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Oxygen Isotopes and Metolachlor Residues in Water Samples
from a Portion of the Canajoharie Creek Watershed,
Central New York

Abstract of
a thesis presented to the Faculty
of the University at Albany, State University of New York
in partial fulfillment of the requirements
for the degree of
Master of Science
College of Arts and Sciences
Department of Earth and Atmospheric Sciences

John M. Nadeau
2000

Abstract

Increased ground and surface water contamination has fueled the need for a better understanding of factors affecting hydrogeological settings. Seasonal variability in the recharge of an aquifer can affect the rate and amount of contamination that can occur. Stable isotopes have been previously investigated as tracers to determine flow paths of the water and contaminants. In this study, oxygen isotopes were used to determine the factors that influence seasonal variations in ground and surface water, such as well location, aquifer type, surface water sites, and soil type. Samples were collected from different locations around the Canajoharie Field Site, including wells that were screened in an unconfined aquifer, wells screened in confined aquifers, tile drains, and surface water sites, in an attempt to determine differences in seasonal variation.

The proximity of the wells to the Canajoharie Creek affected the seasonal variation of both water table elevation and oxygen isotopic composition of well water. The closer the well to the stream, the greater the response to storm events and seasonal changes. Wells along fence and tree lines show more of an influence during spring snowmelts than wells located in the middle of the fields, due to snow drifting from open areas to the fence and tree lines, resulting in a disproportionately large amount of recharge. The confined aquifers show little to no seasonal and storm event response.

Samples collected from two tile drains show that soil type also affects the recharge response. Soils with lower porosity, i.e. clayey soils, displayed macro pore flushing following storm events, whereas more porous sandy soils showed better water mixing capabilities. The samples collected from the tile drains were also analyzed for the herbicide metolachlor, and two metabolite compounds, metolachlor ESA (ethanasulfonic

acid) and metolachlor OA (oxanilic acid), that are found in higher concentrations and persist longer than the parent compound. The oxygen isotopic composition of the tile drain water was compared with the ratios of metolachlor ESA to metolachlor (SAM ratio) and metolachlor ESA to metolachlor OA (SAO ratio) to illustrate macropore flushing and to determine how residence time of groundwater affects the herbicide degradation. A larger decrease in SAO ratios in the clay soil is the result of macropore flow which causes the breakdown of the less stable metolachlor OA in the infiltrating water. Pore water has a longer residence time in clayey soil, resulting in a higher SAM ratio in the water subsequently flushed out during storm events. Sandy soil retains less water in the pores, the briefer soil-water interaction resulting in lower metolachlor ESA production and lower SAM values.

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Part 1

Introduction

Herbicides and pesticides have been used in increasing amounts on agricultural land to improve crop yields. This increased usage has the potential to cause an increase in the pollution of ground and surface waters. To better comprehend the means by which the contamination occurs, a more thorough understanding of the hydrogeological cycle, including the seasonal variability of input water (recharge), ground water and output water (discharge), is necessary. One possible means of studying the seasonal variability of the water cycle is to analyze the oxygen and hydrogen isotopic composition of the water. Combined with water table elevation measurements, isotopic composition can provide us with a means to trace the water through the whole cycle, from recharge to discharge. A micro-scale look into the seasonal variability of the groundwater aquifer can be accomplished by sampling water from wells located in different regions around an agricultural site. This sampling can provide us with information on how land usage and distance from a stream can influence the seasonal variability of the isotopic composition and water table elevation.

In 1991, the United States Geological Survey (USGS) established the National Water Quality Assessment (NAWQA) program to investigate the effects of land use practices on water quality. Study units were established at 60 sites in the U.S., including the Hudson River (Leahy and Thompson, 1994). The Hudson River Basin unit established a network of sites comprising all aspects of the basin, from the small tributaries to the Hudson River itself. The Canajoharie Field Site (CFS) was chosen because its location in the headwaters of an agricultural basin.

The CFS is an 110-hectare agricultural site (Figure 1.1) located within a 165-km² watershed in western Montgomery County, approximately 113 km (70 miles) northwest of Albany, New York. Canajoharie Creek flows eastward and borders the CFS on both the northern and western sides. The CFS elevation ranges between 210 and 220 meters above mean sea level (amsl) except for an east-west trending drumlin found on the southern boundary with an elevation of approximately 245 meters amsl. The watershed is predominately (66%) agricultural, consisting of field corn, alfalfa, and soybean production (row crop and pasture), with forest (29%), and residential development (5%) constituting the rest. The USGS maintains a streamflow gage station approximately 10 km downstream from the CFS at the mouth of the watershed.

Previous work at the CFS determined how land use affects water quality. Initially, the concentration of the herbicide atrazine was measured in ground and surface waters. Atrazine is widely used to control the growth of broad-leaf weeds and grasses in corn, sorghum and other row crops (Mandelbaum *et al.*, 1993). Hollister (1997) focused on determining the flowpaths and travel velocities of the groundwater on the site. Knowledge of groundwater flow direction and velocity can determine the fate of herbicides. If groundwater velocity is slow, the herbicide might degrade before it reaches surface waters. A second aspect of Hollister's work was to determine locations where the creek may either be influent or effluent, a critical factor in determining whether the creek contaminates the groundwater and/or groundwater flow contaminates creek water (Fetter, 1994). These studies were designed to investigate herbicide movement in these waters.

The first objective of this current project was to use oxygen isotopes to further understand the hydrogeological settings of the CFS. Sampling sites were chosen that

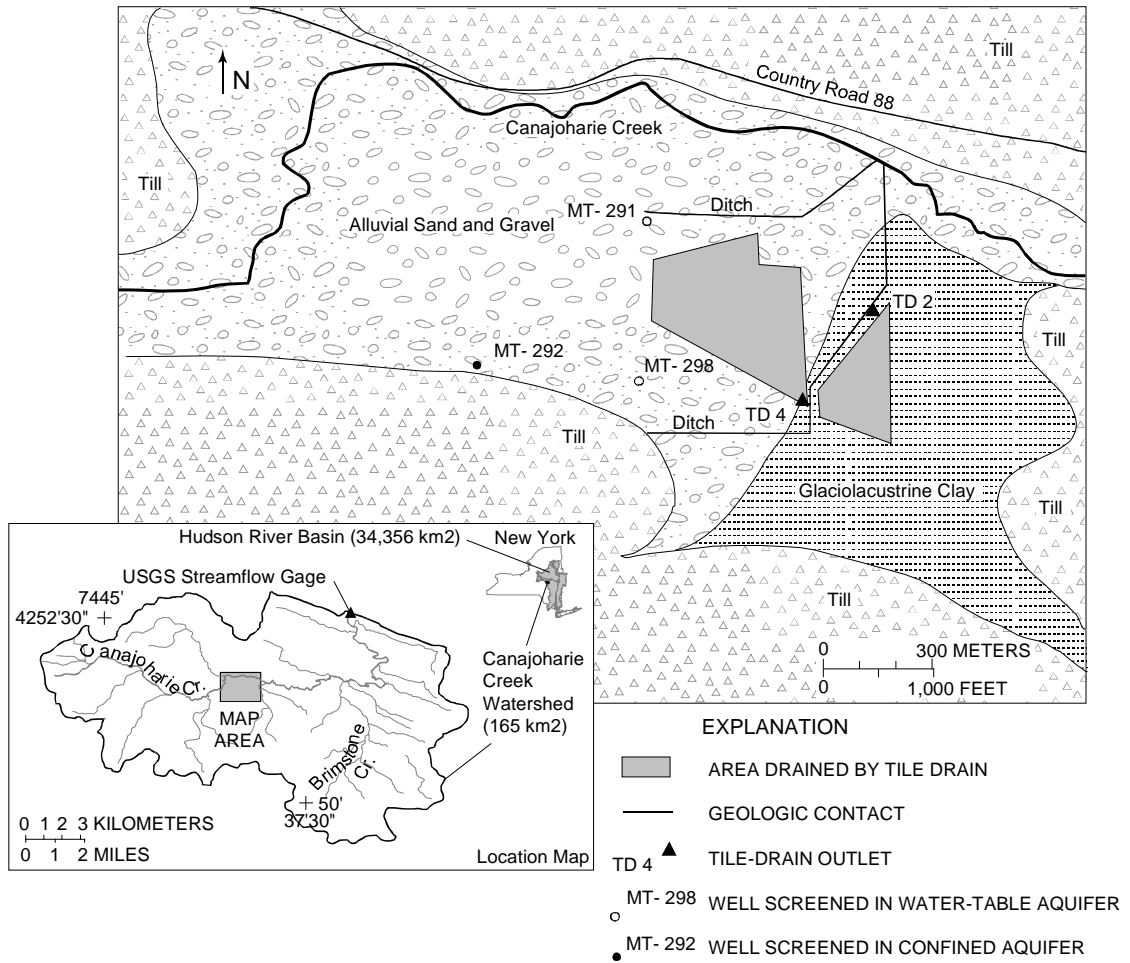


Figure 1.1 Site Location Map (Phillips *et al.*, 1999)

showed varying land use, geology, and geography to determine how each of these characteristics may influence the aquifer during seasonal changes. Among the factors that might influence groundwater-surface water interactions is farm field usage. For example, agricultural fields are usually separated by fence or tree lines, which trap snow that drifts from the unprotected growing fields. The aquifer water could also show temporal and spatial differences in oxygen isotopic composition.

To better understand the causes for seasonal oxygen isotopic composition variations at the CFS, a discussion of environmental factors critical to the hydrologic cycle is essential. Precipitation is the most important form of input into the local hydrologic cycle. Precipitation is formed by the condensation of atmospheric water vapor that was derived from the evaporation of bodies of water (Dansgaard, 1953; Craig, 1961; Gonfionini *et al.*, 1998). Oxygen isotope fractionation occurs both during evaporation, in which the isotopically lighter molecules ($^{16}\text{O}_2$) evaporate preferentially, and condensation, in which the isotopically heavier molecules ($^{18}\text{O}_2$) condense preferentially.

It is well known that the two major factors that affect the oxygen isotopic composition of precipitation are temperature and the composition of the condensing parent vapor (Dansgaard, 1953; Craig, 1961; Ingraham, 1998). Temperature affects the phase of the condensing precipitation as well as the fractionation factor. Precipitation falling in solid form, i.e. snow or ice, is not subject to evaporation and exchange during its descent through the atmosphere. Composition of the vapor affects the precipitation because it regulates the isotopes available for partitioning to the liquid phase. The fractionation factor determines the partitioning of the isotopes between the parent vapor and the condensate.

Ingraham (1998) and Gonfiontini *et al.* (1998) have summarized the factors that influence the isotopic composition of parent vapor as:

1. The continental effect; meteoric water becomes more depleted in the heavier isotope the further inland away from the source.
2. The latitude effect; the vapor becomes more depleted at higher latitudes. There is also a greater amount of precipitation and fractionation at cooler temperatures. The evaporation sources for vapor become more depleted in higher latitudes.
3. The greater the amount of precipitation, the more depleted the remaining vapor becomes.
4. The elevation factor results in vapor becoming more depleted due to increased precipitation as the air mass rises and cools.

The ^{18}O isotope can be used as a conservative tracer in groundwater due to the previously mentioned seasonal input variations, which will in turn produce seasonal variations in the oxygen isotopic composition of the groundwater. Maloszewski and Zuber (1982), using the properties of water mixing, set up conceptual models to determine water residence times. The variations of the isotopic composition of input water (precipitation and snowmelt) and output water (groundwater and surface water) can provide insight into factors such as evaporation, aquifer residence time, and stormflow components (Kendall *et al.*, 1995; Burns and McDonnell, 1997).

Analyses of oxygen isotopic composition, and of herbicide and metabolite concentrations, may prove useful for tracing the movement of water through the

subsurface and may also provide a better understanding of herbicide degradation pathways. The herbicide metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide] is a chloroacetanilide herbicide used for the control of annual grasses and broadleaf weeds on corn (*Zea mays*) and soybean (*Glycine max*) crops (Aga *et al.*, 1996; Kolpin *et al.*, 1996). Recently, metolachlor has been shown to break down into two metabolite components, metolachlor ethanesulfonic acid (metolachlor ESA: 2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)] amino)-2-oxoethanesulfonic acid) and metolachlor oxanilic acid (metolachlor OA: 2-[2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoacetic acid) (Aga *et al.*, 1996; Field and Thurman, 1996; Kalkhoff *et al.*, 1998). Recent studies have shown that these metabolites are more soluble than the parent metolachlor and that concentrations of these metabolites in ground water, surface water, and soils may greatly exceed concentrations of the parent compound (Gaynor *et al.*, 1995; Aga *et al.*, 1996; Field and Thurman, 1996; Ng and Clegg, 1997; Fenelon and Moore, 1998; Eckhardt *et al.*, 1999; Phillips *et al.*, 1999).

The objective of this part of the study was to trace water movement through two different soil types overlying tile drains at the CFS. Water residence time may be a factor in the preferred degradation pathway of the herbicide. Two tile drains were chosen, one in clayey soil and one in sandy soil, to determine how the residence time of the pesticide in the water table would affect the breakdown process and the concentration levels. The clayey soil provides macro-pore flow following precipitation events and the sandy soil displays a longer release of water as the water table subsides. Concentrations of metolachlor and its metabolites provided by the USGS (P. Phillips, written comm., 2000)

were compared to the oxygen isotopic composition of ground and surface waters to attempt to determine any correlations.

Previous investigations of metolachlor and its metabolites at the CFS has shown that both can persist in groundwater for three or more years after application. In order to distinguish application of new herbicide from residence of previously applied herbicide, the following two ratios are used: the ratio of metolachlor ESA to metolachlor (SAM ratio) and metolachlor ESA to OA (SAO ratio) (Phillips *et al.*, 1999). It has been determined that the flow paths influence the ratio results, with the SAM ratio found to be higher where the water has a longer period of contact with the soil and the SAO ratio found to be lower in open water and after storm events (Phillips *et al.*, 1999).

Part 2

Field Site Description

The surficial deposits at the CFS formed during the period of the Sacandaga and Mohawk glacial lobes, and consist of Pleistocene glacial and alluvial deposits, overlying Upper Ordovician bedrock. During several readvancements of the glaciers, layers of till and outwash were deposited until the Yost Readvance formed Lake Schoharie, which deposited sandplains, clay plains, and deltas throughout the Mohawk and Schoharie valleys (Dineen and Hanson, 1985). Sand, silt and clay were received from Lake Sacandaga via Hale Creek, and outwash was received from an ice margin at Galway Lake (Dineen and Hanson, 1985). The waters of Lake Schoharie slowly subsided and stabilized to form Lake Amsterdam until the ice sheet retreated. Figure 2.1a shows the location of the site geology cross sections displayed in Figures 2.1b and 2.1c.

The field site consists of three aquifers. The overlying unconfined aquifer consists of Holocene alluvium, which is the same composition as the banks of the Canajoharie Creek (Hollister, 1997). The surficial aquifer ranges in thickness from 0 to 3 meters thick, thickening from east to west. The aquifer material is comprised of Fredon series soil (Aeric Haploquepts: coarse-loamy over sand on a sandy-skeletal, mixed, non-acidic mesic) and has a permeability of 1×10^{-3} cm/s (Davis and Landry, 1978; Phillips *et al.*, 1999).

A varved glaciolacustrine clay layer with a thickness ranging from 3-12 meters, generally underlies the surficial aquifer but reaches the surface in the eastern third of the field site (Figure 1.1). The clay soil is characterized as Wayland series soil (Mollic

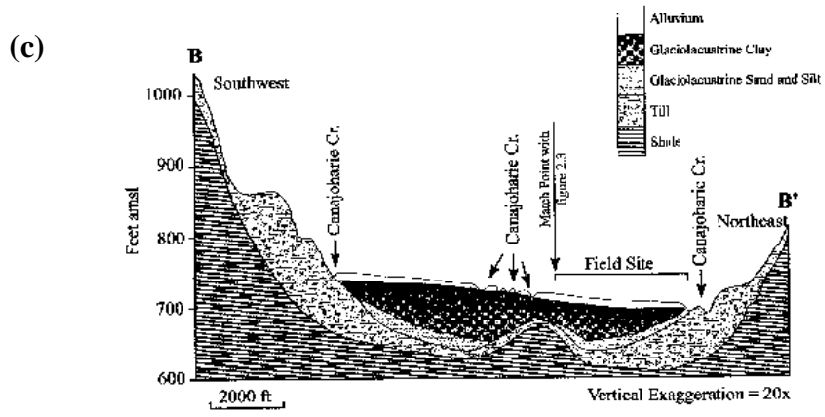
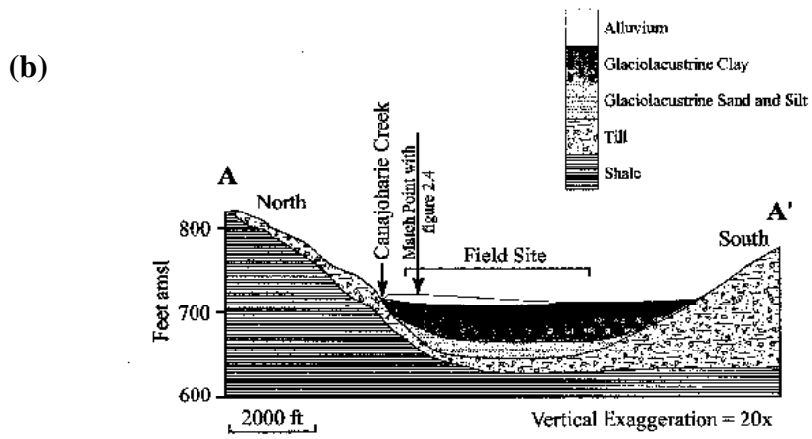
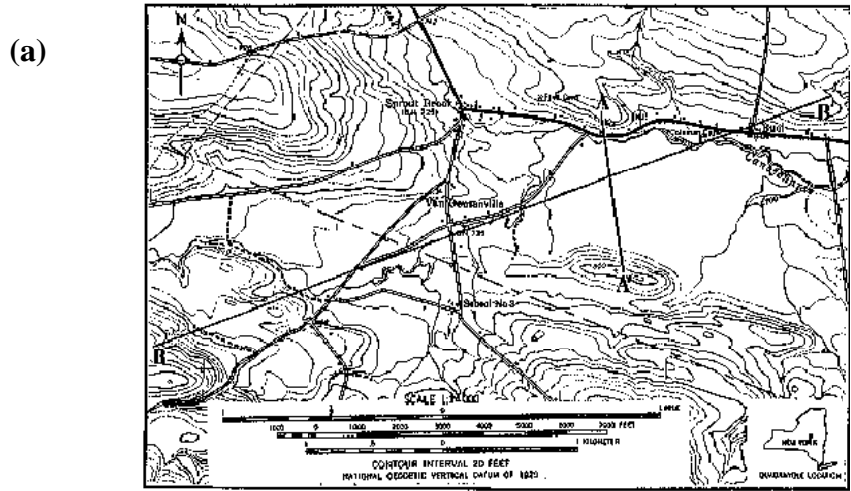


Figure 2.1 a) Location of cross sections A-A' and B-B', b) idealized geological cross section along A-A' section, c) idealized cross section along B-B' section (modified from Hollister, 1997).

Fluvaquents: fine silty, mixed, non-acidic mesic) and has a permeability of less than 1×10^{-4} cm/s. Well boring logs indicate that this layer thins to the north and south (Lang, 1995; Hollister, 1997).

A confined aquifer consisting of glaciolacustrine sand and silt lies beneath the glaciolacustrine clay, and above the glacial till. The till mantles bedrock north of the field site but forms a drumlin to the south (Hollister, 1997). A second confined aquifer is found at a shallow depth beneath the drumlin at the southern border margin of the site.

Recharge of the unconfined and confined aquifers located at the field site is believed to be from several areas, including upland runoff, direct infiltration, and possibly influent upstream sections of the Canajoharie Creek during portions of the year (Hollister, 1997).

Aerial photographs indicate the presence of filled stream channels in the central and southern portions of the site. The stream channels are likely the result of flow from an ancestral Canajoharie Creek and its tributaries that traversed the field site (Lang, 1995).

The eastern part of the site is drained by tile drains that discharge into drainage ditches which in turn flow into the Canajoharie Creek (Figure 1.1). The tile drains are employed in the areas where the clay layer approaches and reaches the surface. In areas where the sediments consists of sands, tile drains may be employed if there is a low hydraulic gradient. Where used, tile drains have been emplaced between three and four feet below the ground surface. The tile drains were installed by digging a small (<46 cm) horizontal trench in which perforated pipes were placed. Native material was used to back fill the areas surrounding the drains (Hollister, 1997).

The basic premise behind the tile drain system is to remove excess water from the fields and to raise the soil temperature thereby allowing earlier planting with increased production. The drains can affect the water table in two ways: 1) As precipitation infiltrates through the vadose zone, a percentage is carried through the drain to drainage ditches, and 2) An increase in groundwater flow through the aquifer can result in the water table rising to the level of the drains, and the excess water is transported away to the drainage ditches.

The USGS and Rensselaer Polytechnic Institute (RPI) have installed and currently maintain a total of twenty-four wells at the site. The monitoring wells consist of two-inch (5.08 cm) (outside diameter) poly-vinyl chloride (PVC) pipe. Well screens are 0.01-inch (0.03 cm) machine-slotted PVC pipe. Morie sand #0 was used as a filter screen pack, which was then sealed with two feet (0.61 m) of hydrated bentonite pellets. Most wells have five-foot (1.52 m) screens located at the bottom of the well. The USGS wells were installed using methods described by Lapham *et al.* (1997). Well location, surface water collection sites and tile drain locations are shown in Figure 2.2.

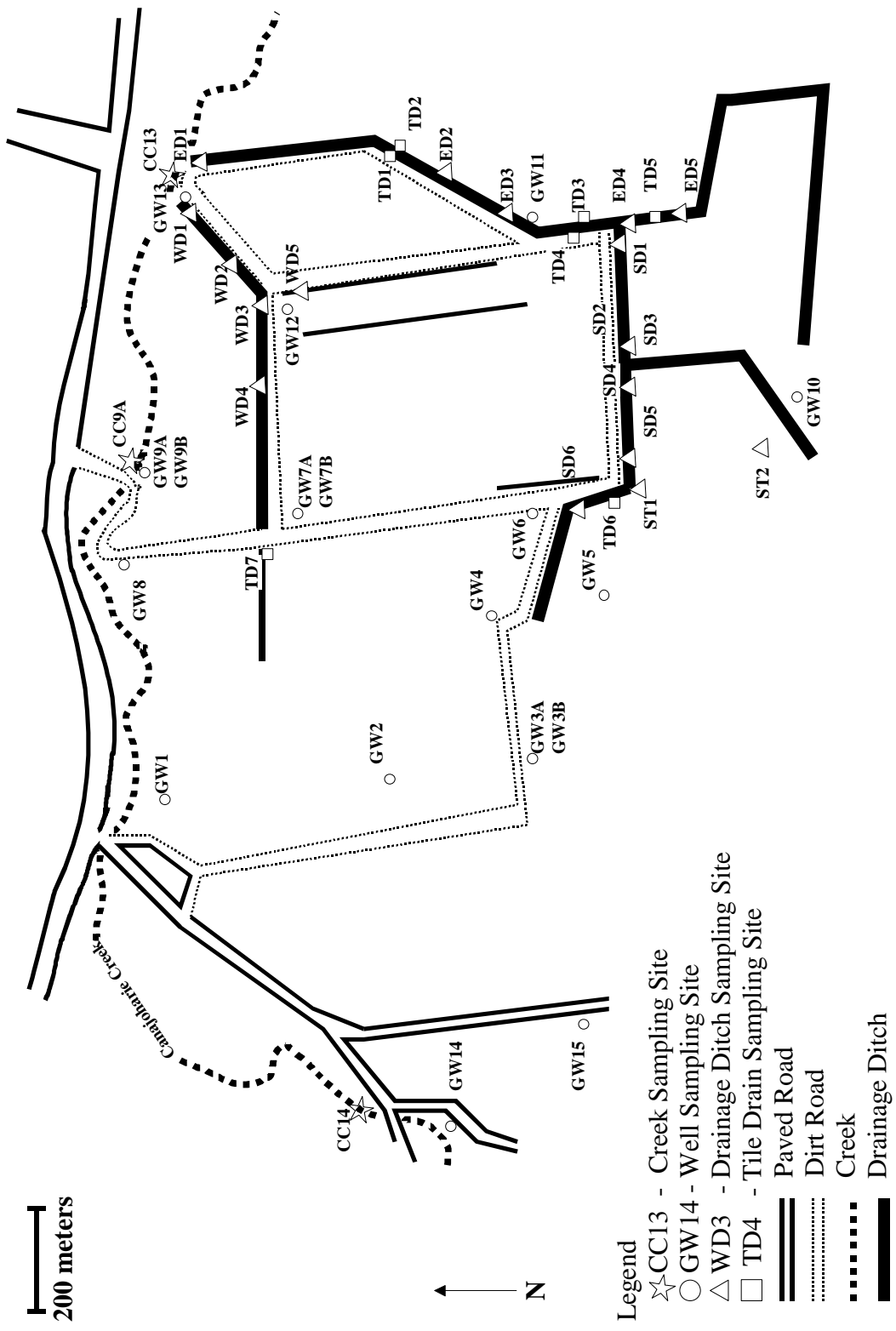


Figure 2.2 Location of wells and previous sampling sites.

