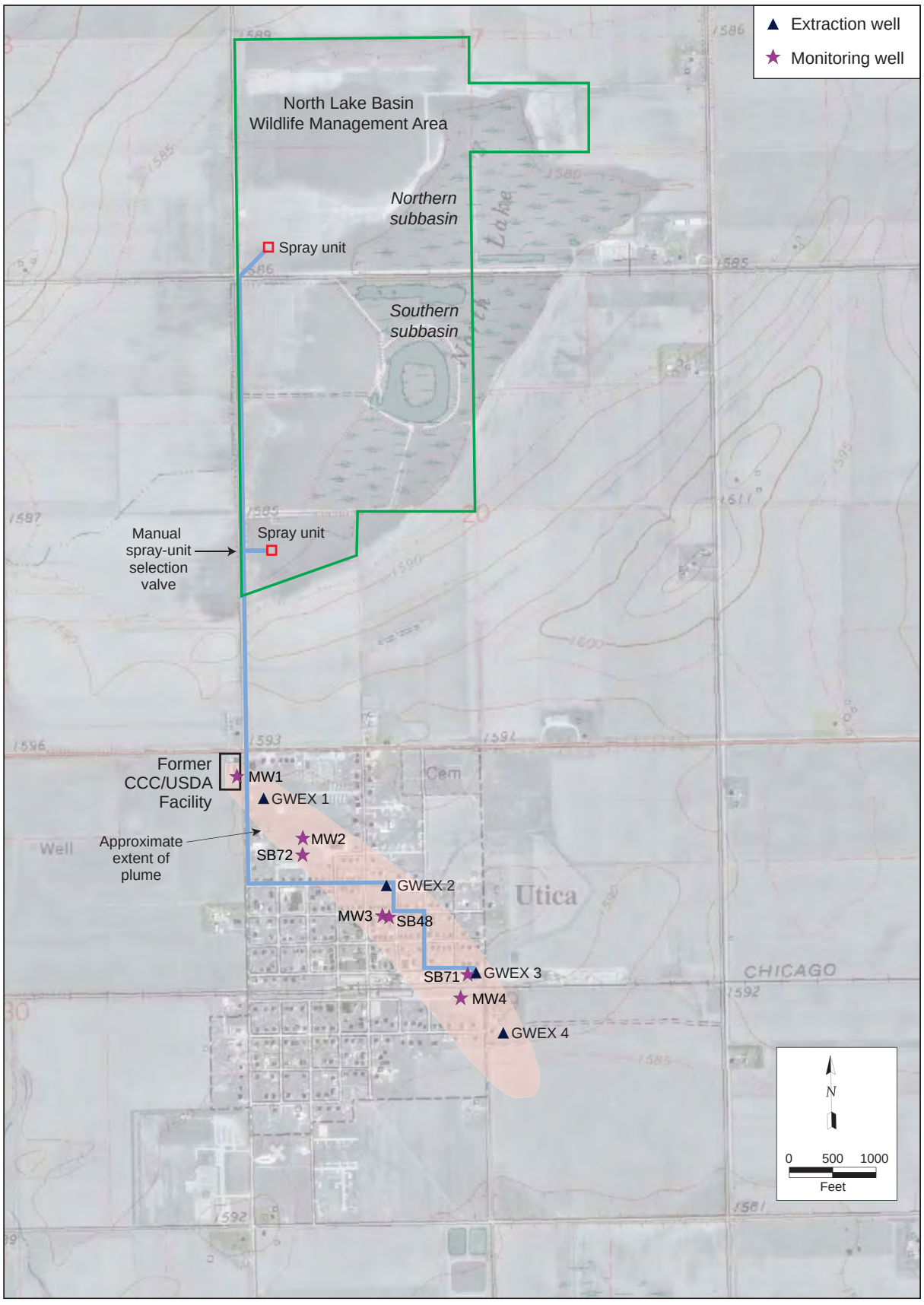

FIGURE 1.8 Locations of the restoration facilities, contaminant plume, and permanent monitoring wells at Utica.

FIGURE 1.9 Spray irrigation unit in operation at Utica.

2 Regulatory Status and Performance of the Utica Program

The CCC/USDA's primary objective for the aquifer restoration at Utica is the treatment of carbon tetrachloride contamination in the shallow aquifer. The combined aquifer and wetlands restoration effort was undertaken voluntarily by the CCC/USDA, in cooperation with the agencies listed in Table 1.1. Throughout the conception, planning, design, and implementation of this program, the CCC/USDA has maintained specific communication with the U.S. Environmental Protection Agency (EPA) Region VII, the Nebraska Department of Environmental Quality (NDEQ), and NGPC to keep these agencies apprised of the CCC/USDA's activities at Utica and the North Lake Basin.