Part 3

Techniques

3.1 Sample Collection/Storage

Water samples were collected from April to September, 1997, and from October, 1998 to October, 1999, on a weekly to bi-weekly basis, and following major precipitation events. Tile drain and creek samples obtained for pesticide analysis were collected in 3-l Teflon bottles cleaned and rinsed following procedures described by Shelton (1997). Samples obtained for oxygen isotopic analysis were collected in 20-ml Wheaton high-density polyethylene liquid scintillation vials.

Precipitation samples were collected from a rain gage installed on the roof of the Earth Science Building at the University at Albany approximately 110 km from the CFS. Water was collected from the rain gage either during, immediately following, or less than 12 hours after storm events. Snowpack was melted at room temperature and the melt water collected in sample vials for storage and analysis.

Wells located on the site were installed in 1993 and are screened in both unconfined and confined aquifers (Hollister, 1997). The screen depths of the wells are shown in Table I. The wells screened in the unconfined aquifer were sampled using a PVC bailer, employing techniques described in Koterba *et al.* (1995) where the well was purged three times prior to sampling. The wells screened in the deep confined aquifer (wells 7B and 11) were sampled using a purge pump. Samples were collected from the artesian well (3B) by filling a sample vial with water flowing out of the well casing.

Table I Well Screen Depths

Well Number	USGS Well Number*	Well Depth (feet from surface)	Screen Depth (feet)
GW2	MO-315	11.5	6-11
GW3B	MO-292		
GW6	MO-298	17	12-17
GW7A	MO-291	16	10.5-15.5
GW7B	MO-303	74	67-72
GW9A	MO-313	11	5.5-10.5
GW9B	MO-304	17	12-17
GW11	MO-311	47	42-47
GW13	MO-302	17	12-17
GW14	MO-297	14	9-14

* - The USGS changed the well nomenclature from MT-# (as shown in Figure 1.1) to MO-#. These well numbers correspond with the locally used well numbers.

Table II Surface Water Sample Sites

Site Index	Type of Site
CC-13	Creek
CC-14	Creek
ED	Drainage Ditch
WD	Drainage Ditch
TD-2	Tile Drain
TD-4	Tile Drain
GS	Creek (Gage station)

Samples collected from Canajoharie Creek at the gaging station followed the equal-width, depth-integrated sampling techniques of Shelton (1997). Samples collected from other surface water sites (Table II) employed a grab technique.

Samples were stored and transported from the field site in an ice-filled cooler and remained refrigerated until analyzed.

3.2 Analysis

3.2.1 Pesticide Analysis Techniques

The samples were analyzed for the parent metolachlor and the OA and ESA metabolites following methods described in Phillips *et al.* (1999), as follows:

Samples were filtered through a 0.7 μm baked glass fiber filter, and sample splits were sent to two laboratories: the National Water Quality Laboratory (NWQL) in Denver, and the USGS Organic Research Laboratory (ORL) in Lawrence KS. The parent compound (metolachlor) was analyzed at the NWQL by gas chromatography/mass spectrometry with selected ion monitoring after extraction on a C-18 solid-phase extraction cartridge (Zaug *et al.*, 1995).

The two metabolites were analyzed by high-performance liquid chromatography (HPLC) with diode array detection and quantitation after solid-phase extraction on C-18 cartridges (Zimmerman and Thurman, 1999). A subset of samples was analyzed by HPLC for confirmation by negative ion electrospray. Metolachlor ESA standard was prepared according to methods described by Aga *et al.* (1996). Metolachlor OA standard was obtained from Novartis Corporation in Greensboro, NC. Detection limits for the two metabolites were 0.2 $\mu\text{g/L}$.

3.2.2 Isotopes

3.2.2.1 Preparation

The water samples were removed from the refrigerator and warmed to room temperature approximately 12-16 hours before analysis. Sub-samples consisting of 200 μl of water were pipetted into glass chromatography V-vials and the vials placed into a plastic rack. The rack was then placed into a plastic glove bag which could be opened and

closed at one end. Carbon dioxide was first introduced into the glove bag to flush out air. The glove bag was then purged of CO₂ and resealed. The bag was then sequentially both filled and purged with CO₂ three more times, each time taking care to direct a gentle stream of CO₂ into the glass vials above the contained water samples during the filling stage. Finally, the glove bag was filled with CO₂ and the vials capped with Kel-F lined silicone rubber septa and removed from the bag.

3.2.2.2 Isotope Analysis

The samples were analyzed using a Micromass Optima gas-source magnetic-sector triple collector isotope ratio mass spectrometer located in the Department of Earth and Atmospheric Sciences at the University at Albany. The mass spectrometer is equipped with a dual inlet and interfaced with a Multiprep automated sample preparation device used to equilibrate water samples with carbon dioxide. The Multiprep is adapted from a Gilson 222 XL liquid handler. The septum-capped glass chromatography V-vials were loaded into a rack heated to 40°C and controlled to $\pm 0.1^\circ\text{C}$. A needle sequentially punctured each vial's septum, removing the equilibrated CO₂ which passed through a water trap prior to passage into the mass spectrometer's dual inlet.

The equilibrated carbon dioxide was analyzed by comparing its 46/44 ratio to that of reference carbon dioxide repeatedly during a 7-minute analysis. The reference gas was standardized using two international standards (NBS-18 and LSVEC) and two laboratory standards (ALB-1 and UVM-3). An average difference in isotopic composition between the sample and the working reference gas is determined using the following general equation:

$$[(R_{\text{sample}} - R_{\text{standard}}) / (R_{\text{standard}})] \times 1000 = \delta_{\text{sample-standard}}$$

where here R_{sample} = ratio of mass 46 to mass 44 the sample, R_{standard} = the same ratio in the working reference gas, and $\delta_{\text{sample-standard}}$ = the difference in isotopic composition of the sample relative to that of the reference, expressed in parts per thousand (per mil [‰]). Through careful calibration, R_{standard} of the working reference gas is known with respect to an internationally accepted standard, and hence R_{sample} can be determined relative to the same international standard. Thus, the oxygen isotopic composition of a water sample can be expressed as $[(^{18}\text{O}/^{16}\text{O}_{\text{water sample}} - ^{18}\text{O}/^{16}\text{O}_{\text{ref}}) / (^{18}\text{O}/^{16}\text{O}_{\text{ref}})] \times 1000 = \delta^{18}\text{O}_{\text{water sample}}$, expressed in per mil. As long as the $^{18}\text{O}/^{16}\text{O}$ of the reference carbon dioxide is known with respect to an international standard such as Vienna Standard Mean Ocean Water (VSMOW), the $\delta^{18}\text{O}$ of the water sample can be expressed relative to VSMOW.

The samples collected in 1997 were analyzed in August, 1998, and the samples collected in 1998-1999 were analyzed from September, 1999 to November, 1999. A local deionized water standard, ALB-3, was analyzed periodically as an internal standard.

3.3.2.3 Precision of Analysis

The standard deviation of the $\delta^{18}\text{O}$ values of VSMOW for the 1997 samples and the 1998-1999 samples were 0.05 per mil and 0.02 per mil, respectively. The standard deviation of analyses of ALB-3 during August, 1998 was 0.13 per mil and 0.11 per mil for analyses between September and November, 1999. The average standard deviation of replicate analyses of selected samples was 0.03 per mil during 1998 and 0.03 per mil during 1999.

Part 4

Water Chemistry

4.1 Introduction

Water samples were collected from the CFS and the streamflow gaging station to evaluate two major aspects of site hydrology. Figure 4.1 shows the location of the sampling sites at the Canajoharie Field Site utilized for this study. The first objective concentrated on evaluating seasonal $\delta^{18}\text{O}$ variations at the site. The second objective was to examine the relationship between the $\delta^{18}\text{O}$ of water samples collected from tile drains and the degradation of the herbicide metolachlor. The raw data used to construct the plots found in this section can be found in Appendix A. More detailed plots of the discharge, precipitation, and oxygen isotopic composition from all sampled sites can be found in Appendix B.

4.2 Seasonal Variations

4.2.1 Seasonal Climate Variations

The variation in the $\delta^{18}\text{O}$ of the ground and surface waters and of the water table elevation at the field site can be separated into three distinct periods: Autumn to early Winter, Winter through the Spring snow melt, and Spring through early Autumn. The 30 year (1961-1990) average daily mean precipitation for these periods is relatively constant with the respective values of 0.25 cm, 0.21 cm, and 0.23 cm (National Weather Service, 1999).

The Autumn season is characterized by the end of agricultural production, leaving the fields bare and more susceptible to direct infiltration from precipitation. The

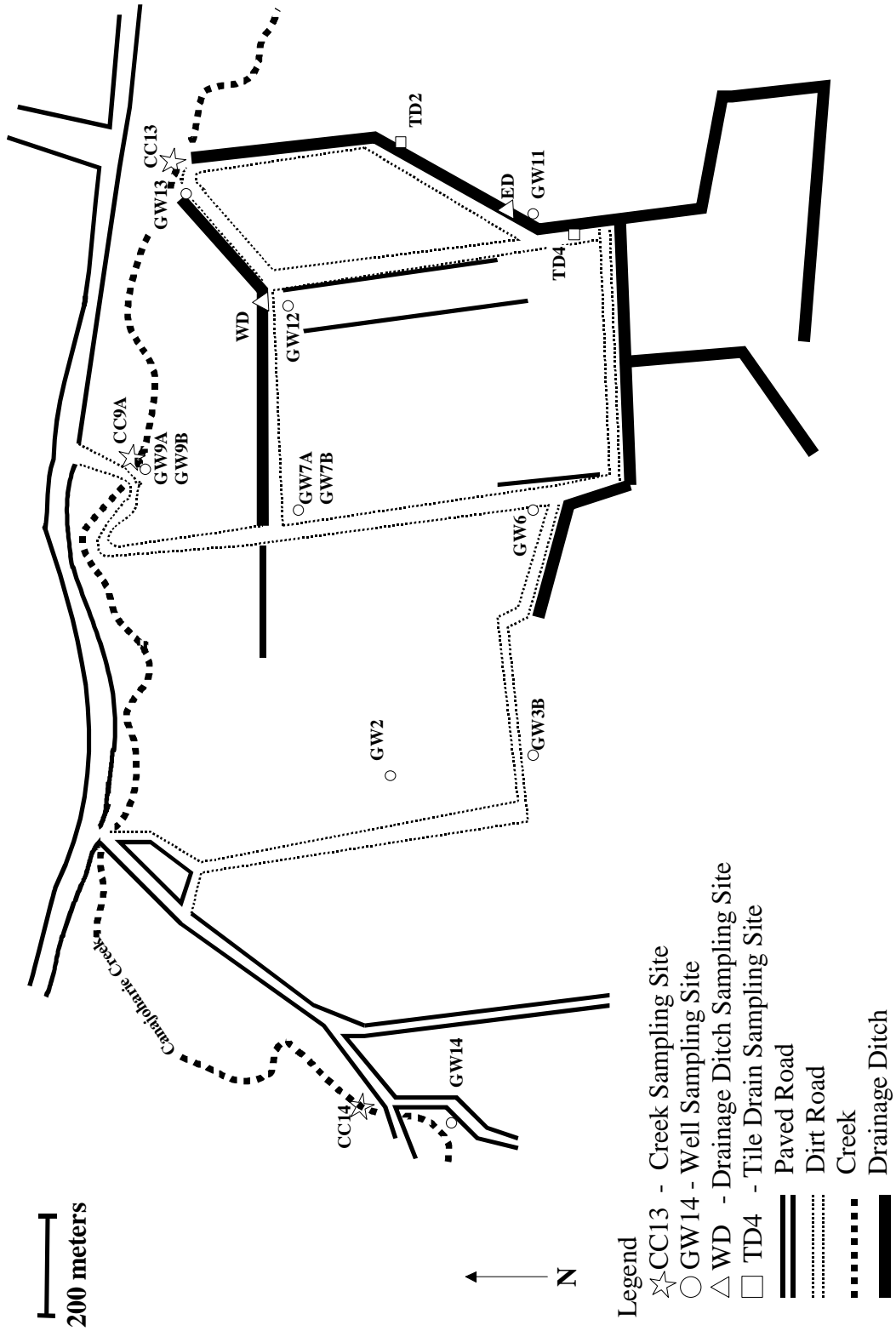


Figure 4.1 Location of sampling sites.

Autumn 1998 months had a daily mean precipitation of 0.16 cm and cooler than normal temperatures.

The Winter 1998-99 season brought an increase in precipitation (0.29 cm daily mean), generally in the form of snow. This snow build-up tended to remain until temperatures rose sufficiently to cause melting. Flooding occurred during these melting periods due to ice damming in stream channels and/or large increases in runoff that are not contained by the stream channel. Heavy precipitation occurred into the early Spring, falling in the form of both snow and rain.

The 1997 and 1999 Spring through Summer growing seasons were characterized by an increase in temperature and a daily mean precipitation of 0.24 cm and 0.37 cm (0.25 cm when the July 4th and September 16th, 1999 storms are removed from the 1999 season), respectively. As the crops take hold and begin to flourish, the uptake of water by plant root systems reduces the infiltration of precipitation to the subsurface.

Geological and geographical factors at the field site influence the seasonal variability in water oxygen isotopic composition and water table elevation, including the distance between the creek bed and individual wells, and the location of the wells with respect to barricades, such as fences or tree lines, and whether the aquifer is confined or unconfined.

4.2.2 Seasonal Variations – Autumn to Early Winter

The 1998 Autumn to early Winter season (October through December) had several small rainstorms providing less than 1.25 cm of precipitation with each event (Figure 4.2b). There was only one storm with precipitation over 3 cm, an approximately 8-cm snowfall on December 22nd. However, this snow event represents very little input of

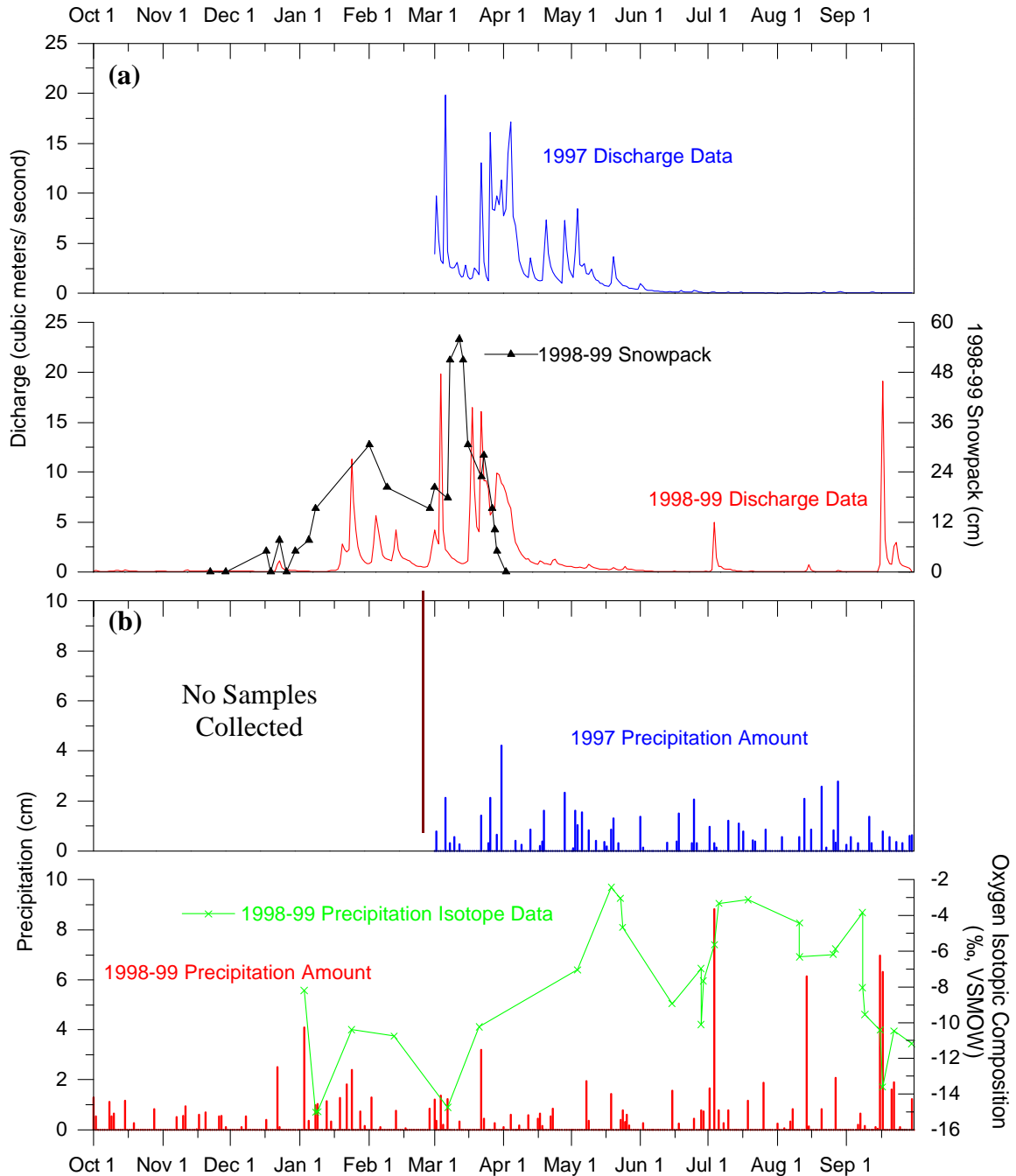


Figure 4.2 (a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997 and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. (b) Precipitation amounts, March to October, 1997 and October, 1998 to October, 1999, measured at the Cherry Valley 2NNE National Weather Service sampling site, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999. The precipitation $\delta^{18}\text{O}$ results were not elevation corrected due to the small elevation difference from the CFS (~100m).

new water into the system during this timeframe. There is no $\delta^{18}\text{O}$ data available for the precipitation (Figure 4.2b) that occurred during this period.

Stream discharge rate at the gaging station was low during the Autumn season (Figure 4.2a), and only fluctuated following the December 22nd storm. The $\delta^{18}\text{O}$ of the surface water samples (Figure 4.3a) displays an overall trend towards a more negative $\delta^{18}\text{O}$ from October to January, with fluctuations following each precipitation event. The East Ditch (Figure 4.3b) shows a large increase in $\delta^{18}\text{O}$ in late November, which is the result of increased flow from the tile drains into the ditch.

Over this time period, the water table elevation throughout the field site decreased slightly, from 0.02 to 0.20 meters in most unconfined wells (Figures 4.4a and b), until the December 22nd storm, when the water table rose as much as 0.09 meters. The confined wells (Figure 4.6a) were inaccessible after the middle of November as the water in the well casings was frozen.

The $\delta^{18}\text{O}$ values of the water samples show considerably more variability than the water table elevation after individual precipitation events. The wells located adjacent to the creek (Figure 4.5a) displayed a greater response to recharge events, and a more pronounced decrease in $\delta^{18}\text{O}$ than the “inland” wells 2, 6, and 7A (Figure 4.5b). Water $\delta^{18}\text{O}$ values decreased slightly at the inland well 6 but increased slightly at wells 2 and 7A through the time period.

4.2.3 Seasonal Variations – Winter through Spring Snow Melt

At the beginning of 1999, precipitation increased both in the form of rain and snow. Total water equivalent of the precipitation amount for January was approximately 15 cm with 3 storms of greater than 1.9 cm. Continued precipitation in the first week of

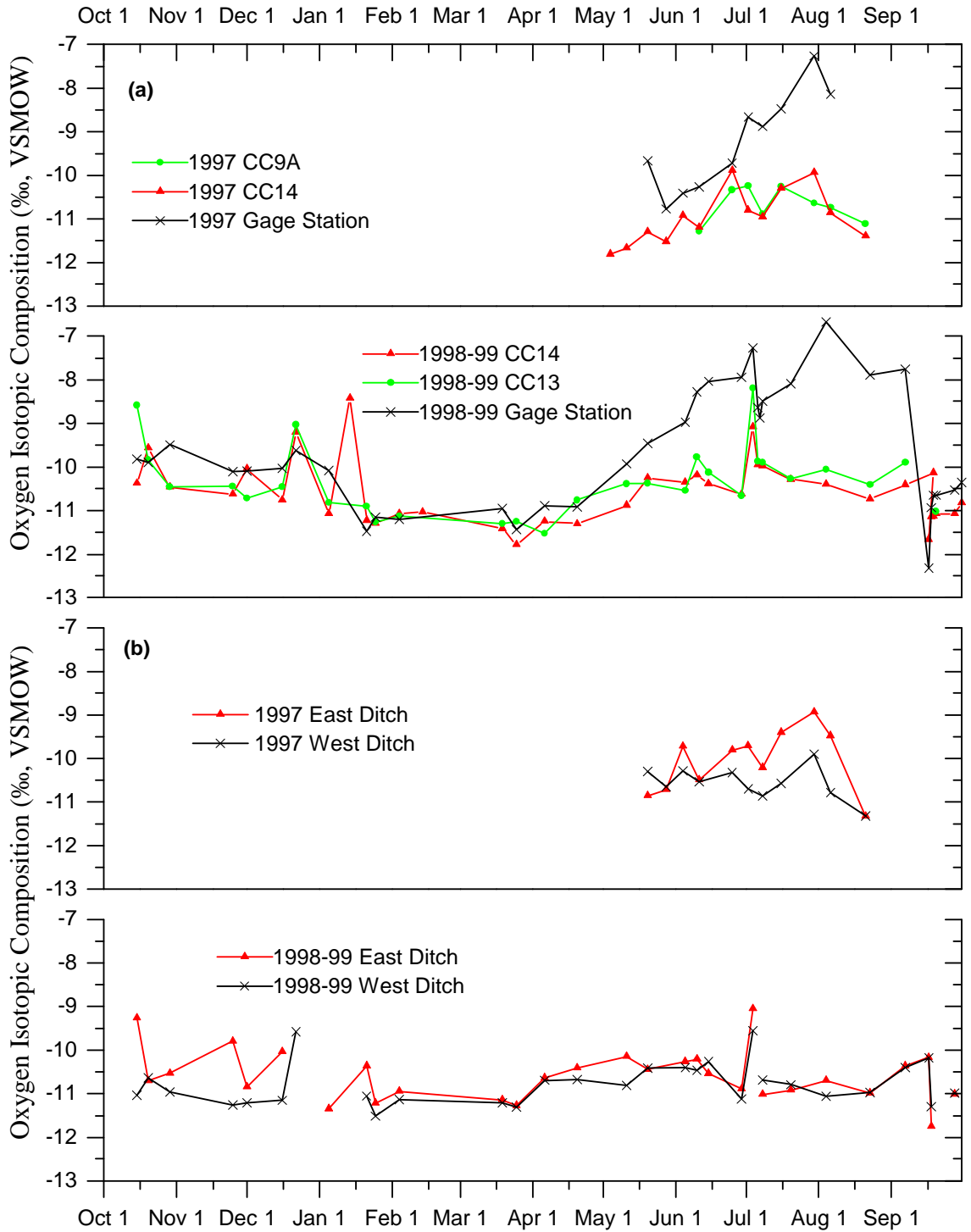


Figure 4.3 (a) Oxygen isotopic composition of water samples collected from CC13, CC14, the Streamflow Gaging station, and CC9A, from May to September, 1997, and October, 1998 to October, 1999. (b) Oxygen isotopic composition of water samples collected from the east (ED) and west (WD) drainage ditches, from May to September, 1997, and October, 1998 to October, 1999.