2.1 Regulatory Status and Compliance Monitoring

The only regulatory instrument presently governing the CCC/USDA operation at Utica is a National Pollutant Discharge Elimination System (NPDES) permit (No. NE0137456) granted by the NDEQ, which specifies certain water quality criteria (pH, carbon tetrachloride content, and chloroform content) that must be met by the treated groundwater discharged to the waters of Nebraska. The permit identifies three separate outfalls from the groundwater treatment operations at the site, representing discharges from (1) the north spray irrigation unit, (2) the south spray irrigation unit, and (3) the air stripper at GWEX4 (Figure 1.8). The results of groundwater compliance monitoring performed in accord with the NPDES permit requirements are reported to the NDEQ on a quarterly basis (under the Discharge Monitoring Reports system). The results are summarized in *Operations and Performance* reports prepared by Argonne for each year of system operation at the site (Argonne 2005, 2006, 2008, 2009).

The results of the NPDES compliance monitoring for the period November 2004 to September 2009 are summarized in Table 2.1. *To date, all regulatory requirements established under the NPDES permit for the Utica restoration systems have been achieved.*

2.2 Restoration of the Utica Aquifer

In cooperation with the agencies listed in Table 1.1, the CCC/USDA and Argonne developed and have implemented a supplemental *Monitoring Plan* for the Utica aquifer restoration program (Argonne 2004). The *Monitoring Plan* identifies both initial (conducted at system start-up) and subsequent long-term monitoring activities intended to (1) document the

effectiveness of the individual groundwater treatment processes, and (2) provide data necessary to demonstrate the performance of these systems in achieving restoration of the contaminated shallow aquifer. The results of the monitoring activities conducted under this program are included in the annual *Operations and Performance* reports for Utica (Argonne 2005, 2006, 2008, 2009).

The long-term monitoring activities recommended (in the accepted *Monitoring Plan*) to track the restoration of the Utica groundwater include the following (Argonne 2004):

- Monthly recording of the volumes of groundwater extracted by wells GWEX1-GWEX4
- Monthly sampling of the untreated groundwater extracted by wells GWEX1-GWEX4, for VOCs analyses
- Quarterly sampling of monitoring wells MW1-MW4, SB48, SB71, and SB72 for VOCs analyses
- Reassessment of the carbon tetrachloride distribution in groundwater at 5-yr intervals following the start-up of the treatment facilities

The results of the monitoring activities performed under this program to date are briefly summarized in Table 2.2 and Figures 2.1-2.5. Figures 2.1-2.4 illustrate the carbon tetrachloride concentrations measured at GWEX1-GWEX4, respectively, since the routine operation of these wells began in November 2004. Complete monitoring data for wells MW1-MW4, since sampling at these points began in September 2005, are depicted in Figure 2.5.

Table 2.2 indicates that *approximately 414 million gallons of contaminated groundwater have been extracted and treated at Utica (as of September 2009), resulting in the removal of approximately 97 kg of carbon tetrachloride from the contaminated shallow aquifer.* The identified carbon tetrachloride concentrations at downgradient wells GWEX2-GWEX4 (Figure 1.8 and Figures 2.2-2.4) have shown a slow decline during the period of record, although short-term variability is apparent within the generally decreasing trend for each well. In contrast, carbon tetrachloride concentrations at upgradient well GWEX1 (Figures 1.8 and 2.1) have been highly variable and show no consistent trend.

Except for MW1, carbon tetrachloride concentrations at all of the monitoring wells (Figure 2.5) have been relatively stable, with no persistently rising or falling trends. Carbon tetrachloride concentrations at MW1 have been consistently greater than those at downgradient monitoring wells MW2-MW4 (Figures 1.8 and 2.5). Concentrations at MW1 increased to a maximum in June-October 2007 (Figure 2.5). Since October 2007, the concentrations observed at MW1 have decreased significantly.

Wells MW1 and GWEX1 are located, respectively, on and near the former CCC/USDA facility property (Figure 1.8). Together, the data for MW1 and GWEX1 (Figures 2.1 and 2.5) might reflect a transient, localized influx of carbon tetrachloride to the upgradient shallow groundwater, from residual contamination in the soils beneath the former CCC/USDA facility (Argonne 2000, 2003). The stable or decreasing contaminant levels observed at all of the downgradient monitoring and GWEX wells suggest, however, that GWEX1 has acted effectively as an upgradient capture well.

TABLE 2.1 Results of NPDES groundwater compliance monitoring at Utica, November 2004 to September 2009.