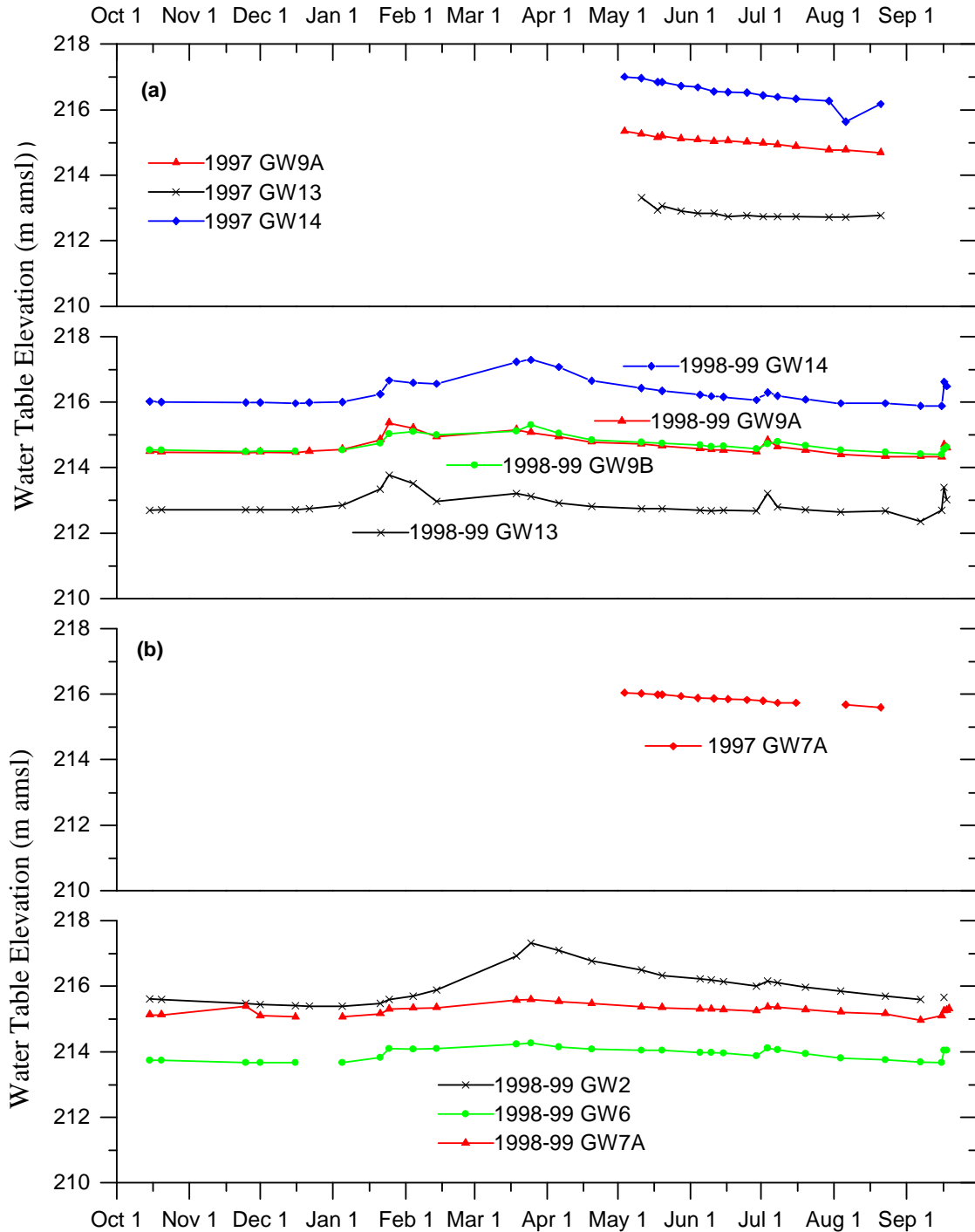


Figure 4.4 (a) Water table elevations from wells 9A, 13, and 14 in the unconfined aquifer and 9B in the confined aquifer, located adjacent to the creek, May to September, 1997, and October, 1998 to October, 1999. **(b)** Water table elevations from wells 2, 6, and 7A, located inland from the creek, May to September, 1997 and October, 1998 to October, 1999.

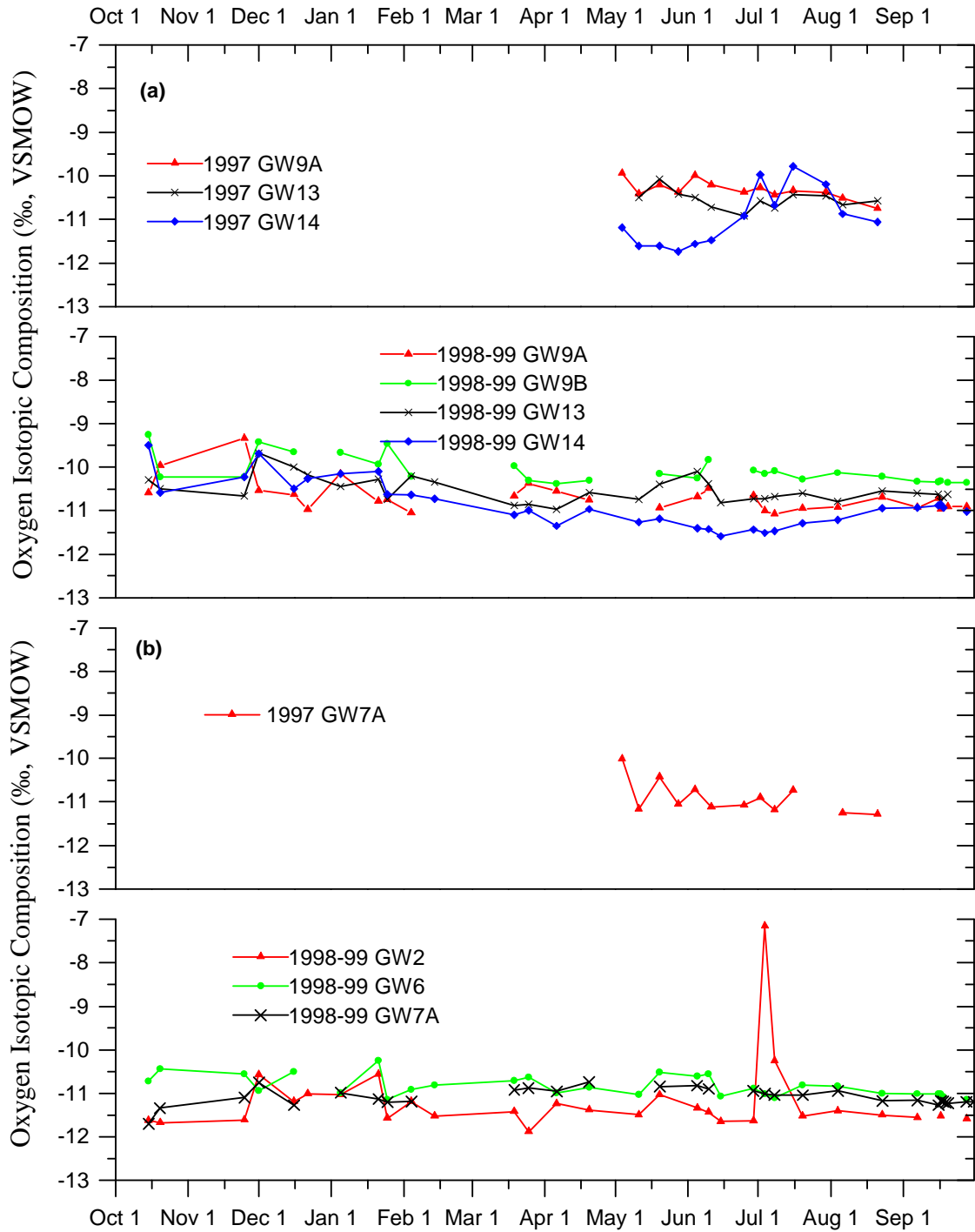


Figure 4.5 (a) Oxygen isotopic composition of water samples from wells 9A, 13, and 14 in the unconfined aquifer and 9B in the confined aquifer, located adjacent to the creek, May to September, 1997, and October, 1998 to October, 1999. **(b)** Oxygen isotopic composition of water samples from wells 2, 6, and 7A, located inland from the creek, May to September, 1997 and October, 1998 to October, 1999.

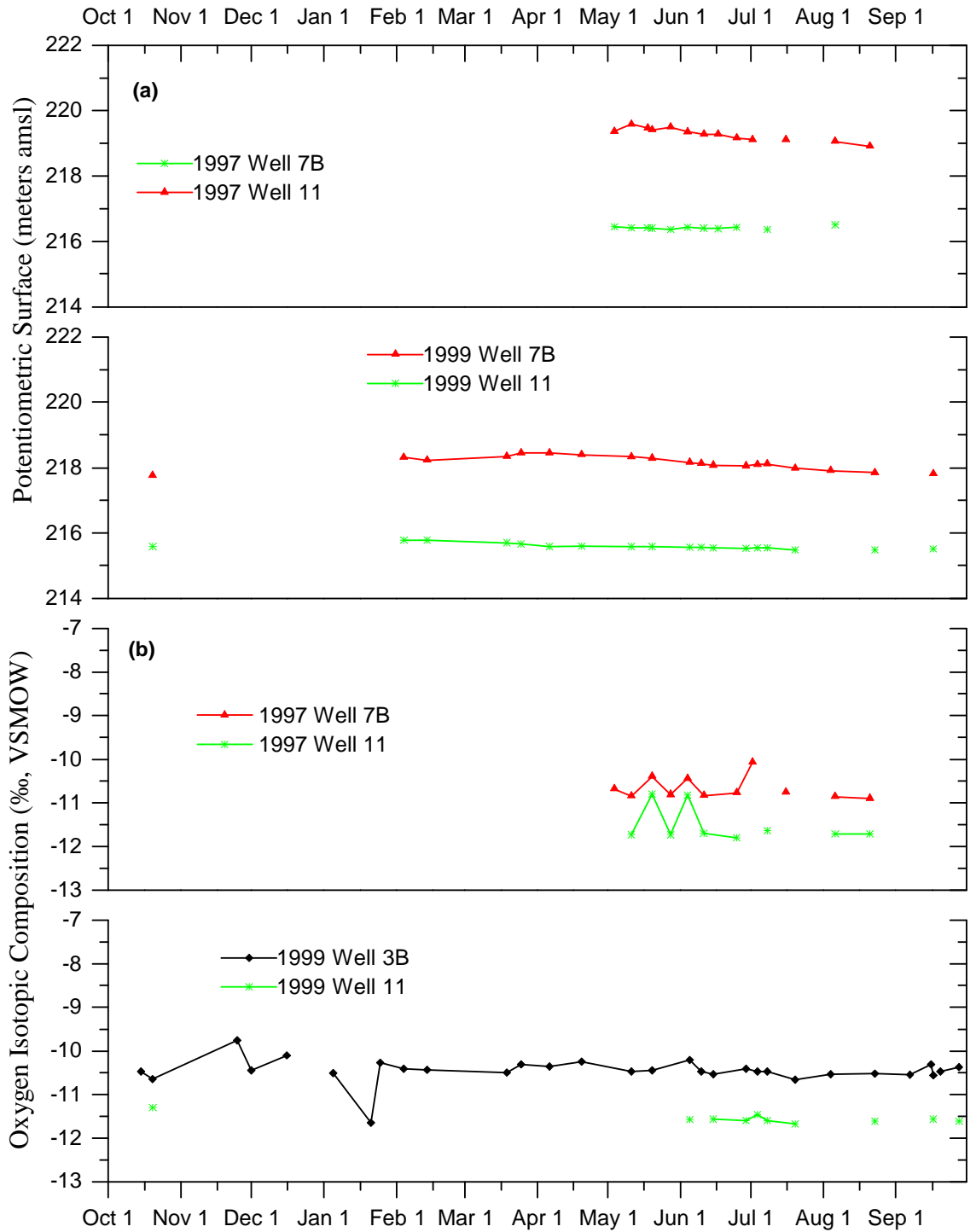


Figure 4.6 (a) Potentiometric surfaces for confined wells 7B and 11, May to September, 1997 and October, 1998 to October, 1999. **(b)** Oxygen isotopic composition of water samples collected from wells 3B, 7B, and 11, May to September, 1997 and October, 1998 to October, 1999.

February and a drop in temperatures brought the total snowpack (Figures 4.2a) to 30.48 cm. After the first week of February, there were no significant precipitation events until February 28th. A storm during March 1st and 2nd produced about 2.54 cm of rain equivalent snowfall. Continued snowfall through the 12th of March brought the snowpack up to its seasonal maximum value of 56 cm. A warming trend began melting the snow almost immediately, and the melting was accelerated by a significant rain event on the 22nd of March (3.2 cm). The snowpack had disappeared by April 1st.

Beginning with the January 5th storm, precipitation samples were collected and analyzed for oxygen isotopic composition. Although there were large $\delta^{18}\text{O}$ variations depending on the storm, the $\delta^{18}\text{O}$ values of precipitation generally were between -8‰ to -16‰, resulting in an input more depleted in ^{18}O on average than the other seasons sampled in this study.

From January to March, mean stream discharge increased. Beginning with the first snowmelt event in January, the discharge rate remained consistently higher than that of any other season. The high rate of discharge continued until after the late March snowmelt. The general trend of the $\delta^{18}\text{O}$ of the creek water continued to decrease until the end of the snow melt period. The $\delta^{18}\text{O}$ values of water in the drainage ditches continued to decrease until February 4th, at which point sampling was impossible due to freezing. Once the water in the ditches began to melt in March, higher $\delta^{18}\text{O}$ values were apparent which may have resulted from evaporation.

The water table elevation varied during the winter months according to well location and amount of overlying snowpack. Increases began at the beginning of January 1999, and the rate of increase and the date of the maximum elevation (Table III) were

Table III Maximum Well Elevation

Well Number	USGS Well Number	Date	Water Table Elevation (meters amsl)
2	MO-315	03/25/99	217.31
6	MO-298	03/25/99	214.26
7A	MO-291	03/25/99	215.59
7B	MO-303	03/25/99	218.45
9A	MO-313	01/25/99	215.36
11	MO-311	02/04/99	215.78
9B	MO-304	03/25/99	215.30
13	MO-302	01/25/99	213.77
14	MO-297	03/25/99	217.29

dependent on the well location. Creek-side wells 9A and 13 reached their maximum values on the 25th of January due to flooding caused by ice damming in areas surrounding those wells. Well 9B is screened in the confined aquifer and although it showed some response to the January snowmelt, it did not reach its maximum elevation until the end of March. The overall increase in well 9B was less than that of the wells screened in the unconfined aquifer. Well 14 is anomalous because it is both directly adjacent to the creek bed and also along a tree line where snow accumulated. This combination results in well 14 having the largest increase in water table elevation of all the creek side wells.

The unconfined wells located in the middle of the fields, GW6 and GW7A, showed the least response to recharge and the smallest increases in elevation of the unconfined aquifer wells due to wind stripping of the overlying snow. Well 2 which is located along a fence line showed no response to the January melt but displayed a large increase with later snow melting. This rise in water table elevation was the largest

increase among all the sampled wells. The two confined wells, GW7B and GW11, were frozen and thus inaccessible during the early winter months. Once the wells were accessible, the potentiometric surface of both wells remained constant.

The $\delta^{18}\text{O}$ of the well water displayed variations dependent upon the well location and type. The $\delta^{18}\text{O}$ of the water in the wells adjacent to the creek continued to become more depleted in ^{18}O during the winter months, decreasing steadily by 1-1.5 ‰ over the 4-month period. Well 13 followed a similar trend to the other wells but began to show an influence of water from the deep confined aquifer, which is consistent with Hollister's (1997) findings that well 13 has a chemical signature similar to the confined aquifer water. The unconfined wells found "inland" showed less of a decrease in $\delta^{18}\text{O}$ during the winter months with local fluctuations occurring after the snowmelts, possibly the result of "new" water mixing with "older" aquifer water and resulting in a more intermediate oxygen isotopic composition. Water in the confined well 3B (the artesian well located at the foot of the drumlin) showed a 1‰ decrease in $\delta^{18}\text{O}$ following the January snowmelt but quickly rebounded to more average values and then displayed a period of constant $\delta^{18}\text{O}$ for the rest of the winter. Confined wells 7B and 11 were inaccessible due to freezing.

4.2.4 Seasonal Variations – Spring through Early Fall: the Growing Season

For the growing season, there are two separate data sets, the 1997 and 1999 seasons. Although both years were marked by a severe lack of precipitation and prevailing drought-like conditions, the overall precipitation and discharge rates for the 1997 growing season show a consistently wetter season compared to the 1999 growing season. The only major rainfall of 1999 occurred during three storm events, July 4th (8.81

cm), August 14th (6.15 cm), and September 16th and 17th during Hurricane Floyd (13.26 cm). Throughout the rest of the time period, April to October, only six other storms produced rainfall in an amount greater than 1.25 cm.

The $\delta^{18}\text{O}$ of the precipitation varied markedly during the growing season months. Though most storms during the growing season had generally higher $\delta^{18}\text{O}$ values (-8 to -2‰) than storms at other times of the year, several storms had values between -8‰ and -10‰ and during Hurricane Floyd, the isotopic composition approached -14‰.

In contrast, the 1997 season had more moderate precipitation events and only two storms (August 22nd and 28th) that produced rainfall greater than 2.5 cm after April 1st. The creek discharge rate was substantially greater during the spring to early summer months compared to 1999, with several sharp increases during April and May. The 1997 samples did not include precipitation samples so the $\delta^{18}\text{O}$ of this input is not known. The 1999 growing season saw an immediate decrease in the creek discharge following the spring snowmelt. The mean discharge rate tended to be greater throughout the entire 1997 season by approximately 0.3 cubic meter/second.

The $\delta^{18}\text{O}$ of the creek waters (Figure 4.3a) was on average 1 to 1.5 ‰ higher during the spring and summer months for both 1997 and 1999 than during the winter 1998-99 months. During the late summer and early fall, the trends in $\delta^{18}\text{O}$ values of creek waters reversed and began to decrease with fluctuations occurring during precipitation events. The 1997 $\delta^{18}\text{O}$ values were typically lower than the 1999 growing season but display the same seasonal trend. The water at the gage station became more enriched in ^{18}O immediately following the March snowmelt. As the growing season progressed, the difference in the composition of the creek water at the gage station compared to the other

creek sites reached >3%. The source of the variation was evaporation of water around the gaging station during the periods of lower creek discharge (baseflow). Samples collected from 1993 to 1996 by the USGS and analyzed for both $\delta^{18}\text{O}$ and hydrogen (δD) isotopic composition (P. Phillips, written comm., 2000) show that values of water samples collected during summer months vary from the local meteoric water line (Figure 4.7) in a manner consistent with the effects of evaporation.

Water table elevations in both the confined and unconfined aquifers generally decrease during the growing seasons in both years. The 1997 growing season had a water table that was higher in elevation than 1999 because of greater precipitation. The rate of decrease and the response to recharge varies with well location and closely mirrors the increases during the spring melt. The largest decrease is found in the tree and fence-lined areas, wells 2 and 14, after the snowmelt recharge has mixed. The creek-side wells show moderate decreases until baseflow is reached and then the elevations remain relatively constant. The inland wells, 7A and 6, show the least decrease of all the unconfined aquifer wells. The confined wells 7B and 11 decreased slightly with the passing of the season.

The wells located along the creek bed (9A, 9B, 13, and 14) showed a greater response to recharge events than the “inland” wells. Confined well 9B shows the least response of these wells but much greater than the other confined wells, 7B and 11. The inland wells showed a response rate less than that of the creek wells but greater than the confined wells.

The $\delta^{18}\text{O}$ of water from wells located adjacent to the creek generally became depleted in ^{18}O during the beginning of May, although variations occurred depending on

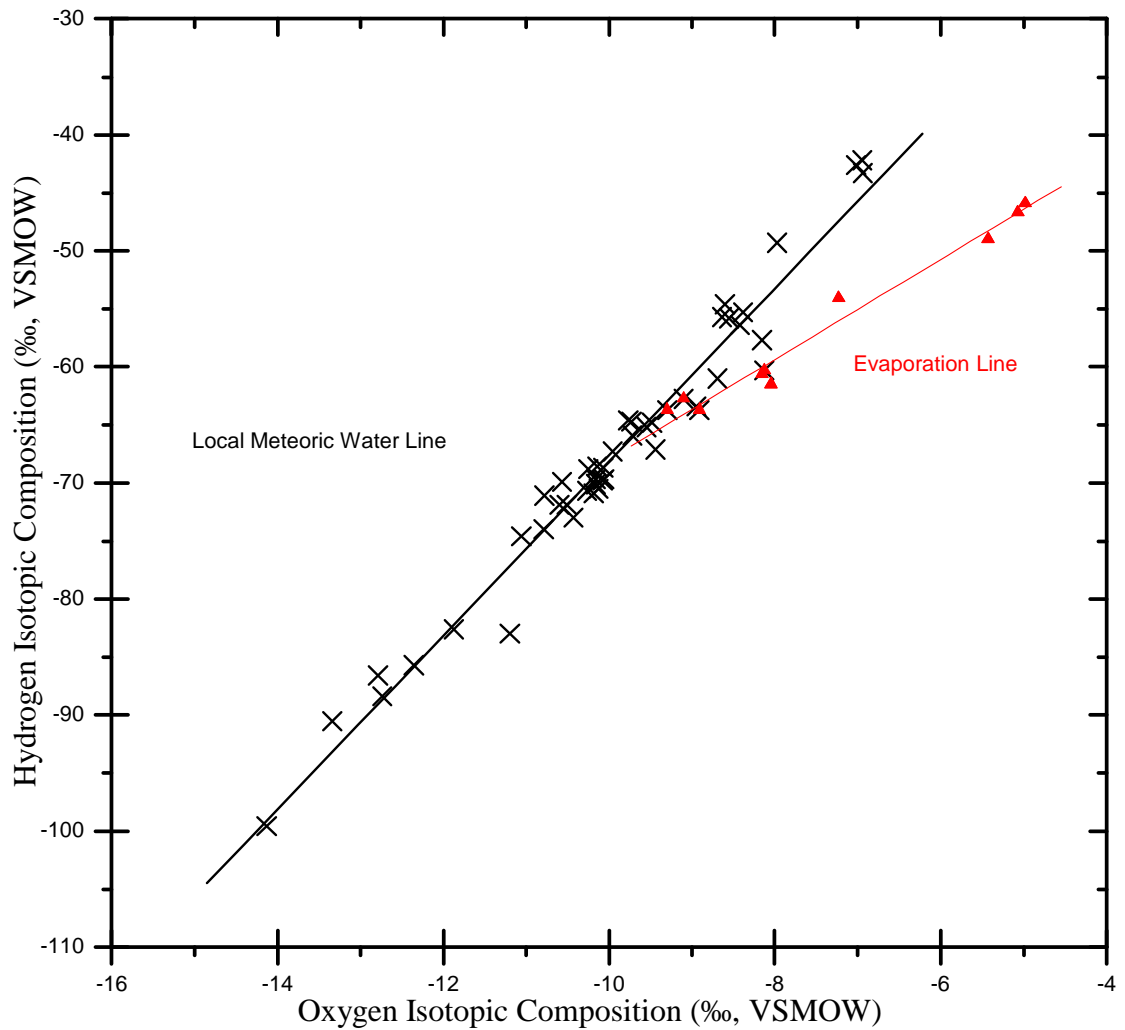


Figure 4.7 The stable isotopic composition of creek water samples collected at the streamflow gaging station located on the Canajoharie Creek, April, 1993, to June, 1996, and the resultant Local Meteoric Water Line of $\delta D = 7.49\delta^{18}O + 6.73$. Also shown is the composition of water samples collected during the Summer of 1995 which show evaporation effects and a resultant line of $\delta D = 4.31\delta^{18}O - 24.89$.

the source of the recharge water. During the 1997 period, for example, the $\delta^{18}\text{O}$ decreased in wells 9A and 13, while well 14 showed an increase through mid July and a decrease through September. This trend is the result of creek recharge of the water surrounding well 14. Previous work by Hollister (1997) showed that the creek provides recharge to the area around well 14. During the 1999 period, the $\delta^{18}\text{O}$ generally increased throughout the summer and into the autumn months. The isotopic composition varied only slightly between the two years; the 1997 water samples were slightly more enriched, ranging from 0.03 to 0.70‰. Water from well 14 largely varied between the two seasons and may be the result of the creek recharge influence in the area. The 1997 $\delta^{18}\text{O}$ values of well water shows a correlation to that of the creek water, in the form of a similar pattern with a short time lag behind the creek values. The 1999 summer values showed a lack of influence by the creek during the drought conditions.

The unconfined “inland” wells showed a slight enrichment in their $\delta^{18}\text{O}$ values during the spring and early summer followed by a slight depletion in ^{18}O . There were generally only minor fluctuations in $\delta^{18}\text{O}$ composition of the well water in response to recharge events. Following the July 4th storm, the $\delta^{18}\text{O}$ of water in well 2 increased by 4.5‰ to a value close to -7‰ (Figure 4.5). This large increase in $\delta^{18}\text{O}$ (confirmed by replicate sample analysis) could be the result of the large precipitation recharge event (8.81 cm) on a drought-influenced water table. The water collected may represent a layer of water at the top of the water table that had yet to fully mix with the aquifer. The confined aquifer wells (3B, 7B, and 11) show no change during the 1999 growing season and slight fluctuations during the 1997 Summer months.

4.3 Seasonal Variations – Results and Discussion

The annual trend of the precipitation (Figure 4.2a) $\delta^{18}\text{O}$ follows the expected path of higher $\delta^{18}\text{O}$ values in the summer months ($>-10\text{‰}$) and lower values in the winter months ($<-10\text{‰}$). The creek water samples (Figure 4.3a) follow a similar trend with slight variations due to location and due to possible evaporation around the gaging station. The isotopic variation of the creek water output showed a more subdued annual pattern than that of the precipitation, indicating the influence of groundwater and older surface water mixing with precipitation.