Period of Operation	GWEX1-GWEX3 Spray Irrigation Discharge				GWEX4 Air Stripper Discharge			
	pH[a]		Carbon Tetrachloride[b]		pH[a]		Carbon Tetrachloride[b]	
	Min	Max	Max (μg/L)	Avg (μg/L)	Min	Max	Max (μg/L)	Avg (μg/L)
2004-2005	7.01	8.18	7.2	1.2	7.01	8.35	< 0.1	< 0.1
2005-2006	7.10	8.32	6.9	1.1	7.50	8.58	< 0.1	< 0.1
2006-2007	7.09	8.36	3.7	0.6	7.79	8.33	< 0.1	< 0.1
2007-2008	7.88	8.51	4.0	1.0	7.48	8.40	< 0.1	< 0.1
2008-2009	7.85	8.43	1.9	0.4	6.73	8.45	< 0.1	< 0.1

[a] The acceptable pH limits for discharges under the NPDES permit are 6.5 to 9.0.

[b] The maximum acceptable carbon tetrachloride concentration for discharges under the NPDES permit is 44.2 μg/L.

TABLE 2.2 Results of the groundwater extraction and treatment effort at Utica, November 2004 to September 2009.

Period of Operation	GWEX1-GWEX3		GWEX4	
	Production (gal)	Carbon Tetrachloride Removed (kg)	Production (gal)	Carbon Tetrachloride Removed (kg)
2004-2005	34,611,960	14.2	31,752,692	9.0
2005-2006	84,365,500	29.2	29,584,010	5.0
2006-2007	90,954,300	21.8	28,320,380	3.0
2007-2008	25,675,200	6.0	29,553,474	2.0
2008-2009	36,867,600	6.0	22,078,421	1.2
TOTALS	272,474,560	77.2	141,288,977	20.2

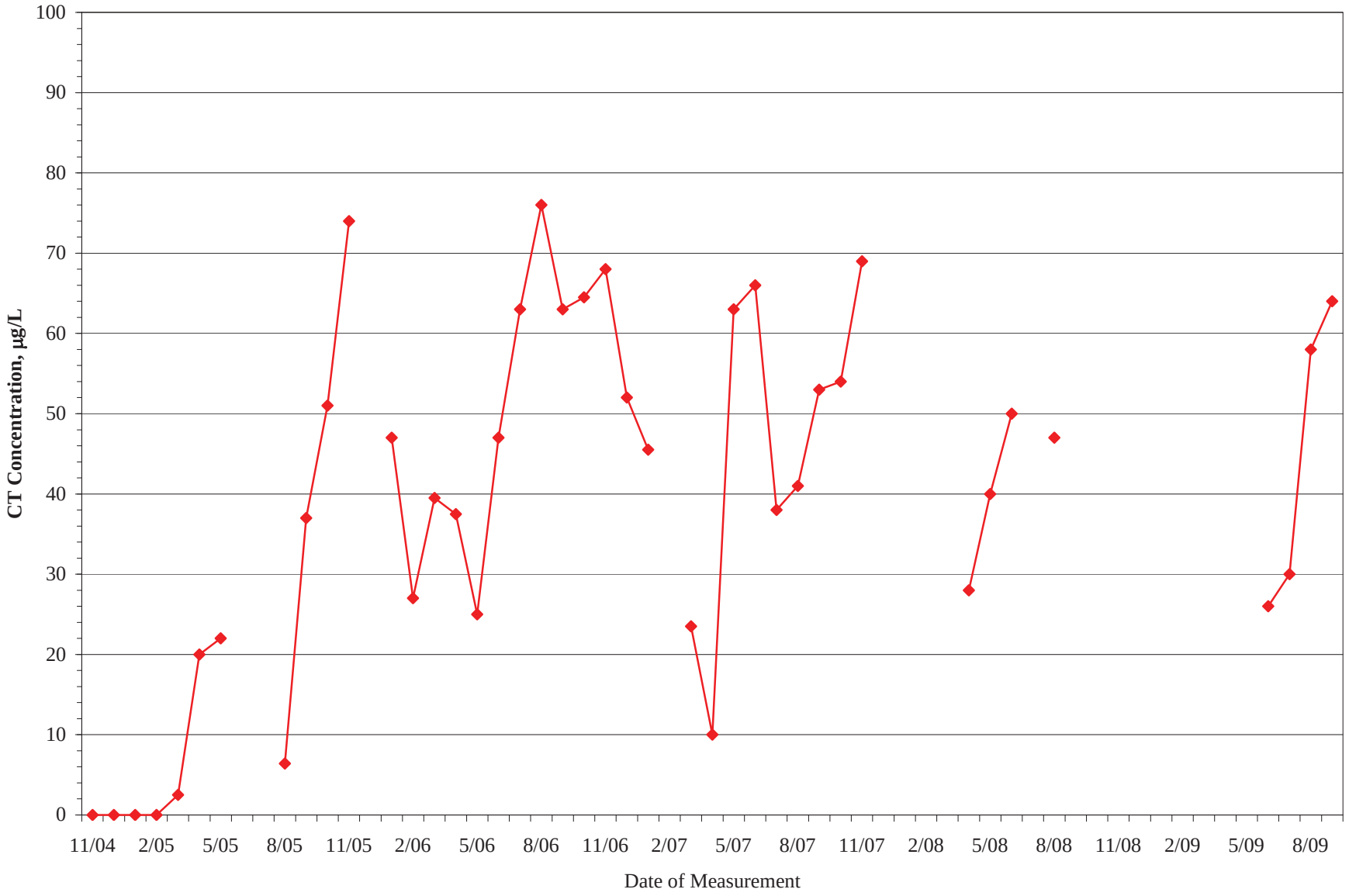

FIGURE 2.1 Measured carbon tetrachloride concentrations (µg/L) in groundwater extracted by GWEX1, 2004-2009.