The annual trends in the well $\delta^{18}\text{O}$ values are controlled by the location of the well with respect to the creek, the aquifer in which the well is screened, amount of recharge, and the water mixing. The wells located adjacent to the creek (Figure 4.5a) show the largest amplitude annual variation of all the wells. This is the result of the creek influence on the recharge of the well water. The wells that are screened in both the unconfined and confined aquifers (9A and 13) show the influence of the deep water mixing during drier baseflow conditions, which can mute the annual trend.

The unconfined wells (Figure 4.5b) more distal to the stream show much less annual response to recharge due to the water mixing in the aquifer and to lower amounts of recharge. The confined wells (3B, 7B, and 11) (Figure 4.6b) show little to no annual variation in both elevation and $\delta^{18}\text{O}$ values due to a lack of immediate influence by recharge events. Well 9B, which lies adjacent to the creek and screened in the confined layer, displays some annual variation. This can be the result of the confined layer pinching out in areas along the creek (Hollister, 1997).

4.4 Single Storm Variations – Results and Discussion

Whereas there was a lack of variation on the annual scale, single storms displayed short-term variations depending on the well sampled. To display how single storms affected the oxygen isotopic composition, two major storms were chosen. The July 4th, 1999 (Figure 4.8) storm produced 8.81 cm of rain in an approximately four-hour time span. The surface water samples display an increase in $\delta^{18}\text{O}$ of between 0.7 to 1.6 ‰ on the 4th followed by an equivalent decrease by July 6th (Table IV). The water table elevation in the unconfined wells showed an increase of ~0.1 m (“inland” wells) to 0.5 m (creek-side wells) with an equivalent decrease in elevation by the 6th. The $\delta^{18}\text{O}$ of the unconfined aquifer water displayed between no change (most “inland” wells) to 0.4 ‰ (creek side wells). Well 2 displayed an abnormally large variation immediately following the storm but returned to a “normal” value by July 20th, which might have been the result of the water sampled consisting mainly of recharge water due to the drought conditions.

The second storm chosen is the September 16-17, 1999 rain event consisting of the remnants of Hurricane Floyd (Figure 4.9). This event is of interest because of the large amount of precipitation (13.26 cm) and the anomalous depletion in ^{18}O found in this precipitation (-13.61 ‰). This depletion was the result of the large amount of precipitation produced by the hurricane during its life span. The surface water samples showed the greatest variation caused by a single storm with between 1.75 and 4.5 ‰ decrease in $\delta^{18}\text{O}$ followed by a more gradual increase of 1 to 2 ‰ by September 20th (Table IV). The water table elevation in the unconfined aquifer shows an increase of between 0.1 m (“inland” wells) to 1 m (creek side wells). The $\delta^{18}\text{O}$ of the unconfined

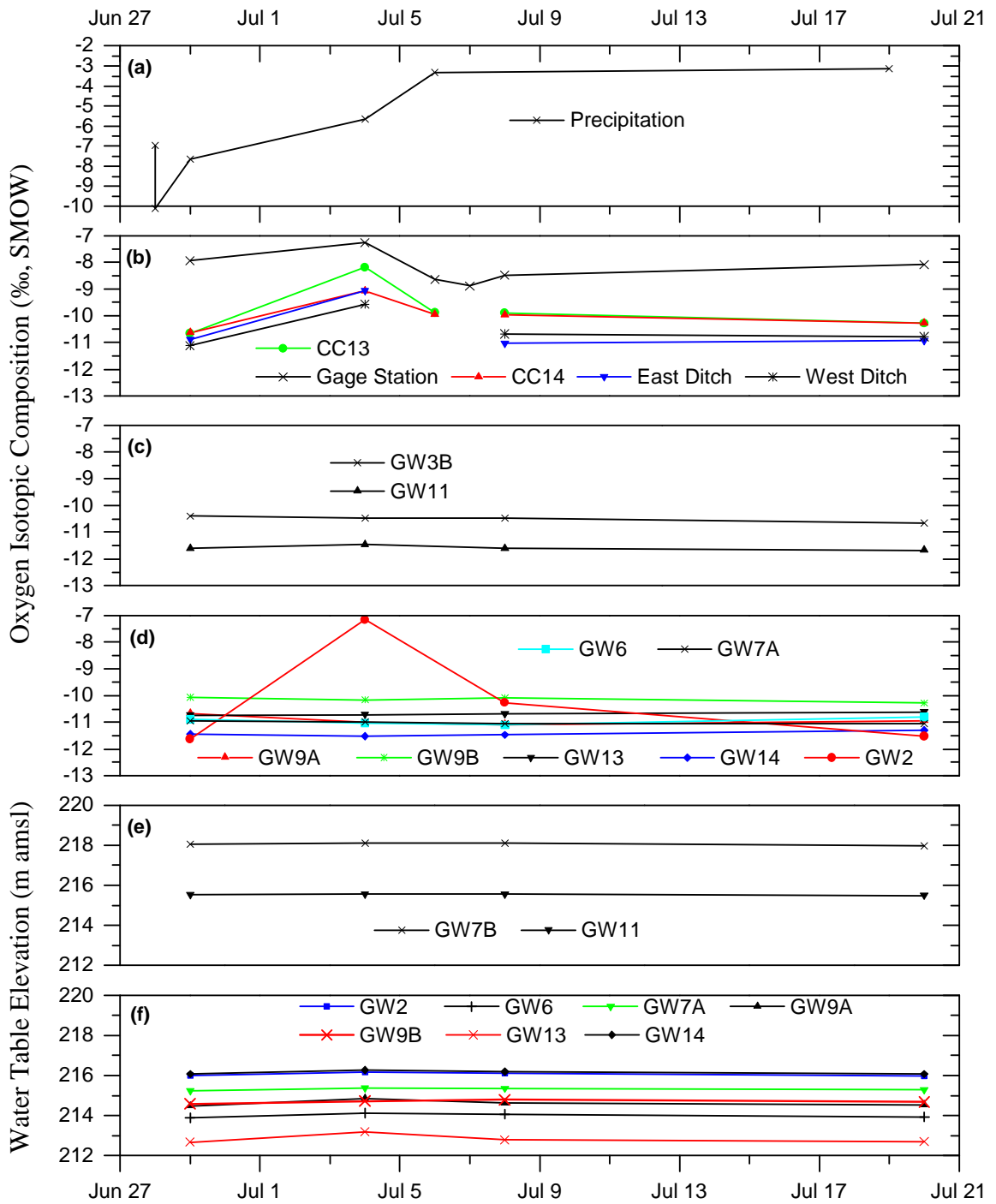


Figure 4.8 Oxygen isotopic composition of (a) precipitation, (b) surface waters, (c) confined well water, (d) unconfined well water, and water table elevation of (e) confined aquifer wells, and (f) unconfined aquifer wells from June 27th to July 21th, 1999.

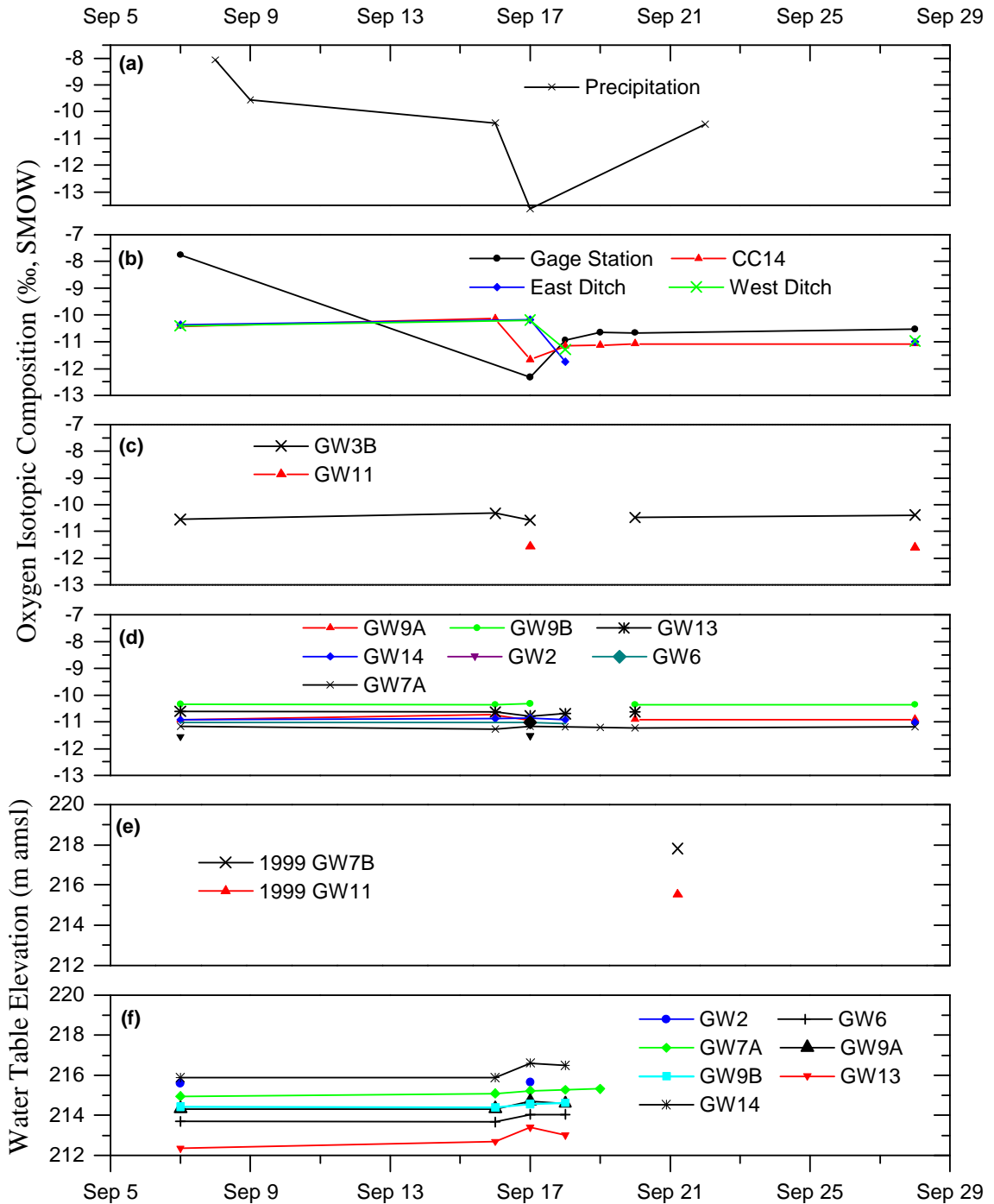


Figure 4.9 Oxygen isotopic composition of (a) precipitation, (b) surface waters, (c) confined well water, (d) unconfined well water, and water table elevation of (e) confined aquifer wells, and (f) unconfined aquifer wells from September 5 to September 29, 1999, displaying the effects of the remnants of Hurricane Floyd.

Table IV Storm Deviation in Water Table Elevation and Oxygen Isotopic Composition

Well Number	July 4, 1999		September 16-17th, 1999	
	Water Table Elevation (Δm)	Oxygen Isotopic Composition ($\Delta\text{‰}$)	Water Table Elevation (Δm)	Oxygen Isotopic Composition ($\Delta\text{‰}$)
GW2	0.16	4.41	0.05	-0.69
GW3B		0.06		-0.06
GW6	0.20	0.18	0.38	-0.06
GW7A	0.11	0.01	0.08	-0.01
GW7B	0.09			
GW9A	0.34	0.20	0.38	-0.04
GW9B	0.09	0.03	0.22	-0.01
GW11	0.03	0.04		0.05
GW13	0.51	0.06	0.70	-0.18
GW14	0.22	0.14	0.73	0.08

aquifer water displays variations of 0 to 0.1 ‰ and the confined aquifer water shows no variation due to the storm.

4.5 Tile Drain Isotopic Variations and Herbicide Correlation - Results and Discussion

Soil type can also indirectly affect the oxygen isotopic composition of groundwater. The field drained by Tile Drain 2 (TD2) is comprised of clay, which displays large quantities of cracks in the surface (Figure 4.10). These cracks appear to allow precipitation to flow preferentially through the ground, without mixing appreciably with water in the aquifers, resulting in the water sampled at TD2 having an oxygen isotopic signature similar to that of the creek water. The area drained by Tile Drain 4



Figure 4.10 Example of clayey soil and mudcracks overlying tile drain 2 (TD2). Photograph taken on July 5th, 1999, less than 24 hours since 8.81 cm of rain fell.



Figure 4.11 Example of gravel and sandy soil overlying tile drain 4 (TD4). Photograph taken on July 5th, 1999, less than 24 hours since 8.81 cm of rain fell.

(TD4) is comprised mainly of sand and gravel (Figure 4.11). The water sampled at TD4 displays temporal variations in $\delta^{18}\text{O}$ more similar to those shown by the water in the shallow aquifer, as precipitation percolates down into the aquifer and mixes with the existing water over a longer period of time. This also explains the less pronounced variation in the $\delta^{18}\text{O}$ of the water sampled at TD4 following storm events.

The oxygen isotopic composition of the water from TD2 is more enriched in ^{18}O than water from TD4 (Figures 4.12c through 4.15c). Although the $\delta^{18}\text{O}$ of the TD2 samples varies temporally in a similar fashion as does that of the creek water, the $\delta^{18}\text{O}$ of the TD2 samples can be up to 3 ‰ heavier than the creek water, a variation similar to that shown between the water in the confined aquifer and in the unconfined aquifer. This could be the result of a longer residence time of the water in the soil overlying TD2. This evidence contradicts the general macropore flow theory, but suggests a possible two-part system, whereby water is trapped in the clay pores and held for long periods of time between storm events and then flushed out by precipitation through the macropore channels, removing a small amount of the older water in the process.

Approximately 1 kg of metolachlor was applied to the field overlying TD4 during late May and early June in both 1997 and 1999. Previous studies by Phillips *et al.* (1999) show that the SAM ratio is found to be the lowest in surface water samples. This is the result of a brief contact with the soil, causing little degradation of the metolachlor into metolachlor ESA. The lowest SAM values occurred in the surface water within the first two months after application of the herbicide, suggesting a large surface runoff of the

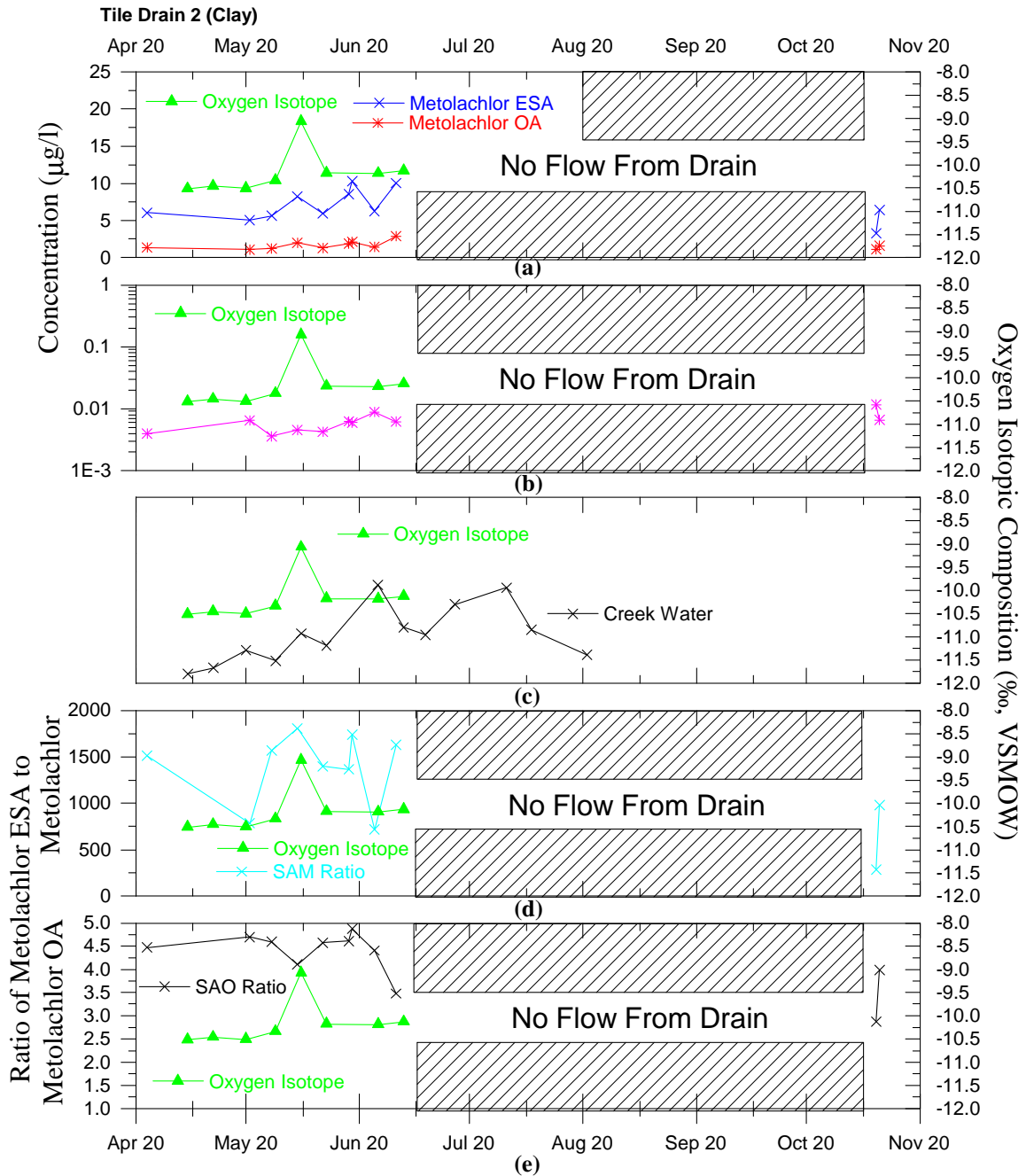


Figure 4.12 Metolachlor, ESA, OA and $\delta^{18}\text{O}$ data for tile drains 2 (TD2) collected from April to November, 1997. $\delta^{18}\text{O}$ values for TD2 are plotted with (a) metolachlor ESA and OA, (b) metolachlor, (c) Canajoharie Creek water, (d) the SAM ratio, and (e) the SAO ratio.

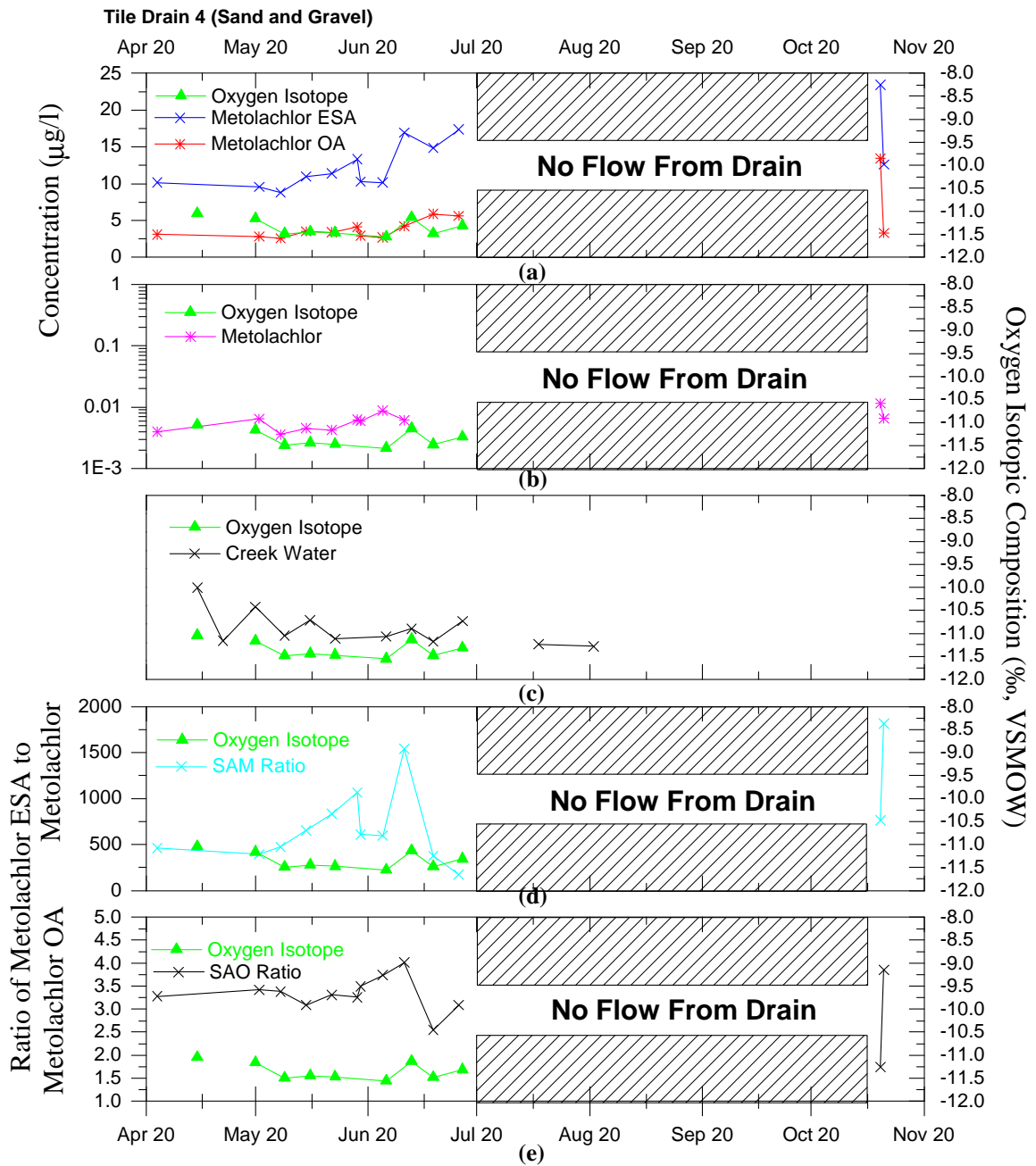


Figure 4.13 Metolachlor, ESA, OA and $\delta^{18}\text{O}$ data for tile drain 4 (TD4) collected from April to November, 1997. $\delta^{18}\text{O}$ values for TD4 are plotted with (a) metolachlor ESA and OA, (b) metolachlor, (c) Canajoharie Creek water, (d) the SAM ratio, and (e) the SAO ratio.

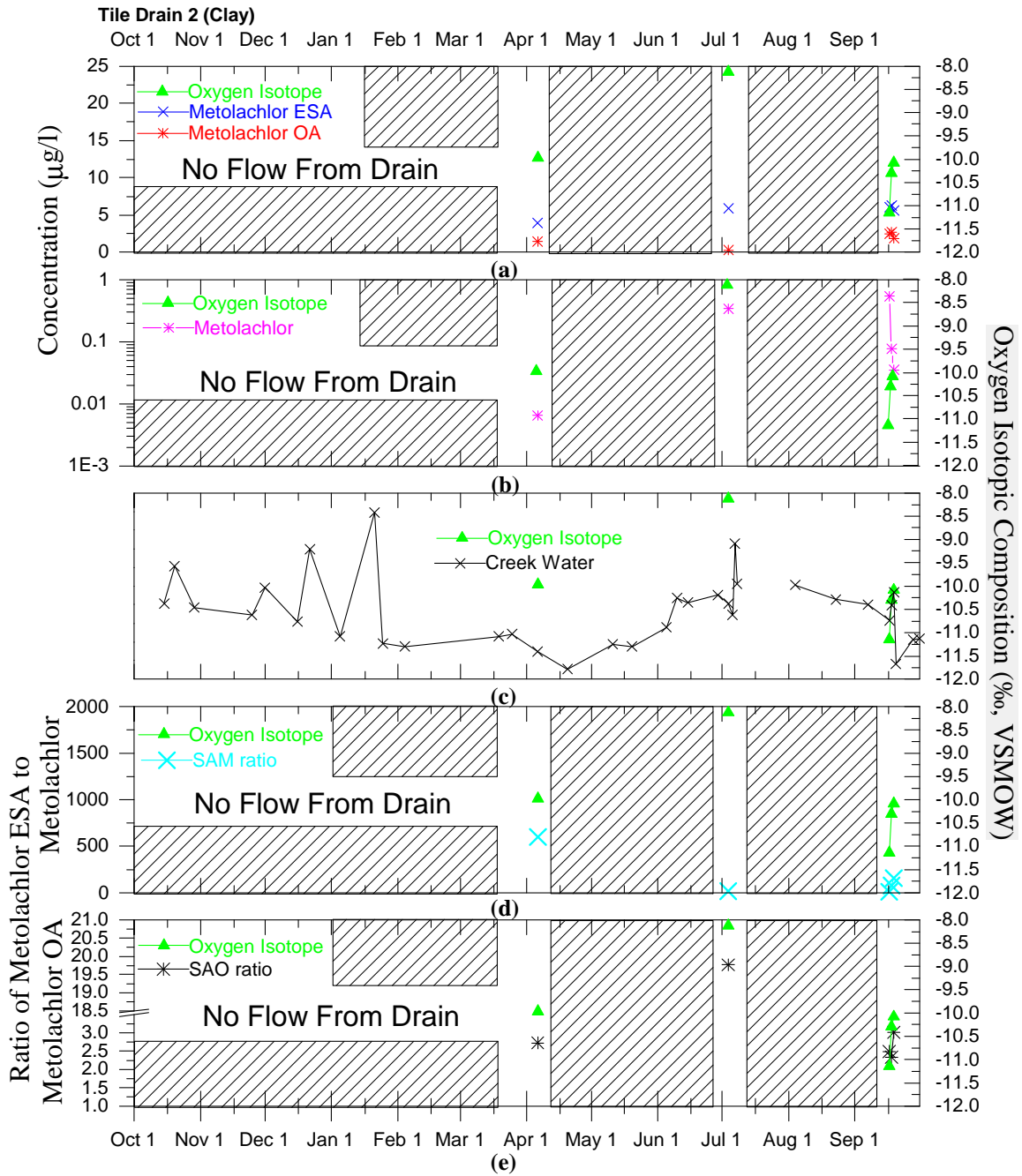


Figure 4.14 Metolachlor, ESA, OA and $\delta^{18}\text{O}$ data for tile drains 2 (TD2) collected from October, 1998 to October, 1999. $\delta^{18}\text{O}$ values for TD2 are plotted with (a) metolachlor ESA and OA, (b) metolachlor, (c) Canajoharie Creek water, (d), the SAM ratio, and (e) the SAO ratio.

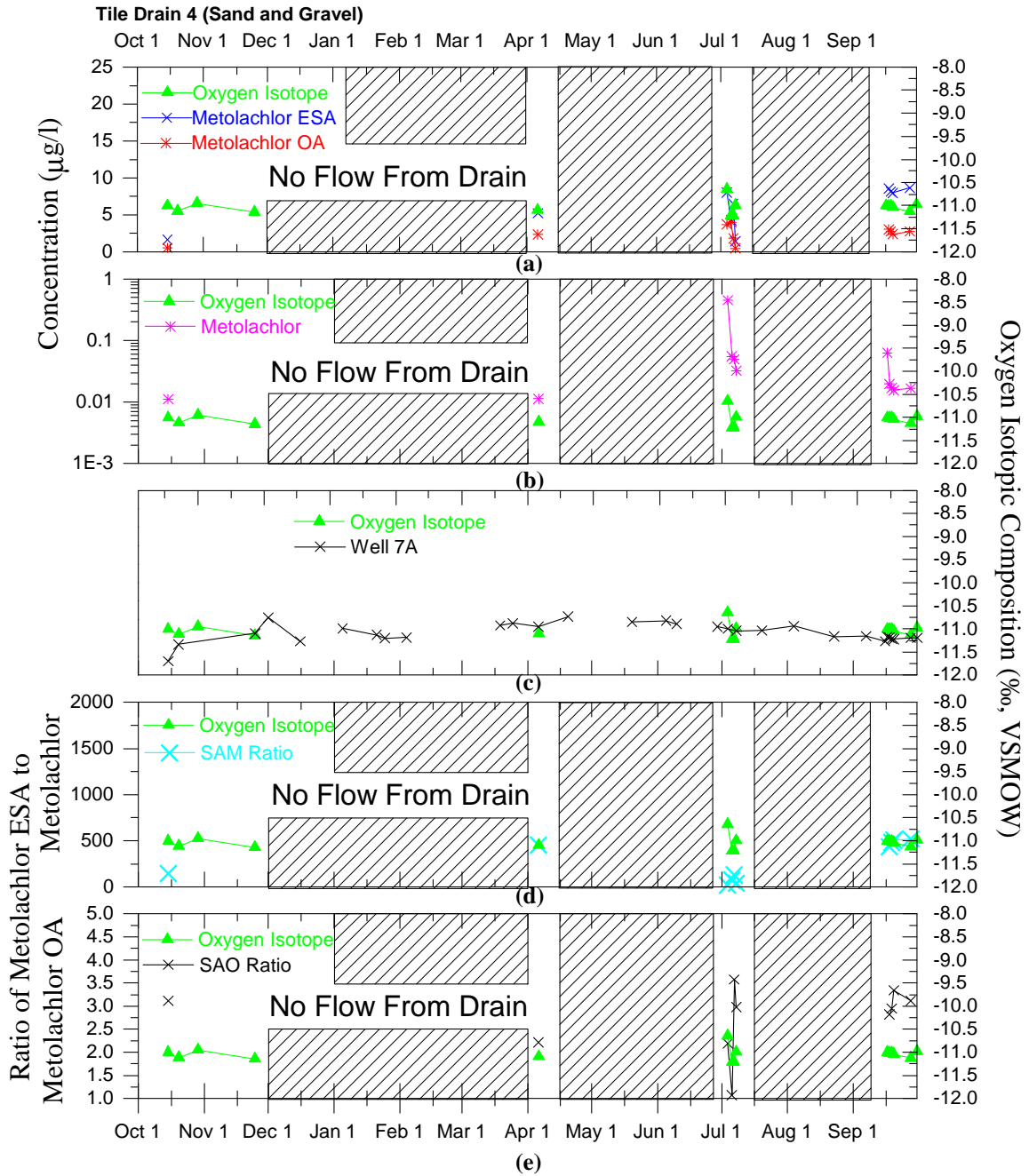


Figure 4.15 Metolachlor, ESA, OA and $\delta^{18}\text{O}$ data for tile drains (TD4) collected from October, 1998 to October, 1999. $\delta^{18}\text{O}$ values for TD4 are plotted with (a) metolachlor ESA and OA, (b) metolachlor, (c) Canajoharie Creek water, (d), the SAM ratio, and (e) the SAO ratio.

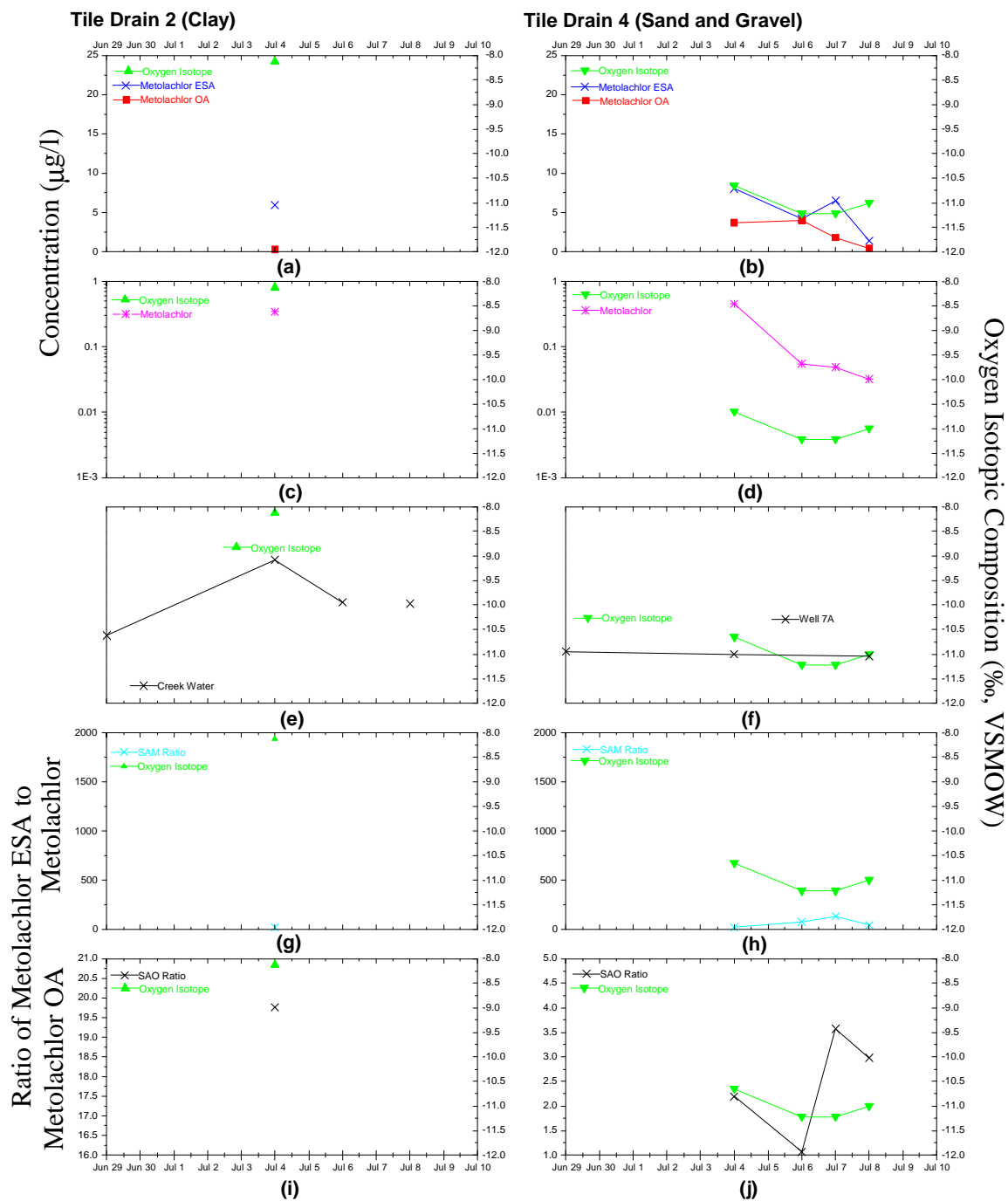


Figure 4.16 Metolachlor, ESA, OA and $\delta^{18}\text{O}$ data for tile drains 2 (TD2) and 4 (TD4) collected from June 29th, 1999 to July 10th, 1999. $\delta^{18}\text{O}$ values for TD2 are plotted with (a) metolachlor ESA and OA, (c) metolachlor, (e) Canajoharie Creek water, (g) the SAM ratio, (i) and the SAO ratio. The $\delta^{18}\text{O}$ values for TD4 are plotted with (b) metolachlor ESA and OA, (d) metolachlor, (f) well 7A water, (h) the SAM ratio, (j) the SAO ratio.

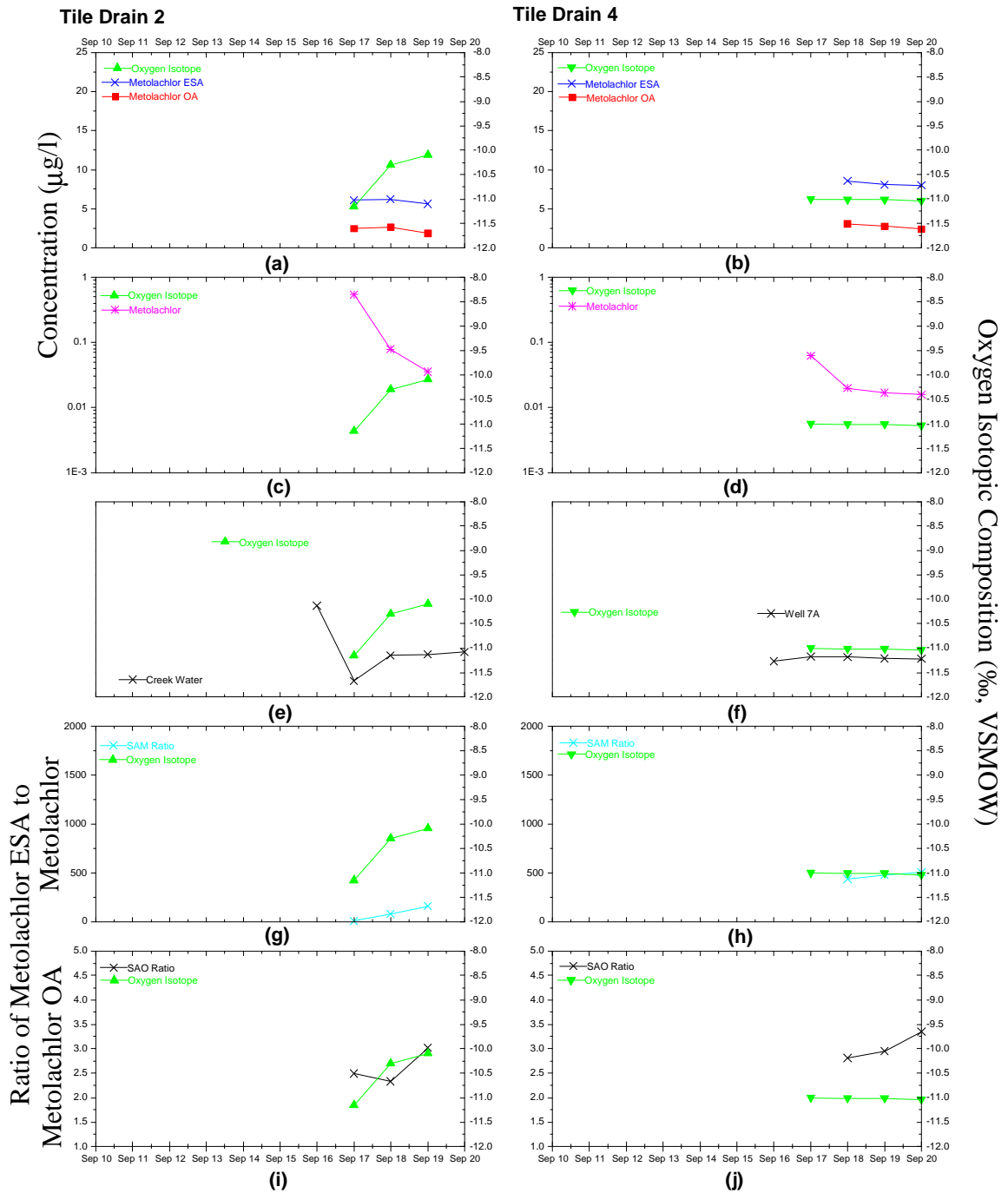


Figure 4.17 Metolachlor, ESA, OA and $\delta^{18}\text{O}$ data for tile drains 2 (TD2) and 4 (TD4) collected from September 10th, 1999 to September 20th, 1999. $\delta^{18}\text{O}$ values for TD2 are plotted with (a) metolachlor ESA and OA, (c) metolachlor, (e) Canajoharie Creek water, (g) the SAM ratio, (i) and the SAO ratio. The $\delta^{18}\text{O}$ values for TD4 are plotted with (b) metolachlor ESA and OA, (d) metolachlor, (f) well 7A water, (h), the SAM ratio, (j) the SAO ratio.

applied amount. Metolachlor OA is less stable than metolachlor ESA and Phillips *et al.* (1999) were only able to detect it a few times in surface water samples.

A more complete data set exists for the 1997 growing season than the 1999 growing season, but both display evidence for the preferential flow of water through the soil at TD2. As the 1997 growing season progressed, the concentrations of both metabolites appear to be greater in TD4 than TD2 (Figures 4.12a and 4.13a). This is due to the fresh application of the herbicide as can be seen in the subsequent larger concentration of metolachlor in TD4 (Figures 4.12b and 4.13b). Once the SAM and SAO ratios (Figures 4.12d-e and 4.13d-e) are calculated, it is apparent that the relative amounts of the metabolites are higher in TD2.

The SAO ratio decreases following 1997 storm events because of its instability. The decrease is more pronounced in the TD2 samples (Figure 4.12e) than the TD4 samples (Figure 4.13e). This provides further evidence for episodic flushing because the large rapid infiltration of the water provides a larger medium for the chemical degradation of the less stable metolachlor OA to occur (Phillips *et al.*, 1999). The SAM ratio in TD2 decreases following a late May storm followed by large increase following an early June storm. The decrease in the SAM ratio is the result of the herbicide being introduced to the field by pooling runoff water from surrounding fields. The SAM ratio in TD4 (Figure 4.13d) shows a decrease following the May-June application and a slow increase during the summer months as the herbicide is allowed to breakdown in the subsurface. Both tile drains show a spike in the metabolite concentration following a November storm because the 3-month period of no flow allows the degradation to occur and the metabolites to build up in the sub-surface.

The 1999 growing season was much drier and subsequently, the data is more sporadic. Figures 4.14 and 4.15 show the data set for the entire year, while Figures 4.16 and 4.17 display the results from two single storms, July 4th, 1999 and September 16-17th, 1999 respectively. The SAM ratio of TD2 shows a large decrease following the July 4th storm (Figures 4.14d and 4.16g) because of large amounts of pooled water overlying the field. Since this was the first storm following the application of metolachlor to surrounding fields, the amount of parent compound was high (Figures 4.14b and 4.16c). The SAM ratio remained low through the September storm because of a lack of flow through the drains to remove the excess metolachlor. The result was lower SAM and SAO values in TD2 than TD4 (Figures 4.14d-e and 4.15d-e) through the Summer months.

Part 5

Conclusions

In terms of the seasonal variability of both the oxygen isotopic composition and the water elevations of the wells and surface water sites sampled in this study the following can be said:

1. The wells located adjacent to Canajoharie Creek show a larger response to precipitation and recharge events than those located further inland. The individual wells show variability in comparison with other creek-side wells in the winter due to localized ice damming and flooding events.
2. The wells located along fence and tree lines (2, and to an extent 14) show a greater change in water table elevation than those located in the middle of the fields (6 and 7A). An increased snowpack resting on the surface above wells 2 and 14 is the result of the fence and trees acting as barricades to wind-blown snow. As these larger snowbanks melt, they provide more recharge than areas in the middle of the fields where surrounding snow has been stripped by blowing winds, such as at wells 6 and 7A. Wells 7A and 6 show the least $\delta^{18}\text{O}$ variation of all the wells screened in the unconfined aquifer. This is in part due to the removal of snow by wind decreasing spring recharge, but could also be due to more homogeneous water mixing. The large open areas cover an even larger shallow unconfined aquifer. As small amounts of recharge percolate into this area at a slow and constant rate, the water can be introduced into the large aquifer without noticeably changing the $\delta^{18}\text{O}$ values of the groundwater.

3. Wells 9A and 13 show characteristics of being screened in both the confined and unconfined aquifer. The $\delta^{18}\text{O}$ of the water sampled in these wells plot somewhere between the composition of other unconfined wells and the deep confined wells during low recharge periods throughout the year. These results, along with specific conductance and other data collected by Hollister (1997), supports the hypothesis that the water in these wells is a mixture of water from both the confined and unconfined aquifers.
4. The confined wells 7B and 11, screened deep within the confined aquifer, show the least variation in both elevation and $\delta^{18}\text{O}$, resulting from a lack of influence by individual recharge events. Since the recharge area for the confined aquifer may be on the order of miles upgradient, single storm events do not have as great an impact compared to the shallow unconfined aquifer which has direct infiltration of precipitation.
5. The confined well 9B, located along the creek, shows more variability and single storm influence than the other confined wells. The water table shows increases following single storms and is influenced, albeit less than well 9A, during the January and March flooding. The oxygen isotopic composition also varies more than the other deep confined wells. This may be the result of the confined aquifer pinching out along the creek in the area.
6. The gage station located at the watershed outlet shows consistently higher $\delta^{18}\text{O}$ values and a greater seasonal change than the surface water sampling locations around the immediate field site. This may be the result of evaporation of water near the gage station during periods of low discharge (baseflow).

In terms of the tile drain systems the following conclusions can be drawn:

1. The oxygen isotopic composition of water samples from TD4 and TD2 closely matches that of well 7A in the shallow unconfined aquifer and that of creek water, respectively. The overlying soil type of TD4 is sand and gravel and shows no cracking following rain events, whereas TD2 is overlain by clayey soil, which displays major cracking following rain events. The conclusion can be made that water emanating from TD4 has mixed well with the shallow unconfined aquifer water and the $\delta^{18}\text{O}$ values from TD2 suggest a greater penetration of new precipitation due to macro-pore flow.
2. The fine-grained clay matrix overlying TD2 traps water in the pore spaces for longer periods of time versus the larger sand and gravel matrix around TD4. This extended residence time in the soil pores allows for increased soil-water interaction resulting in increased metolachlor ESA and OA production and higher SAM and SAO ratios.

The use of stable isotopes allows further insight into the hydrogeology of the Canajoharie Field Site, including insight into the recharge patterns of the aquifer systems. Further work on the site using stable isotopes may be able to determine if a link between isotopes and pesticide concentrations and breakdown pathways can be found. In order to accomplish this task, installation of lysimeters in the areas drained by the tile drains may be helpful in providing information into the unsaturated zone interactions.

Isotopic studies in conjunction with applied conservative tracers, such as bromide or other salts, may be used to better understand other facets of the aquifer systems. The use of the tracers and isotopes may allow the infiltration rates of precipitation to be

quantified, and to further clarify the flow paths and seepage velocities. Continued sampling and analysis of the isotopic composition may also be useful in determining long-term recharge trends.

Part 6

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Appendix A

Raw Data

Appendix A-1: Oxygen isotopic composition of water samples collected around the Canajoharie Field Site from May, 1997 through September, 1997.

Date	Oxygen Isotopic Composition (‰, VSMOW)														Gage Station	
	Sample Location															
	GW7A	GW7B	GW9A	GW11A	GW11B	GW12	GW13	GW14	TD2	TD4	East Ditch	West Ditch	CC9A	CC14		
4-May-97	-10.006	-10.687	-9.945	-11.737	-11.533	-11.406	-10.493	-11.196	-10.521	-11.048					-11.804	
11-May-97	-11.164	-10.848	-10.417	-10.808	-11.462	-11.406	-10.493	-11.606	-10.458						-11.669	
20-May-97	-10.425	-10.399	-10.211	-11.727	-11.630	-10.843	-10.081	-11.610	-10.510	-11.162	-10.863	-10.303			-11.300	-9.670
28-May-97	-11.048	-10.814	-10.380	-11.727	-11.495	-11.172	-10.431	-11.739	-10.341	-11.495	-10.711	-10.652			-11.522	-10.773
4-Jun-97	-10.712	-10.442	-9.989	-10.823	-10.971	-10.250	-10.493	-11.562	-9.072	-11.448	-9.723	-10.295			-10.928	-10.408
11-Jun-97	-11.119	-10.840	-10.209	-11.699	-11.621	-10.606	-10.728	-11.483	-10.174	-11.473	-10.495	-10.529	-11.286		-11.196	-10.267
25-Jun-97	-11.075	-10.774	-10.388	-11.798	-11.153	-10.112	-10.917	-10.916	-10.189	-11.558	-9.808	-10.320	-10.328		-9.889	-9.721
2-Jul-97	-10.902	-10.067	-10.274	-11.632	-11.631	-9.822	-10.580	-9.973	-10.128	-11.134	-9.708	-10.689	-10.242		-10.801	-8.661
8-Jul-97	-11.179	-10.735	-10.443	-11.632	-11.533	-10.333	-10.745	-10.674		-11.487	-10.218	-10.858	-10.890		-10.959	-8.881
16-Jul-97	-10.735	-10.763	-10.339	-11.632	-11.533	-10.333	-10.438	-9.785		-11.316	-9.404	-10.570	-10.252		-10.299	-8.480
30-Jul-97			-10.386				-10.460	-10.202			-8.930	-9.895	-10.640		-9.941	-7.266
6-Aug-97	-11.243	-10.863	-10.517	-11.707			-10.671	-10.872			-9.477	-10.778	-10.742		-10.855	-8.135
21-Aug-97	-11.282	-10.899	-10.751	-11.711			-10.579	-11.063			-11.332	-11.322	-11.107		-11.393	

Appendix A-3: Water table elevations of aquifers located on the CFS from May, 1997 through September, 1997. Elevation is measured in meters above mean sea level.

Date	1997 Water Table Elevation (m amsl)							
	Sample Location							
	GW7A	GW7B	GW9A	GW11	GW13	GW14		
4-May-97	216.05	219.36	215.34	216.45				217.01
11-May-97	216.02	219.58	215.26	216.42	211.17	216.97		216.97
18-May-97	215.98	219.46	215.15	216.42	212.95	216.85		216.85
20-May-97	215.98	219.40	215.19	216.41	213.06	216.85		216.85
28-May-97	215.94	219.49	215.11	216.36	212.91	216.73		216.73
4-Jun-97	215.89	219.35	215.08	216.43	212.84	216.68		216.68
11-Jun-97	215.87	219.27	215.04	216.41	212.84	216.55		216.55
17-Jun-97	215.86	219.27	215.05	216.39	212.75	216.54		216.54
25-Jun-97	215.82	219.16	215.01	216.44	212.78	216.53		216.53
2-Jul-97	215.80	219.11	214.98		212.75	216.44		216.44
8-Jul-97	215.74		214.93	216.36	212.75	216.40		216.40
16-Jul-97	215.74	219.12	214.87		212.75	216.33		216.33
30-Jul-97			214.77		212.72	216.27		216.27
6-Aug-97	215.68	219.06	214.77	216.51	212.72	215.63		215.63
21-Sep-97	215.59	218.91	214.68		212.78	216.18		216.18

Appendix A-4: Water table elevations of aquifers located on the CFS from October, 1998 through October, 1999. Elevation is measured in meters above mean sea level.