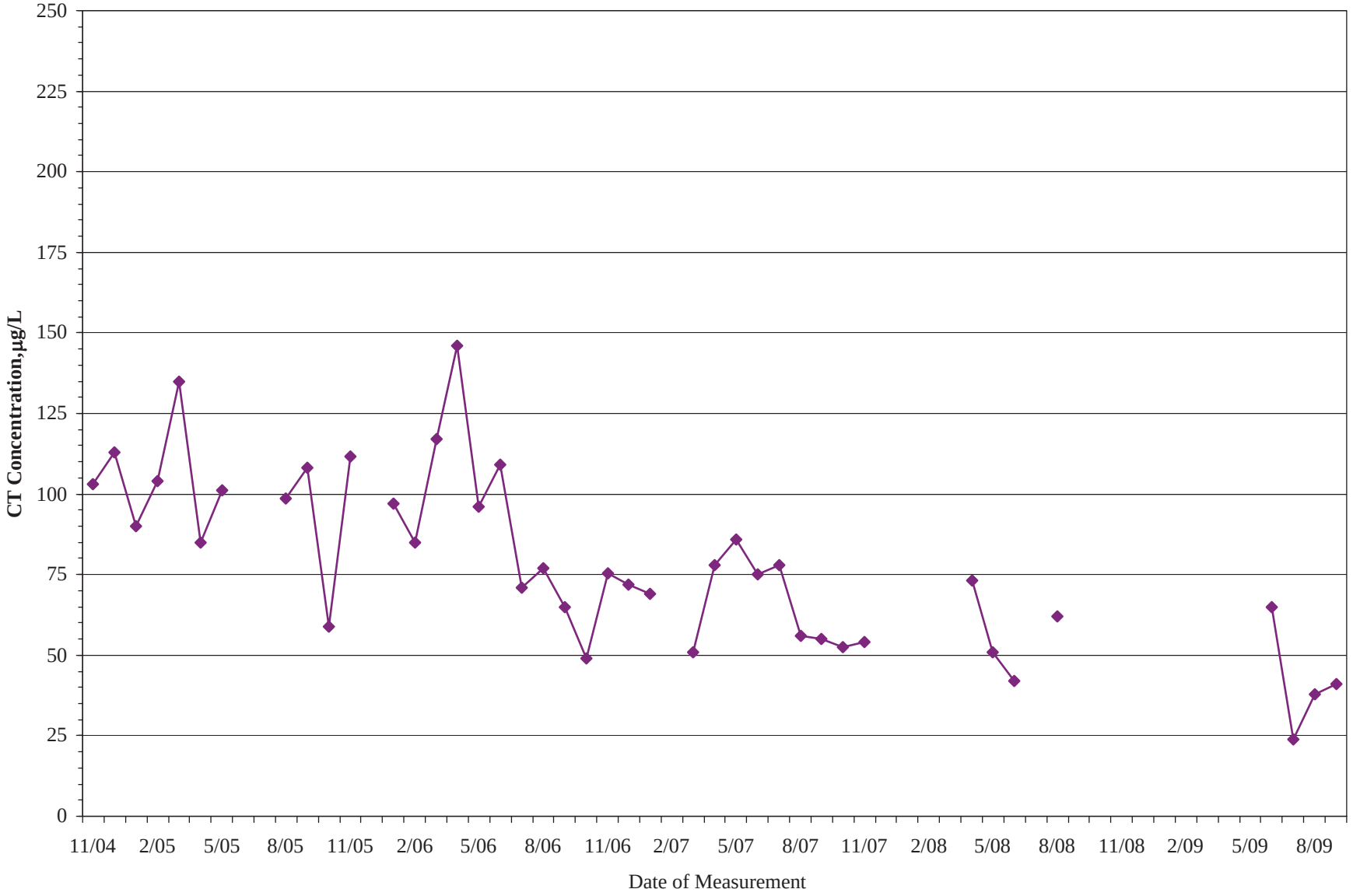

FIGURE 2.2 Measured carbon tetrachloride concentrations (µg/L) in groundwater extracted by GWEX2, 2004-2009.