Date	1998-1999 Water Table Elevation (m amsl)													
	Sample Location													
	GW2	GW6	GW7A	GW7B	GW9A	GW9B	GW11	GW13	GW14					
15-Oct-98	215.62	213.73	215.13		214.48	214.52		212.69	216.01					
20-Oct-98	215.60	213.73	215.12	217.76	214.46	214.53	215.59	212.71	216.00					
29-Oct-98														
25-Nov-98	215.47	213.67	215.39		214.45	214.48		212.70	215.98					
1-Dec-98	215.45	213.68	215.09		214.46	214.49		212.71	215.98					
16-Dec-98	215.42	213.66	215.07		214.45	214.49		212.70	215.96					
22-Dec-98	215.40				214.49			212.75	215.99					
5-Jan-99	215.39	213.66	215.07		214.55	214.54		212.84	216.00					
14-Jan-99									216.03					
21-Jan-99	215.48	213.82	215.16		214.84	214.75		213.34	216.23					
25-Jan-99	215.59	214.10	215.30		215.36	215.02		213.77	216.65					
4-Feb-99	215.70	214.08	215.33	218.31	215.20	215.09	215.78	213.50	216.58					
14-Feb-99	215.89	214.10	215.35	218.22	214.93	215.00	215.78	212.97	216.55					
19-Mar-99	216.93	214.24	215.58	218.34	215.16	215.11	215.71	213.20	217.23					
25-Mar-99	217.31	214.26	215.59	218.45	215.07	215.30	215.66	213.13	217.29					
6-Apr-99	217.09	214.14	215.53	218.45	214.93	215.03	215.59	212.91	217.06					
20-Apr-99	216.78	214.09	215.48	218.39	214.77	214.84	215.61	212.80	216.64					
11-May-99	216.50	214.05	215.37	218.33	214.72	214.77	215.59	212.75	216.42					
20-May-99	216.33	214.04	215.35	218.28	214.66	214.75	215.59	212.74	216.34					
5-Jun-99	216.24	213.99	215.30	218.15	214.57	214.68	215.56	212.69	216.22					
10-Jun-99	216.19	213.97	215.30	218.12	214.54	214.64	215.56	212.67	216.17					
15-Jun-99	216.15	213.95	215.29	218.07	214.53	214.66	215.55	212.69	216.15					
29-Jun-99	216.01	213.89	215.24	218.05	214.46	214.57	215.53	212.67	216.06					
4-Jul-99	216.16	214.11	215.37	218.10	214.83	214.71	215.55	213.19	216.29					
6-Jul-99														
7-Jul-99														
8-Jul-99	216.12	214.06	215.36	218.11	214.63	214.79	215.55	212.79	216.19					
20-Jul-99	215.97	213.94	215.28	217.98	214.53	214.67	215.49	212.70	216.08					
4-Aug-99	215.85	213.81	215.21	217.90	214.39	214.54		212.64	215.95					
23-Aug-99	215.71	213.75	215.16	217.84	214.33	214.47	215.48	212.67	215.95					
7-Sep-99	215.61	213.69	214.96	217.84	214.33	214.41		212.35	215.89					
16-Sep-99	215.66	213.67	215.10	217.81	214.32	214.40		212.69	215.88					
17-Sep-99	215.66	214.05	215.24	217.81	214.70	214.55	215.51	213.39	216.61					
18-Sep-99		214.05	215.27		214.58	214.62		213.02	216.48					
19-Sep-99			215.32											

Appendix A-5: Precipitation amounts for the 1997 season, recorded at the National Weather Service Cherry Valley 2NNE site (#301436) located approximately 8 km from the CFS. Precipitation is measured in inches of rain (cm in parentheses). Data from NCDC (1999).

Day of Month	Precipitation: inches (cm)										
	March	April	May	June	July	August	September	October	November	December	Total
1	-	-	T	0.54 (1.37)	-	-	-	0.1 (0.25)	-	-	-
2	0.31 (0.79)	-	0.04 (0.10)	0.05 (0.13)	0.38 (0.97)	-	-	-	-	-	-
3	T	-	0.63 (1.60)	-	T	0.22 (0.56)	0.22 (0.56)	-	-	-	-
4	T	-	0.41 (1.04)	-	0.12 (0.30)	-	-	-	-	-	-
5	-	-	-	-	0.06 (0.15)	T	-	-	-	-	-
6	0.84 (2.13)	0.16 (0.41)	0.61 (1.55)	-	-	-	0.12 (0.30)	-	-	-	-
7	-	-	T	-	-	-	-	-	-	-	-
8	0.12 (0.30)	T	-	-	-	-	-	-	-	-	-
9	-	0.10 (0.25)	0.32 (0.81)	-	-	-	-	-	-	-	-
10	0.22 (0.56)	-	-	-	0.48 (1.22)	-	-	-	-	-	-
11	T	-	-	-	-	0.22 (0.56)	0.54 (1.37)	-	-	-	-
12	0.11 (0.28)	-	0.16 (0.41)	-	-	-	0.12 (0.30)	-	-	-	-
13	-	0.34 (0.86)	-	0.13 (0.33)	-	0.82 (2.08)	T	-	-	-	-
14	-	-	-	-	-	-	-	-	-	-	-
15	-	-	-	-	0.43 (1.09)	-	-	-	-	-	-
16	T	-	0.14 (0.36)	-	-	0.34 (0.86)	-	-	-	-	-
17	-	0.08 (0.20)	0.07 (0.18)	0.15 (0.38)	0.31 (0.79)	-	0.31 (0.79)	-	-	-	-
18	-	0.15 (0.38)	-	0.59 (1.50)	-	-	-	-	-	-	-
19	-	0.64 (1.63)	0.34 (0.86)	-	-	-	-	-	-	-	-
20	-	-	0.51 (1.30)	T	-	-	-	-	-	-	-
21	-	-	-	-	0.17 (0.43)	1.02 (2.59)	-	-	-	-	-
22	0.56 (1.42)	-	0.12 (0.30)	T	0.15 (0.38)	T	-	-	-	-	-
23	-	-	-	-	-	0.05 (0.13)	0.14 (0.36)	-	-	-	-
24	-	-	-	0.12 (0.30)	-	-	-	-	-	-	-
25	0.12 (0.30)	-	T	0.81 (2.06)	-	-	-	-	-	-	-
26	0.84 (2.13)	-	-	0.12 (0.30)	-	0.32 (0.81)	0.12 (0.30)	-	-	-	-
27	-	-	-	-	0.34 (0.86)	0.13 (0.33)	-	-	-	-	-
28	-	0.92 (2.34)	-	-	T	1.09 (2.77)	-	-	-	-	-
29	0.26 (0.66)	-	-	-	-	-	0.24 (0.61)	-	-	-	-
30	-	-	T	-	-	-	0.25 (0.64)	-	-	-	-
31	1.66 (4.22)	-	-	-	-	-	-	-	-	-	-

T : Trace amount
 - : No recorded precipitation

Appendix A-6: Precipitation amounts for the 1998-1999 time frame, recorded at the National Weather Service Cherry Valley 2NNE site (#301436) located approximately 8 km from the CFS. Precipitation is measured in inches of rain (cm in parenthesis). Data from NCDC (1999).

Day of Month	1999												
	October	November	December	January	February	March	April	May	June	July	August	September	October
1	0.51 (1.30)	-	-	T	-	0.47 (1.19)	0.04 (0.10)	-	-	-	0.09 (0.23)	-	-
2	0.21 (0.53)	-	-	-	0.51 (1.30)	0.14 (0.36)	-	-	0.11 (0.28)	0.65 (1.65)	-	-	-
3	-	-	-	1.61 (4.09)	-	-	-	-	T	-	-	-	-
4	-	-	-	-	-	0.54 (1.37)	0.24 (0.61)	T	-	3.47 (8.81)	0.03 (0.08)	-	-
5	-	-	T	0.14 (0.36)	T	0.08 (0.20)	-	-	-	-	-	-	-
6	-	-	0.04 (0.10)	T	0.04 (0.10)	-	-	-	-	0.31 (0.79)	-	0.08 (0.20)	-
7	-	0.20 (0.51)	-	-	-	0.49 (1.24)	-	-	-	-	-	0.13 (0.33)	0.25 (0.64)
8	0.44 (1.12)	-	0.21 (0.53)	0.39 (0.99)	-	-	0.07 (0.18)	0.77 (1.96)	-	0.11 (0.28)	0.33 (0.84)	T	-
9	0.21 (0.53)	-	-	0.41 (1.04)	-	-	-	0.14 (0.36)	-	T	-	0.06 (0.15)	-
10	0.26 (0.66)	0.22 (0.56)	-	-	-	-	-	-	-	0.31 (0.79)	-	-	-
11	T	0.37 (0.94)	T	-	-	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-	-	-	-	-	-
13	-	-	-	0.45 (1.14)	0.30 (0.76)	0.13 (0.33)	0.23 (0.58)	-	-	-	-	-	-
14	-	-	-	-	-	-	-	-	-	-	-	-	-
15	0.46 (1.17)	-	-	0.13 (0.33)	-	-	-	-	0.62 (1.57)	-	2.42 (6.15)	0.04 (0.10)	-
16	-	0.07 (0.18)	-	-	-	-	0.17 (0.43)	-	-	-	0.05 (0.13)	0.02 (0.05)	-
17	-	0.24 (0.61)	0.16 (0.41)	-	0.03 (0.08)	-	0.26 (0.66)	-	T	-	-	2.74 (6.96)	-
18	-	-	-	-	-	-	0.06 (0.15)	-	0.1 (0.25)	-	-	2.48 (6.30)	-
19	0.11 (0.28)	-	T	0.50 (1.27)	-	T	-	0.57 (1.45)	-	0.46 (1.17)	-	-	-
20	-	0.27 (0.69)	-	-	-	-	-	-	-	-	-	-	-
21	-	T	-	-	-	T	-	-	-	-	0.33 (0.84)	0.64 (1.63)	-
22	-	T	0.98 (2.49)	0.72 (1.83)	-	1.26 (3.20)	0.21 (0.53)	-	-	-	-	0.75 (1.91)	-
23	-	-	0.04 (0.10)	T	-	0.18 (0.46)	0.34 (0.86)	0.16 (0.41)	-	-	-	-	-
24	-	-	-	0.94 (2.39)	-	-	-	0.31 (0.79)	-	-	-	-	-
25	-	-	-	-	-	-	-	0.12 (0.30)	0.17 (0.43)	-	-	0.04 (0.10)	-
26	-	0.21 (0.53)	-	-	T	-	-	0.24 (0.61)	-	0.74 (1.88)	T	-	-
27	-	0.22 (0.56)	-	-	-	-	-	0.07 (0.18)	-	-	0.82 (2.08)	-	-
28	0.33 (0.84)	-	-	0.29 (0.74)	0.34 (0.86)	0.11 (0.28)	-	-	0.31 (0.79)	-	-	-	-
29	-	0.04 (0.10)	-	T	-	-	-	-	0.29 (0.74)	T	-	-	-
30	-	-	-	0.06 (0.15)	-	-	-	-	-	-	-	0.48 (1.22)	-
31	-	-	-	-	-	-	-	-	-	-	-	-	-

T : Trace amount
 - : No recorded precipitation

Appendix A-7: Snow depth measurements for the 1998-1999 winter season measured at the National Weather Service Cherry Valley 2NNE site (#301436). Data from NCDC (1999).

Date	Snow Depth (inches)	Snow Depth (cm)
22-Nov-98	0	0
29-Nov-98	0	0
17-Dec-98	2	5.08
19-Dec-98	0	0
23-Dec-98	3	7.62
26-Dec-98	0	0
30-Dec-98	2	5.08
5-Jan-99	3	7.62
8-Jan-99	6	15.24
1-Feb-99	12	30.48
9-Feb-99	8	20.32
28-Feb-99	6	15.24
1-Mar-99	8	20.32
7-Mar-99	7	17.78
8-Mar-99	20	50.80
12-Mar-99	22	55.88
14-Mar-99	20	50.80
16-Mar-99	12	30.48
22-Mar-99	9	22.86
23-Mar-99	11	27.94
27-Mar-99	6	15.24
28-Mar-99	4	10.16
29-Mar-99	2	5.08
2-Apr-99	0	0

Appendix A-8: 1997 Canajoharie Creek discharge rates measured at the USGS Streamflow Gaging station #1349150 located on Canajoharie Creek near Canajoharie, New York. The units are cubic feet per second (cubic meters per second). Data modified from NWIS-S (1999).

<u>Canajoharie Creek Discharge Rates: cubic feet per second (cubic meters per second)</u>											
Day of Month	March	April	May	June	July	August	September	October	November	December	
1	139 (3.94)	273 (7.73)	67 (1.90)	34 (0.96)	3.4 (0.10)	2.1 (0.06)	3.0 (0.08)				
2	344 (9.74)	298 (8.44)	56 (1.59)	24 (0.68)	3.6 (0.10)	2.1 (0.06)	2.9 (0.08)				
3	189 (5.35)	496 (14.05)	145 (4.11)	15 (0.42)	4.4 (0.12)	2.4 (0.07)	2.9 (0.08)				
4	118 (3.34)	606 (17.16)	299 (8.47)	12 (0.34)	4.1 (0.12)	2.6 (0.07)	2.8 (0.08)				
5	106 (3.00)	271 (7.67)	102 (2.89)	11 (0.31)	3.8 (0.11)	2.7 (0.08)	3.1 (0.09)				
6	701 (19.85)	240 (6.80)	97 (2.75)	9.5 (0.27)	3.6 (0.10)	2.5 (0.07)	2.9 (0.08)				
7	150e (4.25)	177 (5.01)	106 (3.00)	8.5 (0.24)	3.2 (0.09)	2.4 (0.07)	2.8 (0.08)				
8	94e (2.66)	118 (3.34)	71 (2.01)	8.1 (0.23)	3.1 (0.09)	2.3 (0.07)	2.9 (0.08)				
9	90e (2.55)	91 (2.58)	67 (1.90)	7.3 (0.21)	3.4 (0.10)	2.2 (0.06)	2.9 (0.08)				
10	92e (2.61)	70 (1.98)	86 (2.44)	6.6 (0.19)	4.6 (0.13)	2.0 (0.06)	2.8 (0.08)				
11	110e (3.12)	61 (1.73)	60 (1.70)	5.8 (0.16)	4.0 (0.11)	2.0 (0.06)	2.9 (0.08)				
12	70e (1.98)	57 (1.61)	48 (1.36)	5.4 (0.15)	3.2 (0.09)	2.1 (0.06)	4.4 (0.12)				
13	58e (1.64)	126 (3.57)	43 (1.22)	5.4 (0.15)	2.9 (0.08)	2.4 (0.07)	4.7 (0.13)				
14	60e (1.70)	80 (2.27)	37 (1.05)	6.5 (0.18)	2.7 (0.08)	3.4 (0.10)	3.5 (0.10)				
15	100e (2.83)	55 (1.56)	33 (0.93)	5.1 (0.14)	2.9 (0.08)	3.2 (0.09)	3.0 (0.08)				
16	60e (1.70)	47 (1.33)	28 (0.79)	4.7 (0.13)	4.9 (0.14)	2.8 (0.08)	2.9 (0.08)				
17	50e (1.41)	43 (1.22)	26 (0.74)	4.7 (0.13)	3.7 (0.10)	2.8 (0.08)	2.7 (0.08)				
18	54e (1.53)	46 (1.30)	24 (0.68)	5.6 (0.16)	3.3 (0.09)	2.7 (0.08)	2.6 (0.07)				
19	90e (2.55)	158 (4.47)	35 (0.99)	9.3 (0.26)	3.4 (0.10)	2.4 (0.07)	2.5 (0.07)				
20	80e (2.27)	260 (7.36)	128 (3.62)	6.2 (0.18)	2.9 (0.08)	2.2 (0.06)	2.8 (0.08)				
21	66e (1.87)	141 (3.99)	55 (1.56)	5.4 (0.15)	2.7 (0.08)	2.8 (0.08)	2.7 (0.08)				
22	461 (13.06)	96 (2.72)	43 (1.22)	4.7 (0.13)	3.1 (0.09)	6.0 (0.17)	2.8 (0.08)				
23	111 (3.14)	76 (2.15)	35 (0.99)	4.3 (0.12)	3.3 (0.09)	3.7 (0.10)	2.7 (0.08)				
24	60e (1.70)	62 (1.76)	28 (0.79)	4.2 (0.12)	2.8 (0.08)	3.0 (0.08)	2.6 (0.07)				
25	45e (1.27)	52 (1.47)	26 (0.74)	12 (0.34)	2.6 (0.07)	2.7 (0.08)	2.6 (0.07)				
26	567 (16.06)	43 (1.22)	24 (0.68)	7.9 (0.22)	2.5 (0.07)	2.7 (0.08)	2.5 (0.07)				
27	297 (8.41)	36 (1.02)	20 (0.57)	5.5 (0.16)	2.4 (0.07)	2.9 (0.08)	2.6 (0.07)				
28	293 (8.30)	257 (7.28)	18 (0.51)	4.5 (0.13)	2.5 (0.07)	4.9 (0.14)	2.6 (0.07)				
29	344 (9.74)	152 (4.30)	16 (0.45)	4.0 (0.11)	2.7 (0.08)	6.0 (0.17)	2.7 (0.08)				
30	314 (8.89)	85 (2.41)	15 (0.42)	3.7 (0.10)	2.5 (0.07)	4.5 (0.13)	2.6 (0.07)				
31	400 (11.33)		15 (0.42)		2.2 (0.06)	3.3 (0.09)					

e - estimated

Appendix A-9: 1998-1999 Canajoharie Creek discharge rates measured at the USGS Streamflow Gaging station #1349150 located on Canajoharie Creek near Canajoharie, New York. The units are cubic feet per second (cubic meters per second). Data modified from NWIS-W (1999).

		Canajoharie Creek Discharge Rates: cubic feet per second (cubic meters per second)											
		1999											
Day of	1998	October	November	December	January	February	March	April	May	June	July	August	September
Month													
1		4.3 (0.12)	4.5e (0.13)	4.4 (0.12)	5.2e (0.15)	30e (0.85)	150e (4.25)	305 (8.64)	19 (0.54)	5.7 (0.16)	3.8 (0.11)	1.5 (0.04)	1.7 (0.05)
2		6.4 (0.18)	4.2e (0.12)	4.5 (0.13)	4.8e (0.14)	35e (0.99)	120e (3.40)	282 (7.99)	18 (0.51)	5.9 (0.17)	3.9 (0.11)	1.2 (0.03)	1.5 (0.04)
3		4.6 (0.13)	3.9e (0.11)	4.5 (0.13)	4.6e (0.13)	100e (2.83)	100e (2.83)	247 (7.00)	16 (0.45)	5.6 (0.16)	7.7 (0.22)	0.99(0.03)	1.4 (0.04)
4		4.0 (0.11)	3.7e (0.10)	4.3 (0.12)	4.4e (0.12)	200e (5.66)	700e (19.82)	225 (6.37)	16 (0.45)	5.0 (0.14)	177 (5.01)	0.9 (0.03)	1.2 (0.03)
5		3.8 (0.11)	3.5e (0.10)	4.2 (0.12)	4.2e (0.12)	140e (3.96)	150e (4.25)	152 (4.30)	17 (0.48)	4.6 (0.13)	51 (1.44)	1.0 (0.03)	1.2 (0.03)
6		3.6 (0.10)	3.9e (0.11)	4.2 (0.12)	3.9e (0.11)	90e (2.55)	80e (2.27)	106 (3.00)	16 (0.45)	4.2 (0.12)	21 (0.59)	0.94(0.03)	1.1 (0.03)
7		3.6 (0.10)	3.6e (0.10)	4.1 (0.12)	3.7e (0.10)	60e (1.70)	70e (1.98)	92 (2.61)	14 (0.40)	3.9 (0.11)	21 (0.59)	1.1 (0.03)	1.2 (0.03)
8		4.1 (0.12)	3.5e (0.10)	4.2 (0.12)	3.6e (0.10)	50e (1.42)	60e (1.70)	77 (2.18)	16 (0.45)	3.3 (0.09)	13 (0.37)	1.6 (0.05)	1.8 (0.05)
9		5.5 (0.16)	3.4e (0.10)	4.4 (0.12)	3.5e (0.10)	45e (1.27)	50e (1.42)	64 (1.81)	27 (0.76)	3.0 (0.08)	10 (0.28)	2.1 (0.06)	2.6 (0.07)
10		5.4 (0.15)	4.0e (0.11)	4.6 (0.13)	3.4e (0.10)	40e (1.13)	45e (1.27)	55 (1.56)	21 (0.59)	3.1 (0.09)	10 (0.28)	2.5 (0.07)	2.1 (0.06)
11		6.7 (0.19)	5.9 (0.17)	4.3 (0.12)	3.3e (0.09)	40e (1.13)	38e (1.08)	45 (1.27)	16 (0.45)	3.1 (0.09)	8.9 (0.25)	1.8 (0.05)	1.6 (0.05)
12		5.8 (1.60)	7.9 (0.22)	3.9e (0.11)	3.3e (0.09)	80e (2.27)	33e (0.93)	49 (1.39)	14 (0.40)	2.9 (0.08)	6.9 (0.20)	1.6 (0.05)	1.3 (0.04)
13		4.6 (0.13)	5.3 (0.15)	3.7e (0.10)	3.3e (0.09)	150e (4.25)	30e (0.85)	39 (1.10)	13 (0.37)	2.5 (0.07)	5.9 (0.17)	1.6 (0.05)	1.2 (0.03)
14		5.0 (0.14)	4.8 (0.14)	3.6e (0.10)	5.0e (0.14)	80e (2.27)	30e (0.85)	34 (0.96)	12 (0.34)	2.5 (0.07)	5.1 (0.14)	6.7 (0.19)	1.1 (0.03)
15		8.8 (0.25)	4.5 (0.13)	3.6e (0.10)	7.0e (0.20)	60e (1.70)	33e (0.93)	30 (0.85)	11 (0.31)	3.5 (0.10)	4.7 (0.13)	25 (0.71)	1.1 (0.03)
16		5.8 (0.16)	4.5 (0.13)	4.0 (0.11)	6.0e (0.17)	50e (1.42)	40e (1.13)	29 (0.82)	10 (0.28)	4.9 (0.14)	4.1 (0.12)	7.8 (0.22)	27 (0.76)
17		5.0 (0.14)	4.6 (0.13)	3.9e (0.11)	6.0e (0.17)	46e (1.30)	245 (6.94)	40 (1.13)	9.3 (0.26)	3.3 (0.09)	3.7 (0.10)	4.6 (0.13)	676 (19.14)
18		4.6 (0.13)	5.0 (0.14)	3.8e (0.11)	12e (0.34)	42e (1.19)	582 (16.48)	35 (0.99)	8.6 (0.24)	3.6 (0.10)	3.3 (0.09)	3.2 (0.09)	116 (3.29)
19		4.4e (0.12)	4.7 (13.0)	3.8e (0.11)	30e (0.85)	40e (1.13)	295 (8.35)	30 (0.85)	9.9 (0.28)	3.5 (0.10)	3.4 (0.10)	2.5 (0.07)	50 (1.42)
20		4.2e (0.12)	4.6 (0.13)	4.0 (0.11)	100e (2.83)	32e (0.91)	161 (4.56)	30 (0.85)	16 (0.45)	2.8 (0.08)	5.2 (0.15)	2.2 (0.06)	31 (0.88)
21		4.0e (0.11)	5.7 (0.16)	4.4 (0.12)	80e (2.27)	27e (0.76)	143 (4.05)	27 (0.76)	11 (0.31)	2.4 (0.07)	4.6 (0.13)	2.5 (0.07)	29 (0.82)
22		3.9e (0.11)	5.8 (0.16)	27 (0.76)	70e (1.98)	23e (0.65)	568 (16.09)	25 (0.71)	8.8 (0.25)	2.2 (0.06)	3.3 (0.09)	3.4 (0.10)	92 (2.61)
23		3.7e (0.10)	4.8 (0.14)	40 (1.13)	80e (2.27)	20e (0.57)	322 (9.12)	42 (1.19)	8.5 (0.24)	2.0 (0.06)	2.8 (0.08)	3.5 (0.10)	104 (2.95)
24		3.6e (0.10)	4.5 (0.13)	16 (0.45)	400e (11.33)	19e (0.54)	324 (9.18)	46 (1.30)	11 (0.31)	1.7 (0.05)	2.5 (0.07)	2.6 (0.07)	50 (1.42)
25		3.8e (0.11)	4.4 (0.12)	10 (0.28)	250e (7.08)	18e (0.51)	294 (8.33)	32 (0.91)	19 (0.54)	1.6 (0.05)	2.2 (0.06)	2.0 (0.06)	32 (0.91)
26		3.5e (0.10)	4.6 (0.13)	8.0e (0.23)	150e (4.25)	18e (0.51)	203 (5.75)	28 (0.79)	13 (0.37)	1.6 (0.05)	2.0 (0.06)	1.9 (0.05)	24 (0.68)
27		3.5e (0.10)	5.4 (0.15)	7.6e (0.22)	90e (2.55)	20e (0.57)	214 (6.06)	25 (0.71)	12 (0.34)	2.0 (0.06)	3.1 (0.09)	2.9 (0.08)	19 (0.54)
28		4.0e (0.11)	5.4 (0.15)	7.2e (0.20)	60e (1.70)	40e (1.13)	228 (6.46)	23 (0.65)	9.6 (0.27)	2.1 (0.06)	2.4 (0.07)	6.3 (0.18)	17 (0.48)
29		4.8e (0.14)	4.8 (0.14)	6.6e (0.19)	45e (1.27)	351 (9.94)	351 (9.94)	21 (0.59)	8.1 (0.23)	3.8 (0.11)	1.8 (0.05)	4.7 (0.13)	15 (0.42)
30		5.6e (0.16)	4.4 (0.12)	6.0e (0.17)	35e (0.99)	344 (9.74)	344 (9.74)	20 (0.57)	6.9 (0.20)	4.8 (0.14)	1.6 (0.05)	2.6 (0.07)	15 (0.42)
31		5.0e (0.14)		5.6e (0.16)	30e (0.85)	315 (8.92)	315 (8.92)		6.2 (0.18)		1.5 (0.04)	1.9 (0.05)	