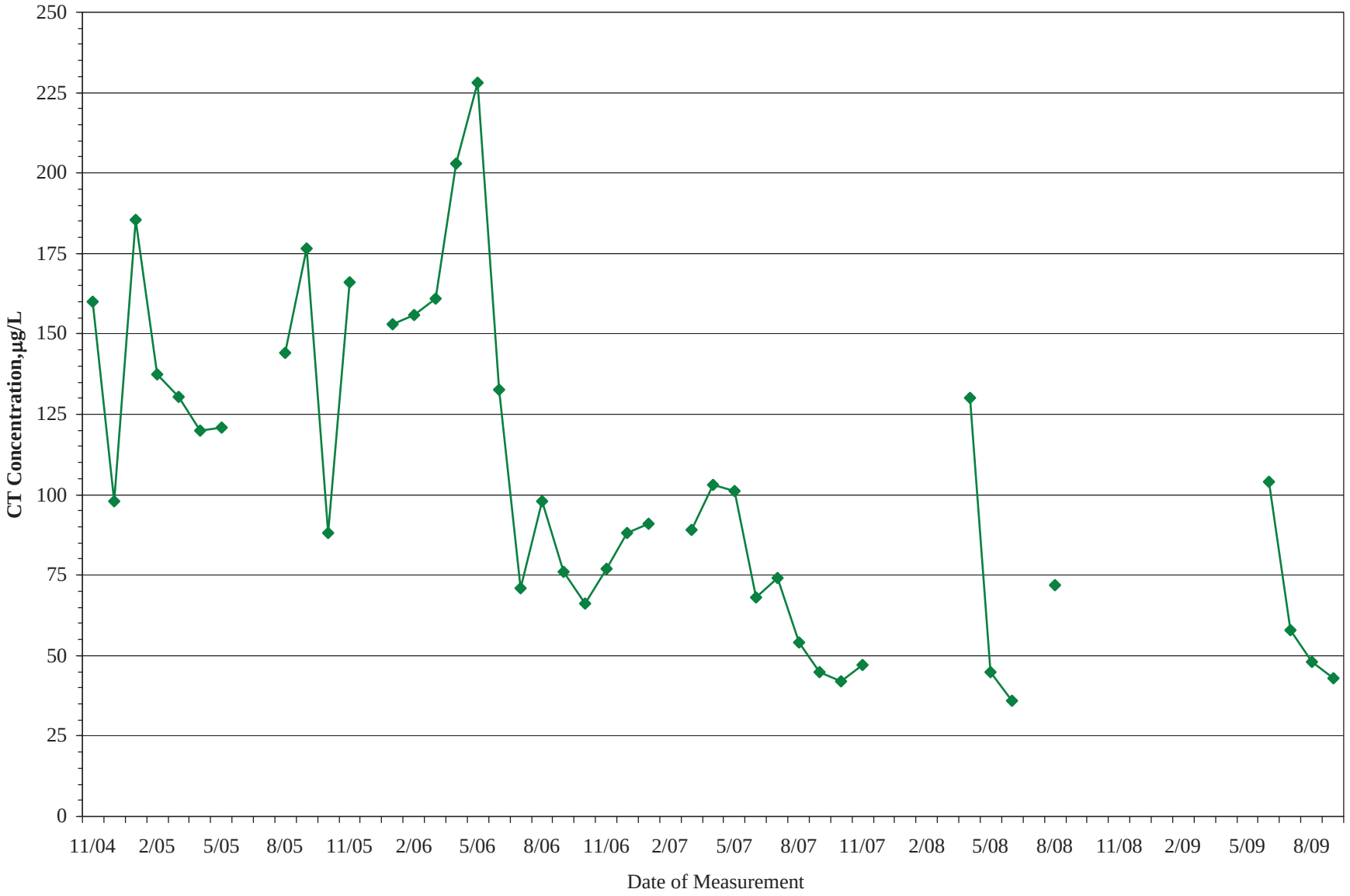

FIGURE 2.3 Measured carbon tetrachloride concentrations (µg/L) in groundwater extracted by GWEX3, 2004-2009.

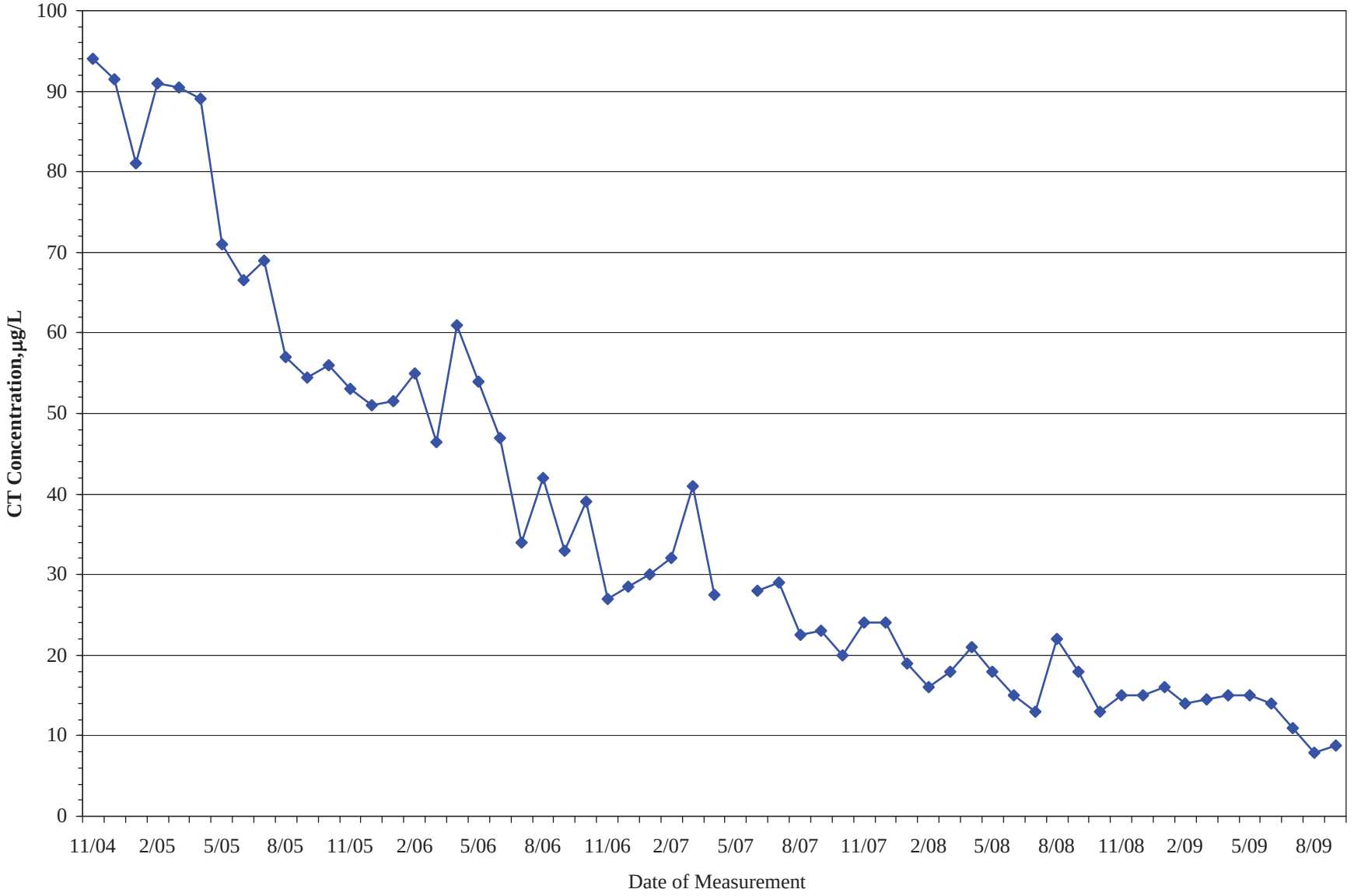

FIGURE 2.4 Measured carbon tetrachloride concentrations (µg/L) in groundwater extracted by GWEX4, 2004-2009.