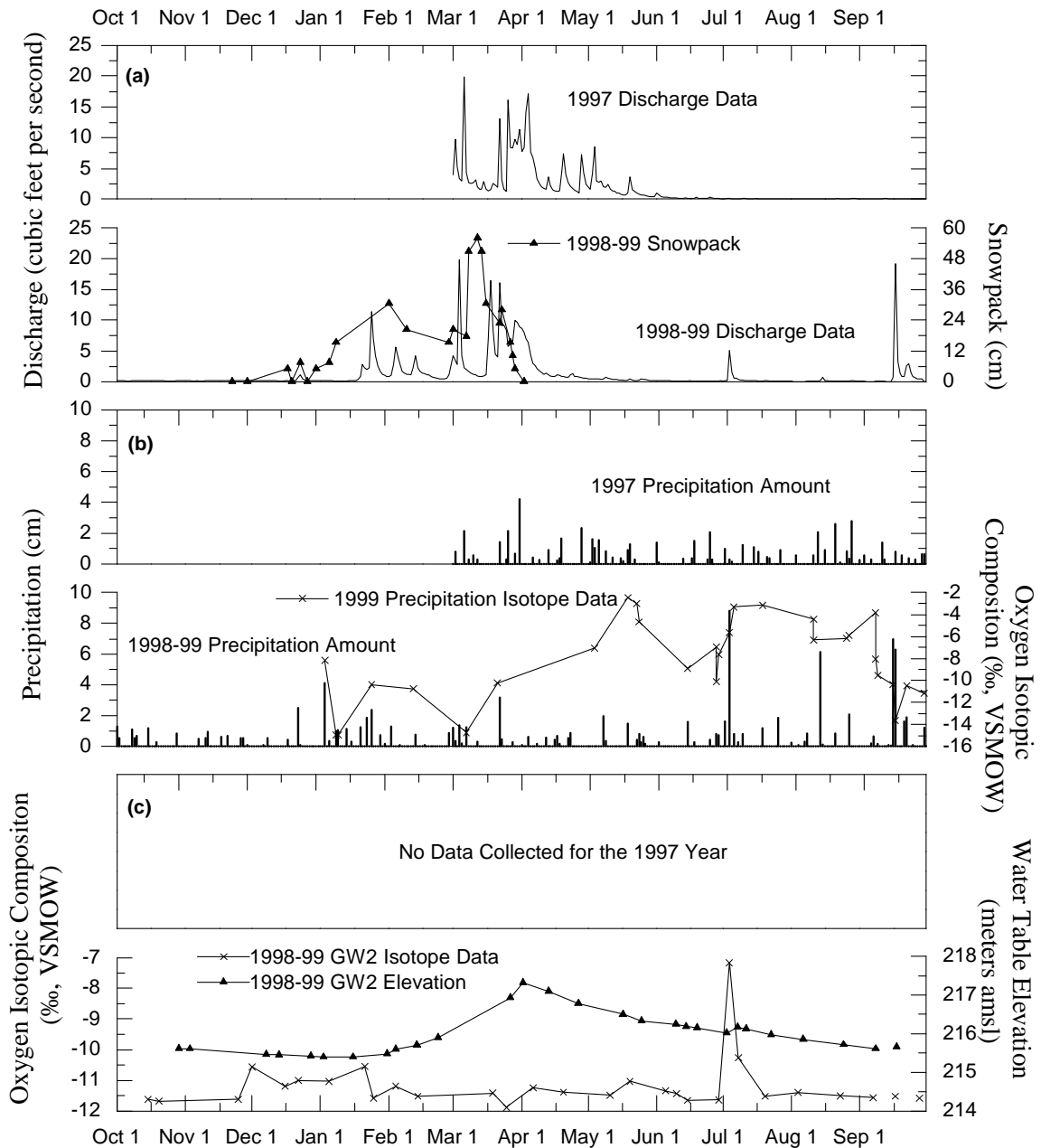
e - estimated

Appendix A-10: Oxygen isotopic composition of precipitation collected at the University at Albany.

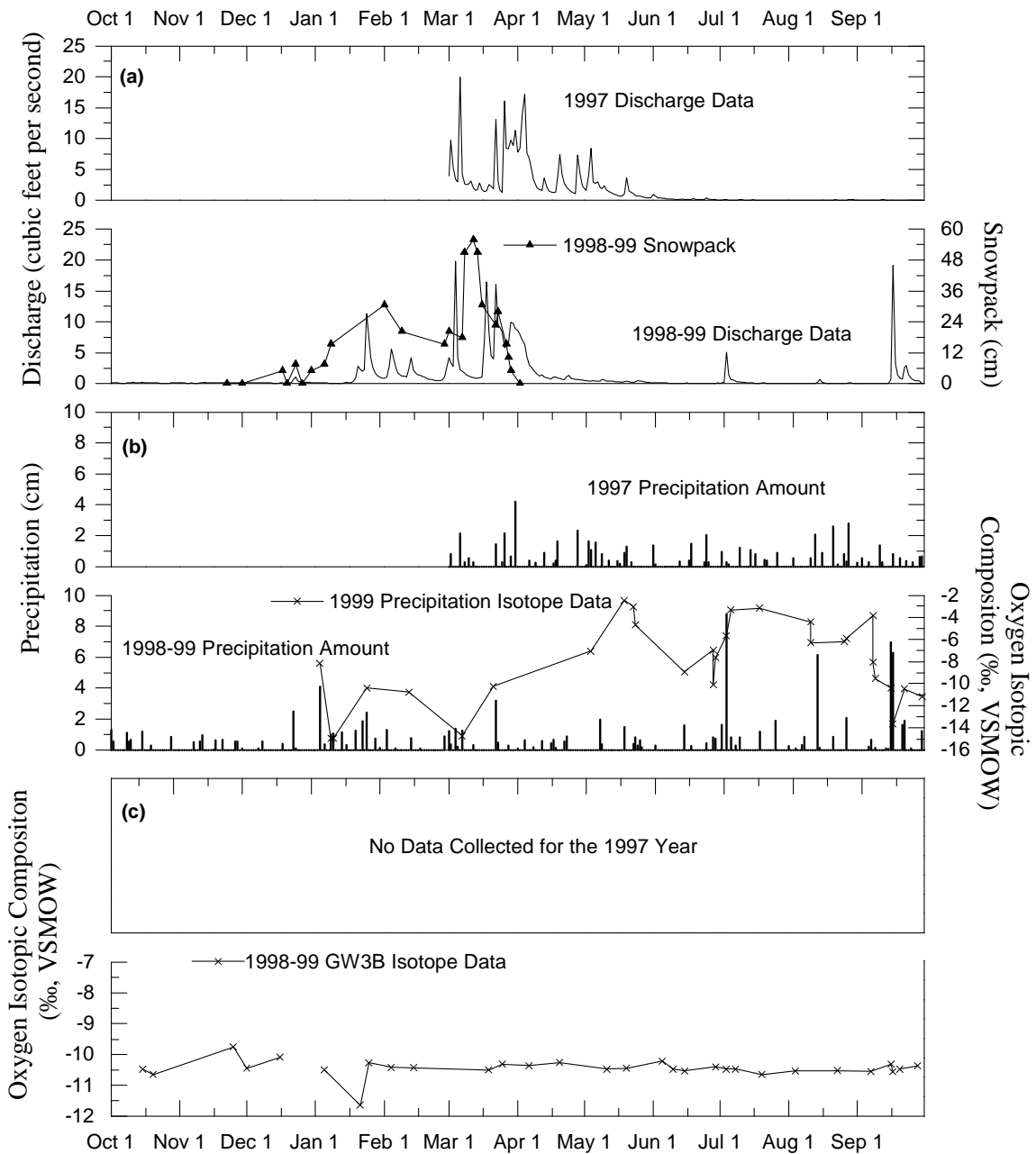
Date	Oxygen Isotopic Composition (‰, VSMOW)
3-Jan-99	-8.200
8-Jan-99	-14.997
9-Jan-99	-14.992
24-Jan-99	-10.392
12-Feb-99	-10.744
7-Mar-99	-14.742
21-Mar-99	-10.248
4-May-99	-7.041
19-May-99	-2.445
23-May-99	-3.035
24-May-99	-4.679
15-Jun-99	-8.937
28-Jun-99	-6.970
28-Jun-99	-10.116
29-Jun-99	-7.660
4-Jul-99	-5.655
6-Jul-99	-3.321
19-Jul-99	-3.133
11-Aug-99	-4.432
11-Aug-99	-6.313
26-Aug-99	-6.173
27-Aug-99	-5.881
8-Sep-99	-3.830
8-Sep-99	-8.050
9-Sep-99	-9.550
16-Sep-99	-10.407
17-Sep-99	-13.614
22-Sep-99	-10.462
30-Sep-99	-11.188

Appendix B

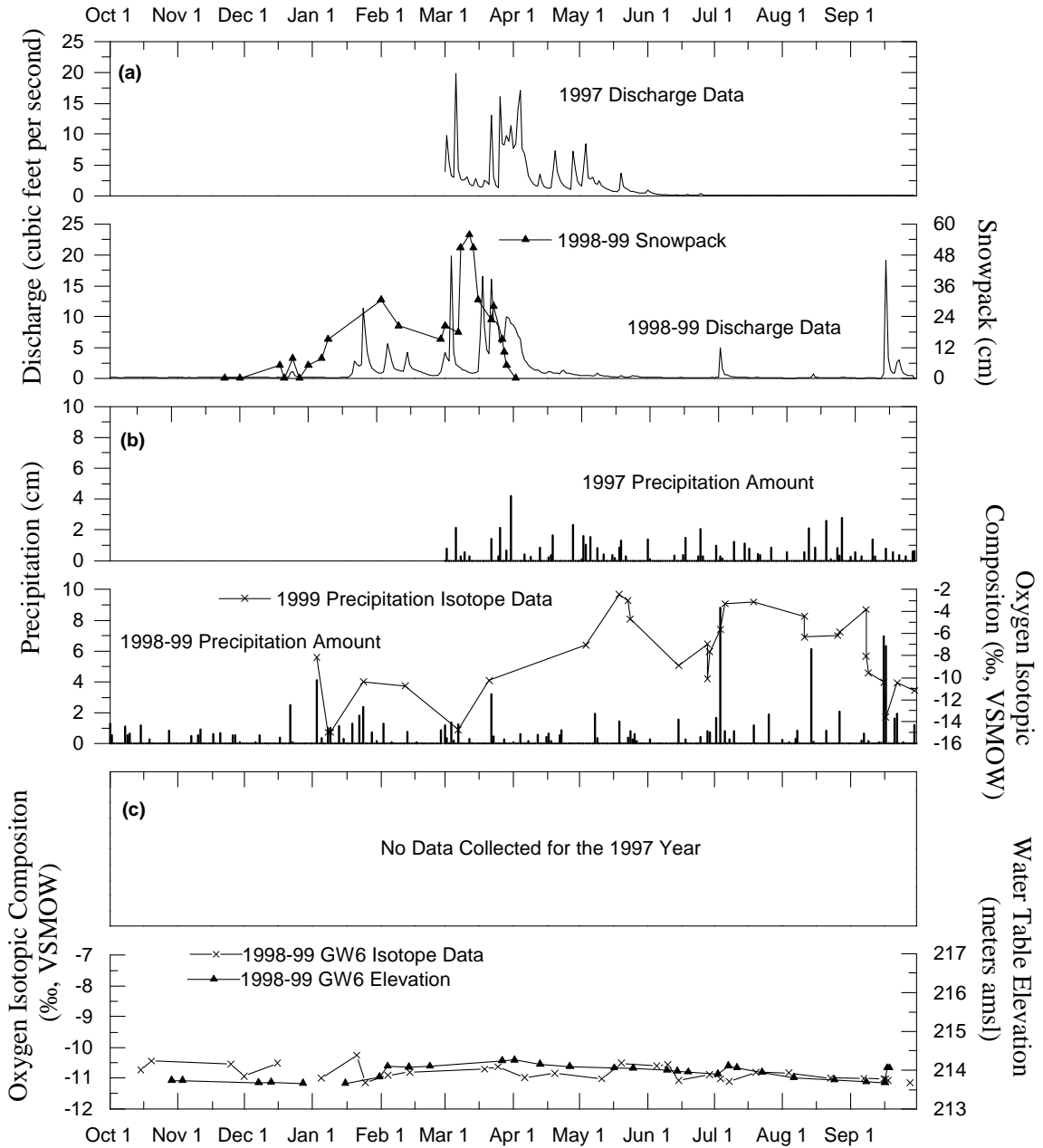
Detailed Graphs of Well and Surface Water Samples



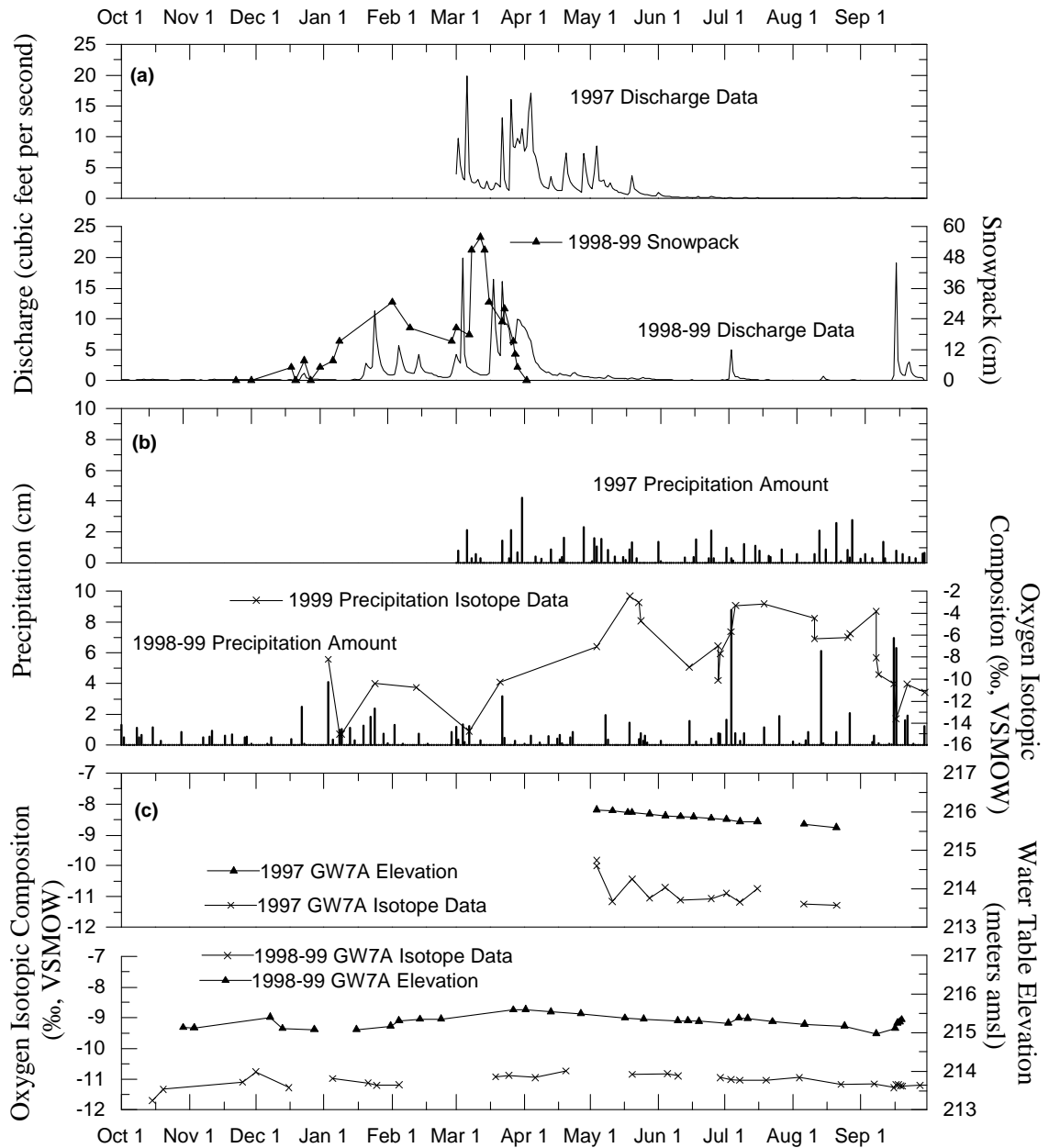
Appendix B-1 (a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999 **(c)** Water table elevation and oxygen isotopic composition of water samples from well 2, October, 1998 to October, 1999.



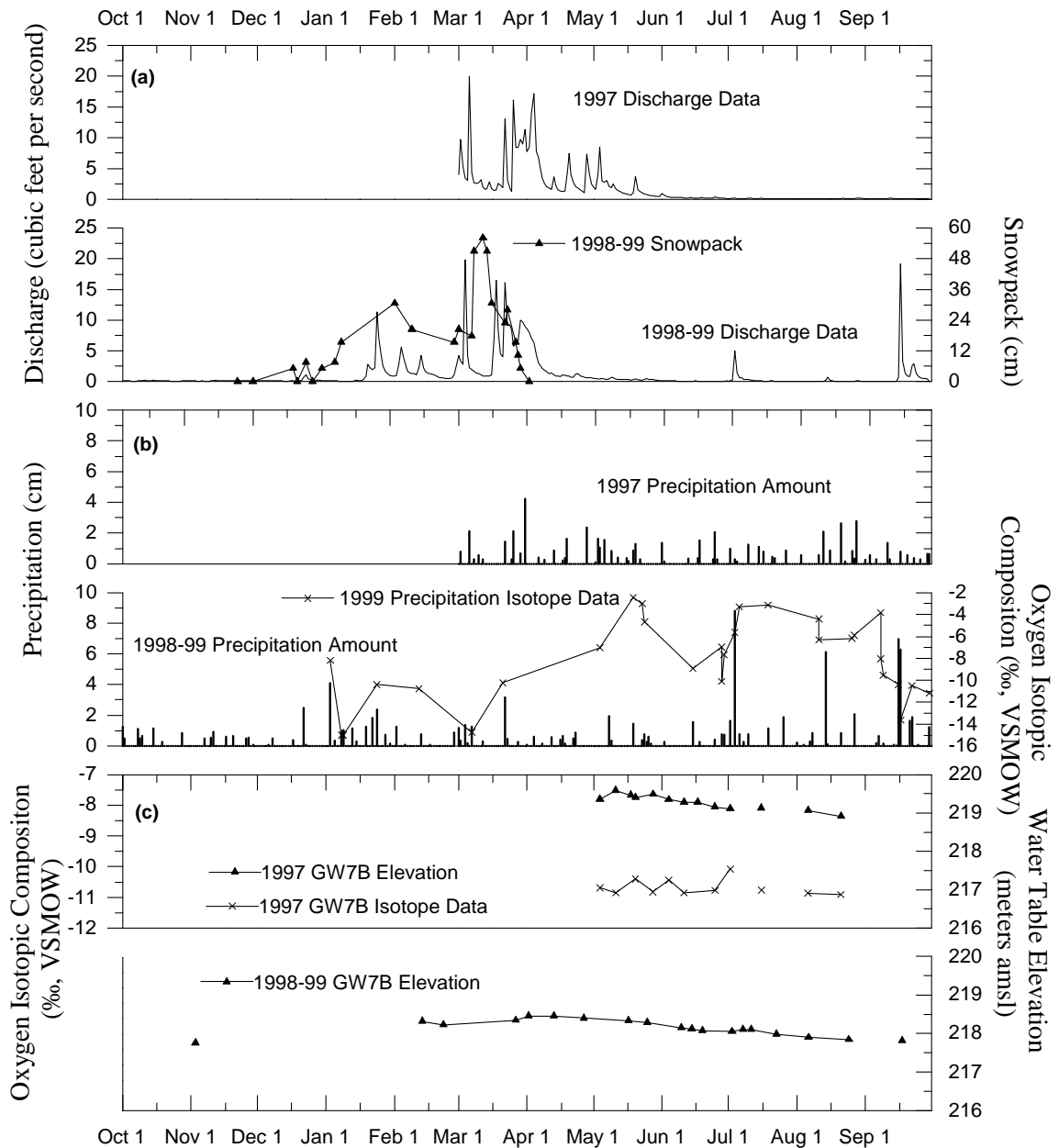
Appendix B-2(a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999 **(c)** Water table elevation and oxygen isotopic composition of water samples from well 3B, October 1998, to October, 1999.



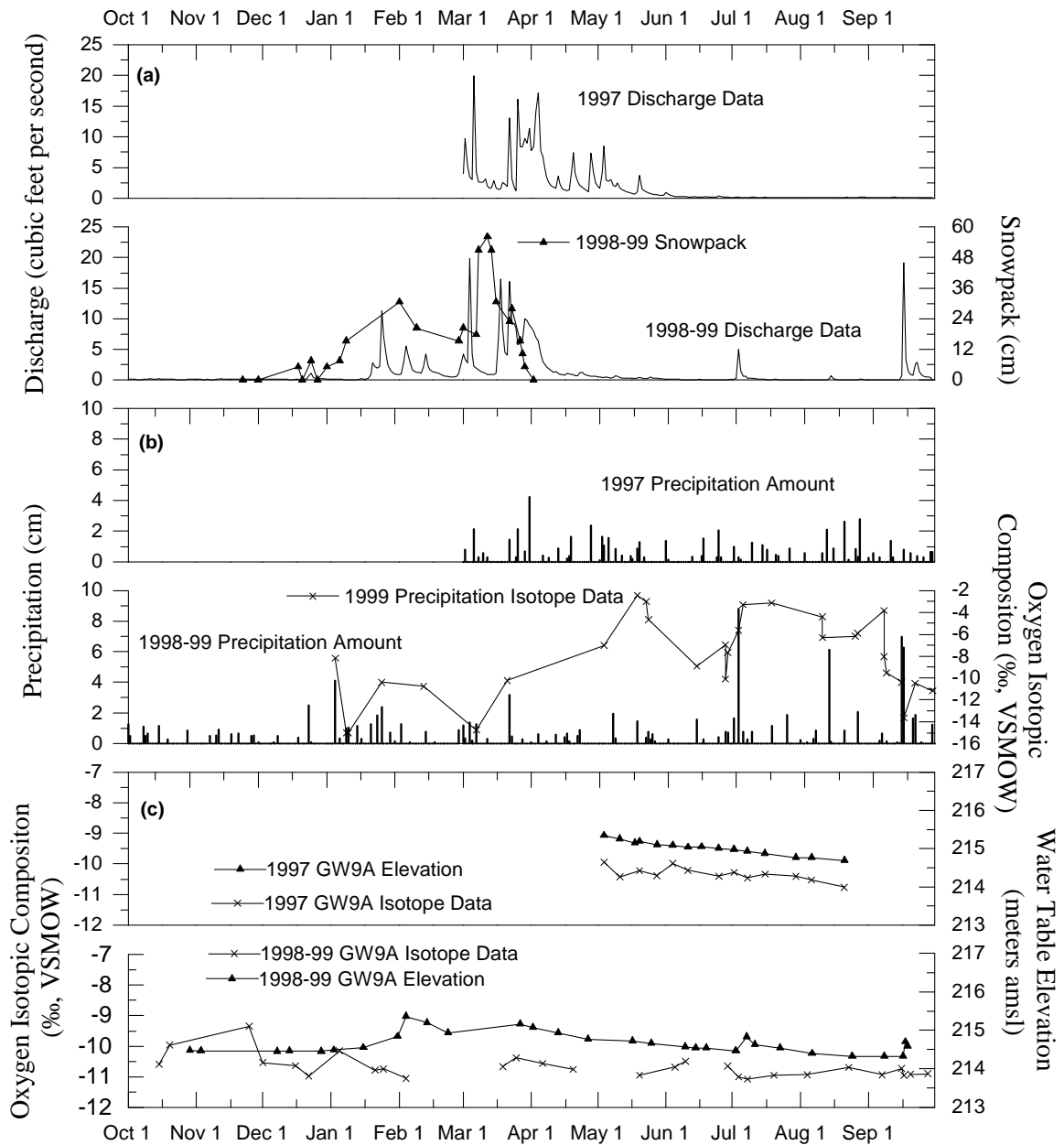
Appendix B-3(a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999 **(c)** Water table elevation and oxygen isotopic composition of water samples from well 6, October, 1998 to October, 1999.