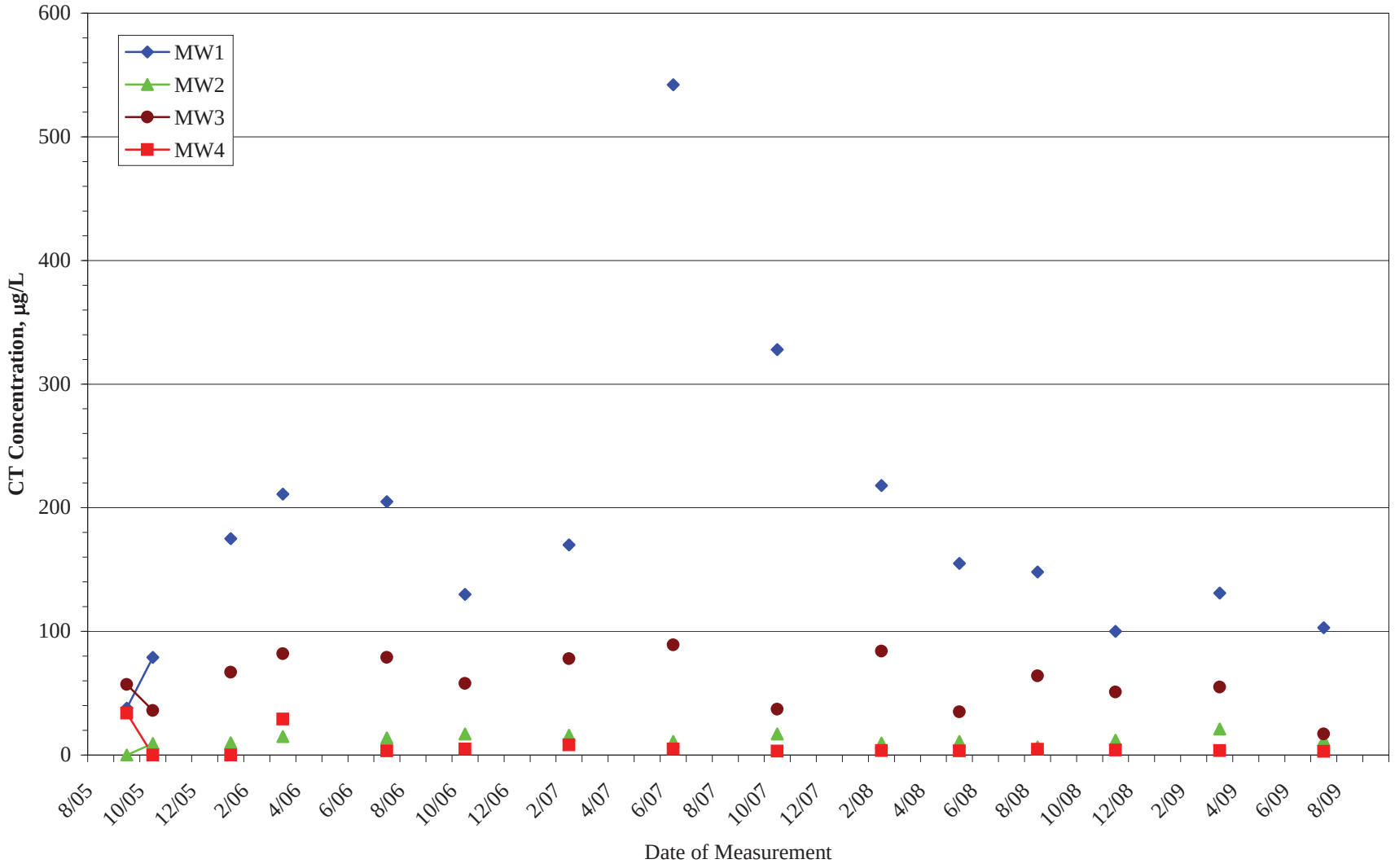

FIGURE 2.5 Measured carbon tetrachloride concentrations (µg/L) in groundwater samples collected from monitoring wells MW1, MW2, MW3, and MW4, 2005-2009.

3 Proposed Remapping of the Carbon Tetrachloride Plume

Predictive groundwater flow and contaminant transport models developed for the groundwater at Utica (Argonne 2000, 2003) were used to estimate a time frame of approximately 15 yr for restoration of the contaminated shallow aquifer, under the treatment approach described in Section 1. The monitoring data discussed in Section 2.2 suggest that the distribution and levels of carbon tetrachloride contamination in the shallow groundwater at Utica have changed significantly since the operation of the treatment systems began in October-November 2004.

The fifth full year of operation of the aquifer restoration systems at Utica will be completed in November 2009. In accord with the elements of the *Monitoring Plan* (Argonne 2004) outlined in Section 2.2, a targeted program of groundwater sampling at the Utica site is therefore recommended. The specific technical objectives of the proposed sampling program are as follows:

- To document the present distribution of carbon tetrachloride contamination in groundwater in the shallow aquifer.

- To identify potential changes in the concentrations and distribution of carbon tetrachloride in the shallow aquifer that have resulted from the restoration efforts to date.

- On the basis of the results obtained, to provide technical recommendations to the CCC/USDA for optimal operation of the groundwater extraction and treatment systems at Utica, in order to address the remaining carbon tetrachloride contamination in groundwater.

The proposed locations for groundwater sampling are shown in Figure 3.1. At each location, the Argonne CPT vehicle will be employed to collect samples for VOCs analyses in a vertical profile, at 10-ft intervals, at the target depths identified in Table 3.1. The proposed sampling locations and depths have been chosen to correspond directly with those of the previous monitoring events conducted with the CPT in 1998 and 2003 (Tables 1.2 and 1.3), to support direct evaluation of potential variations in carbon tetrachloride concentrations within the plume during the first 5 yr of aquifer restoration.

The proposed groundwater sampling will be conducted by using the CPT in accord with the procedures outlined in the EPA- and NDEQ-approved *Master Work Plan* for environmental investigations in Nebraska (Argonne 2002; Sections 6.1.2 and 6.5). Samples for VOCs analyses will be preserved and shipped (on ice at 4°C) by overnight service to the Applied Geosciences and Environmental Management Laboratory at Argonne, for purge-and-trap sample preparation with analysis on a gas chromatograph-mass spectrometer system (EPA Methods 5030B and 8260B; Argonne 2002; Section 6.3.2). To ensure reproducibility, a minimum of 10% of the water samples will also be submitted for verification analysis by a second laboratory (TestAmerica, South Burlington, Vermont) with the EPA's Contract Laboratory Program methods. An index of the EPA methods is online (http://www.epa.gov/epahome/index/).

TABLE 3.1 Target locations and depths proposed for vertical-profile groundwater sampling.

Location	Sampling Interval (ft BGL)	Location	Sampling Interval (ft BGL)
PS01	84-93	PS12	82-93
	94-103		93-102
	104-113		103-112
	114-123		113-122
	124-133		123-132
	134-143		
		PS19	83-92
PS04	80-89		93-102
	90-99		103-112
	100-109		113-122
	110-119		123-132
			133-142
PS05	85-94		
	95-104	PS20	83-92
			93-102
PS06	82-91		103-112
	92-101		113-122
	102-111		123-132
	112-121		133-142
	122-131		
	132-141		
PS07	80-89		
	90-99		
	100-109		
	110-119		
	120-129		
	130-136		

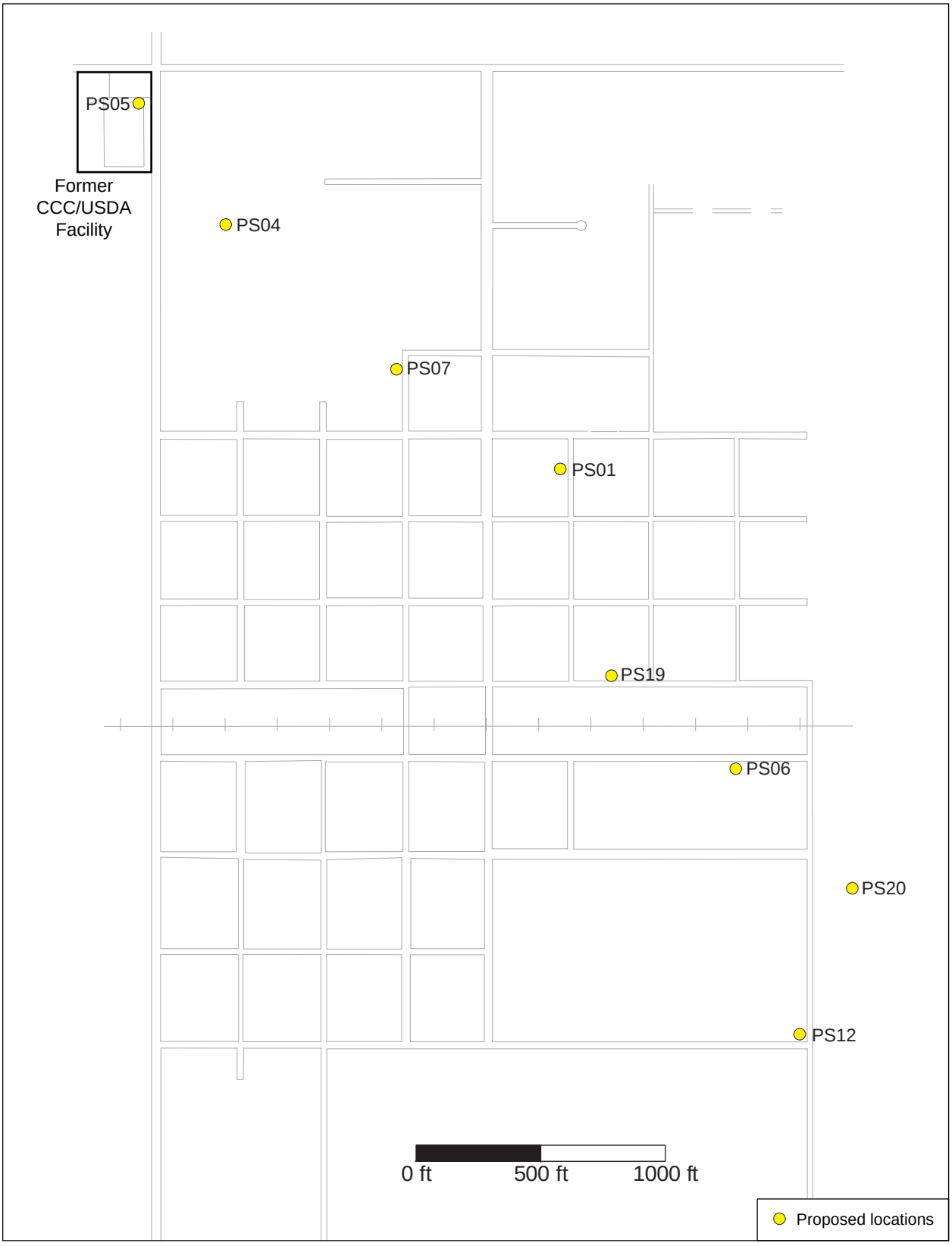

FIGURE 3.1 Proposed locations for vertical-profile groundwater sampling with the Argonne cone penetrometer vehicle.

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