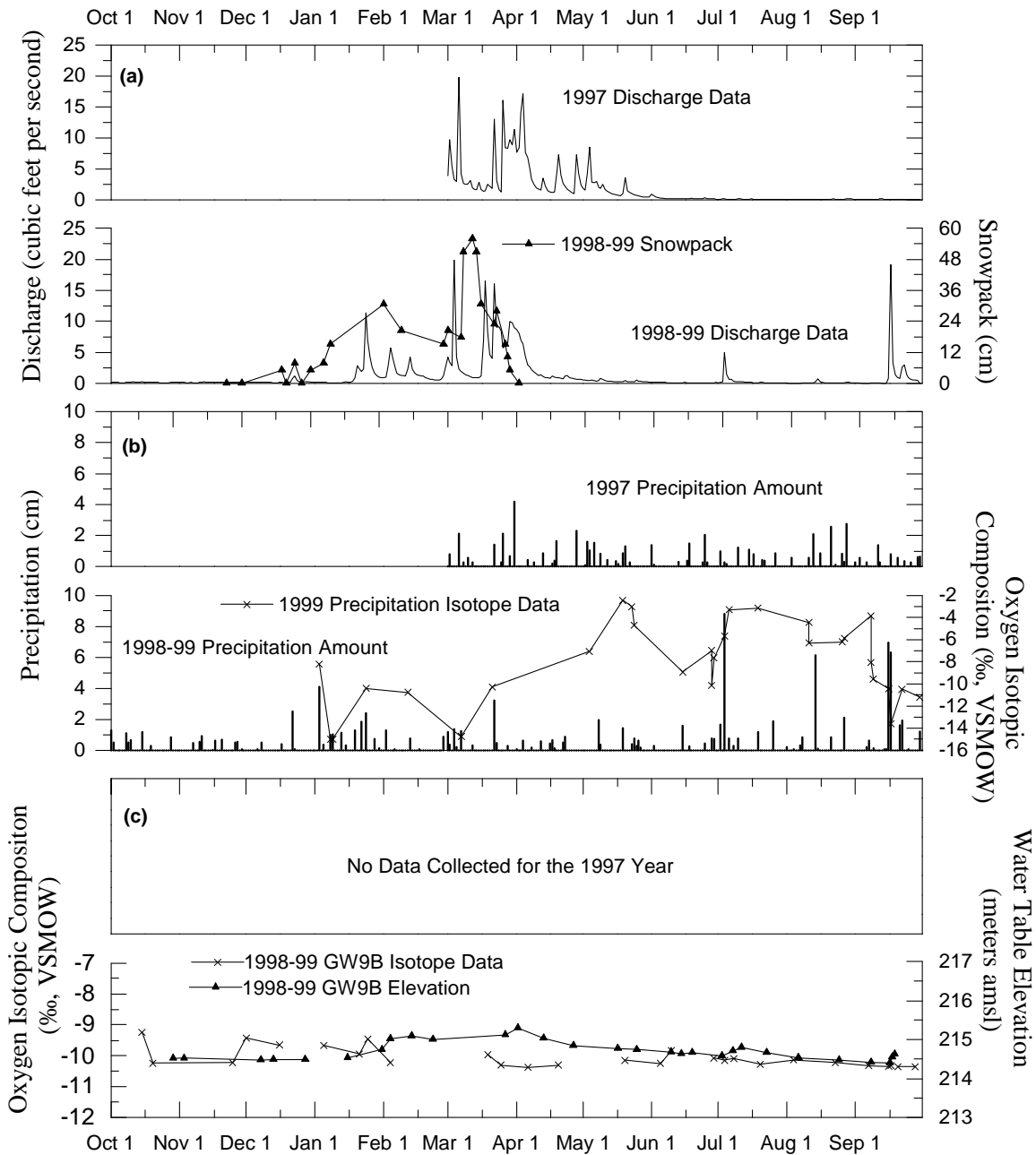
Appendix B-4 (a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. (b) Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999 (c) Water table elevation and oxygen isotopic composition of water samples from well 7A, May to September, 1997, and October, 1998 to October, 1999.



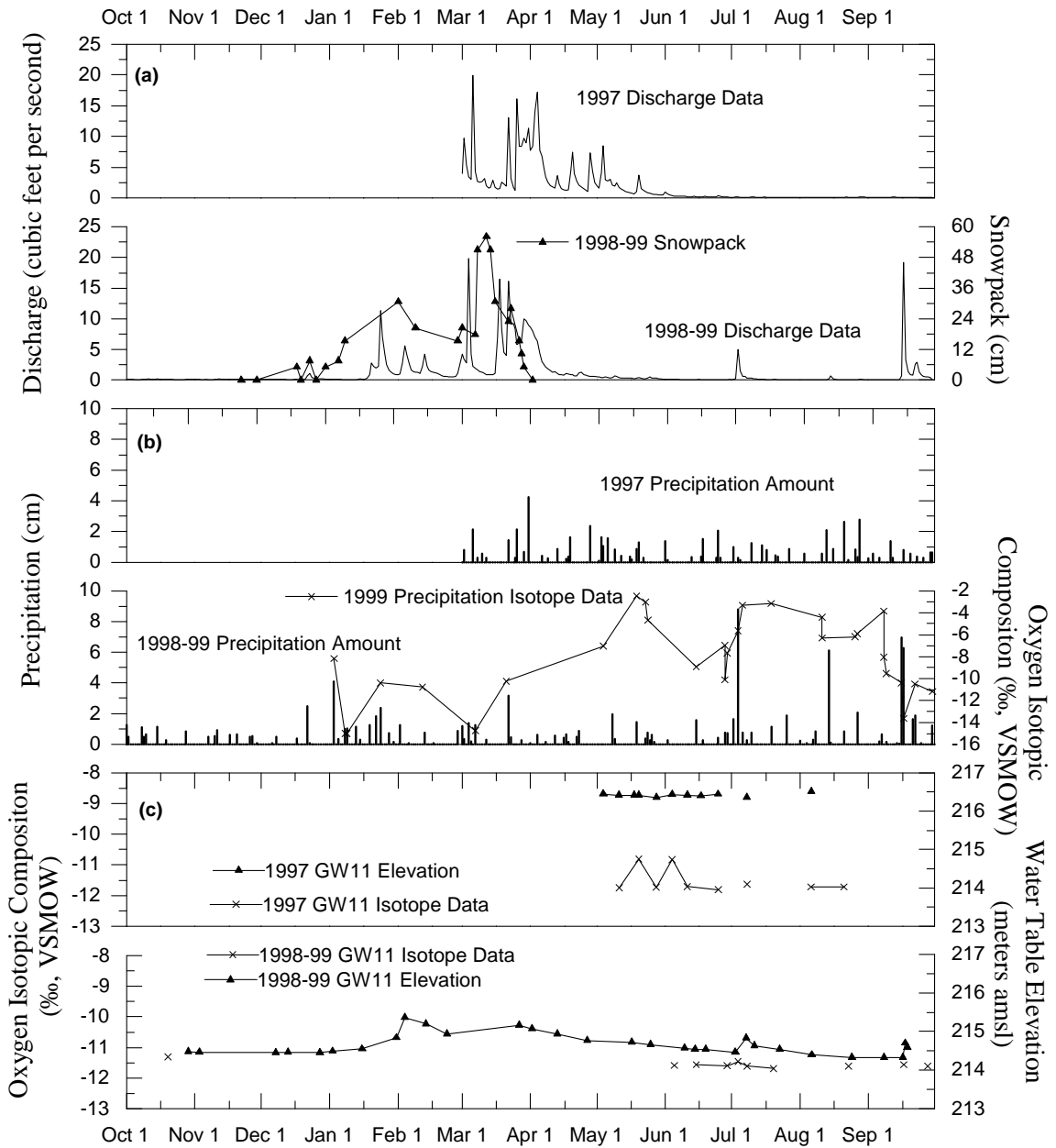
Appendix B-5 (a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. (b) Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999 (c) Water table elevation and oxygen isotopic composition of water samples from well 7B, May to September, 1997, and October, 1998 to October, 1999.



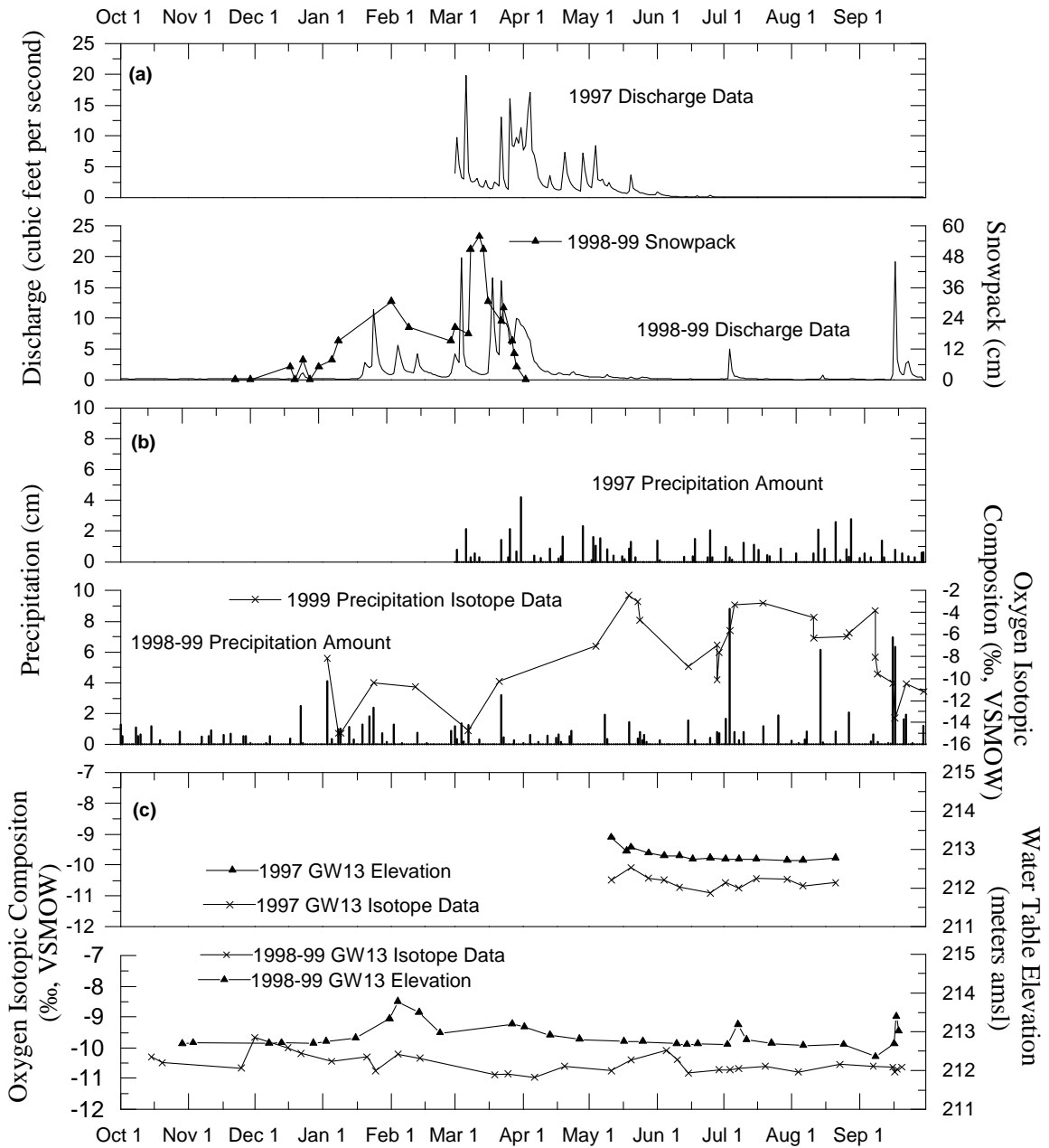
Appendix B-6(a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999. **(c)** Water table elevation and oxygen isotopic composition of water samples from well 9A, May to September, 1997, and October, 1998 to October, 1999.



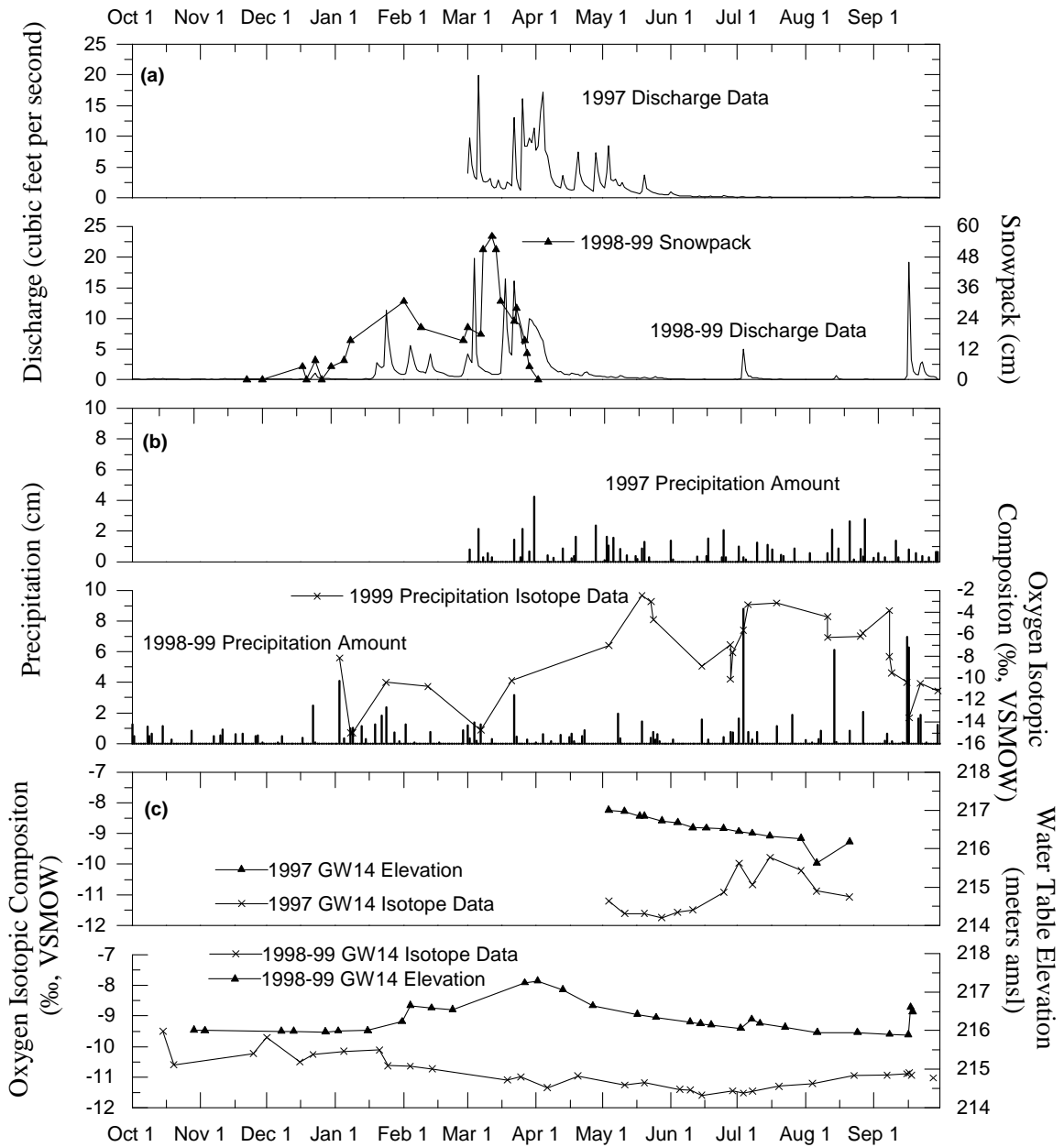
Appendix B-7(a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999. **(c)** Water table elevation and oxygen isotopic composition of water samples from well 9B, October, 1998 to October, 1999.



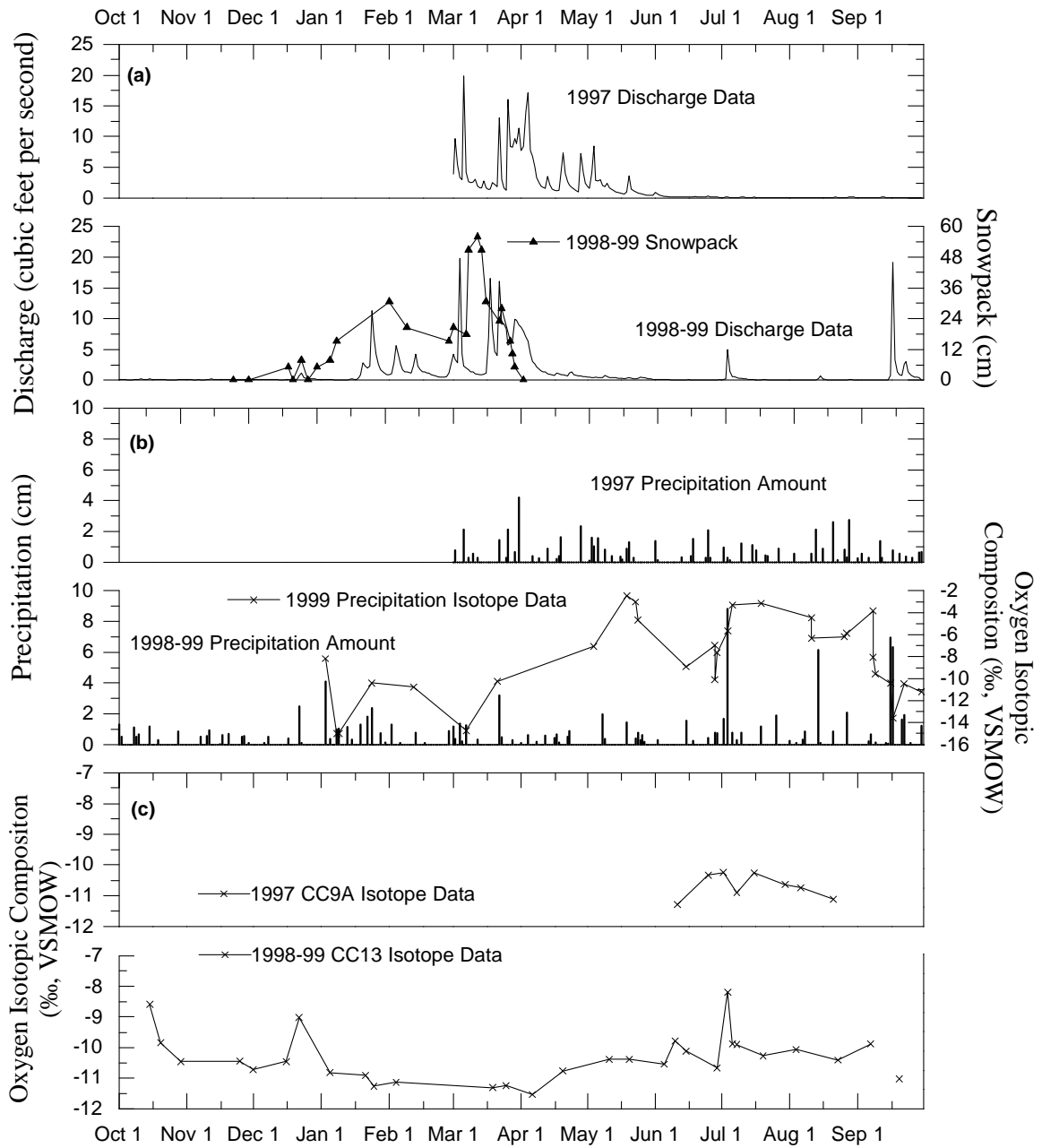
Appendix B-8(a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999. **(c)** Water table elevation and oxygen isotopic composition of water samples from well 11, May to September, 1997, and October, 1998 to October, 1999.



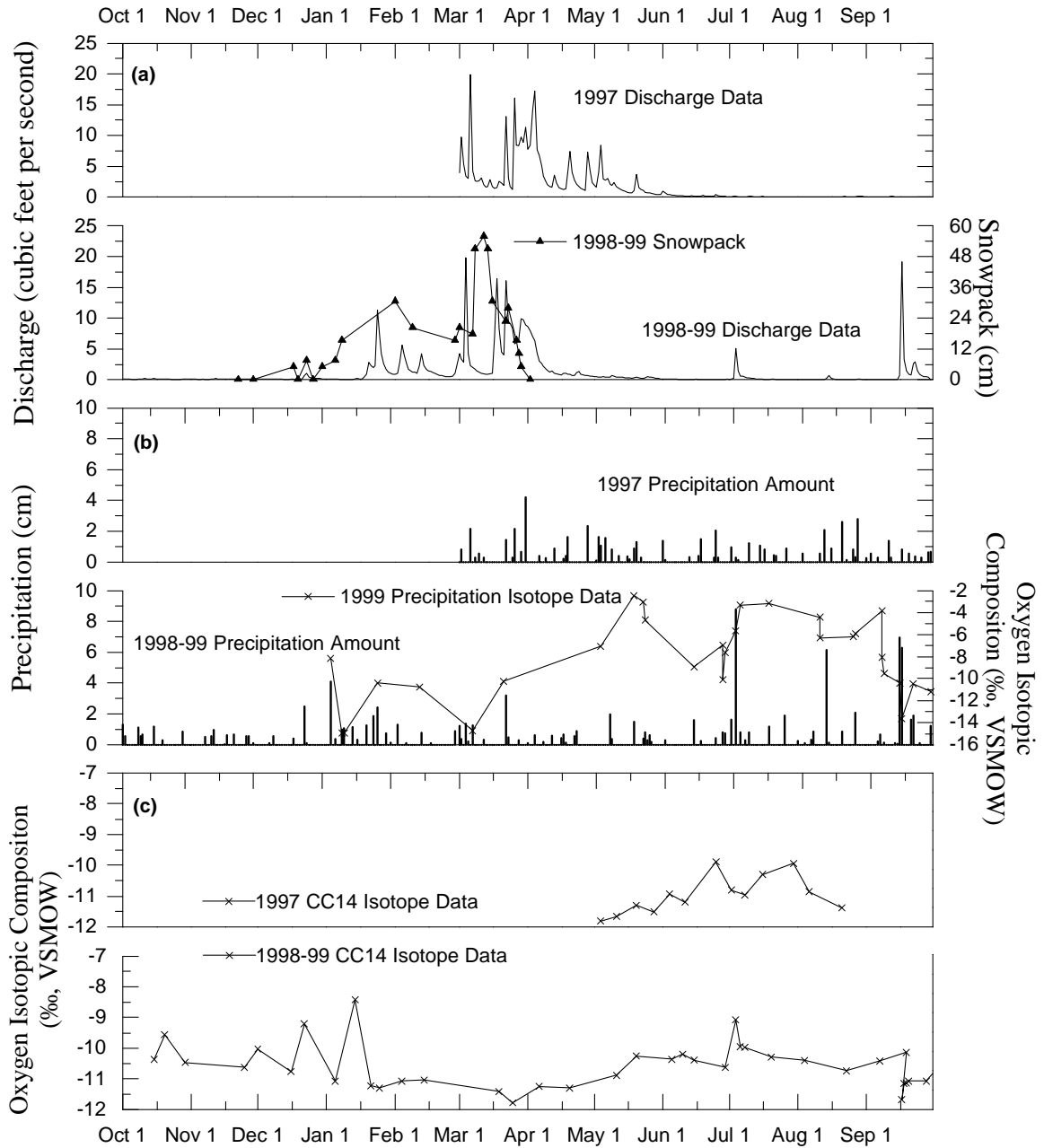
Appendix B-9(a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999 **(c)** Water table elevation and oxygen isotopic composition of water samples from well 13, May to September, 1997, and October, 1998 to October, 1999.



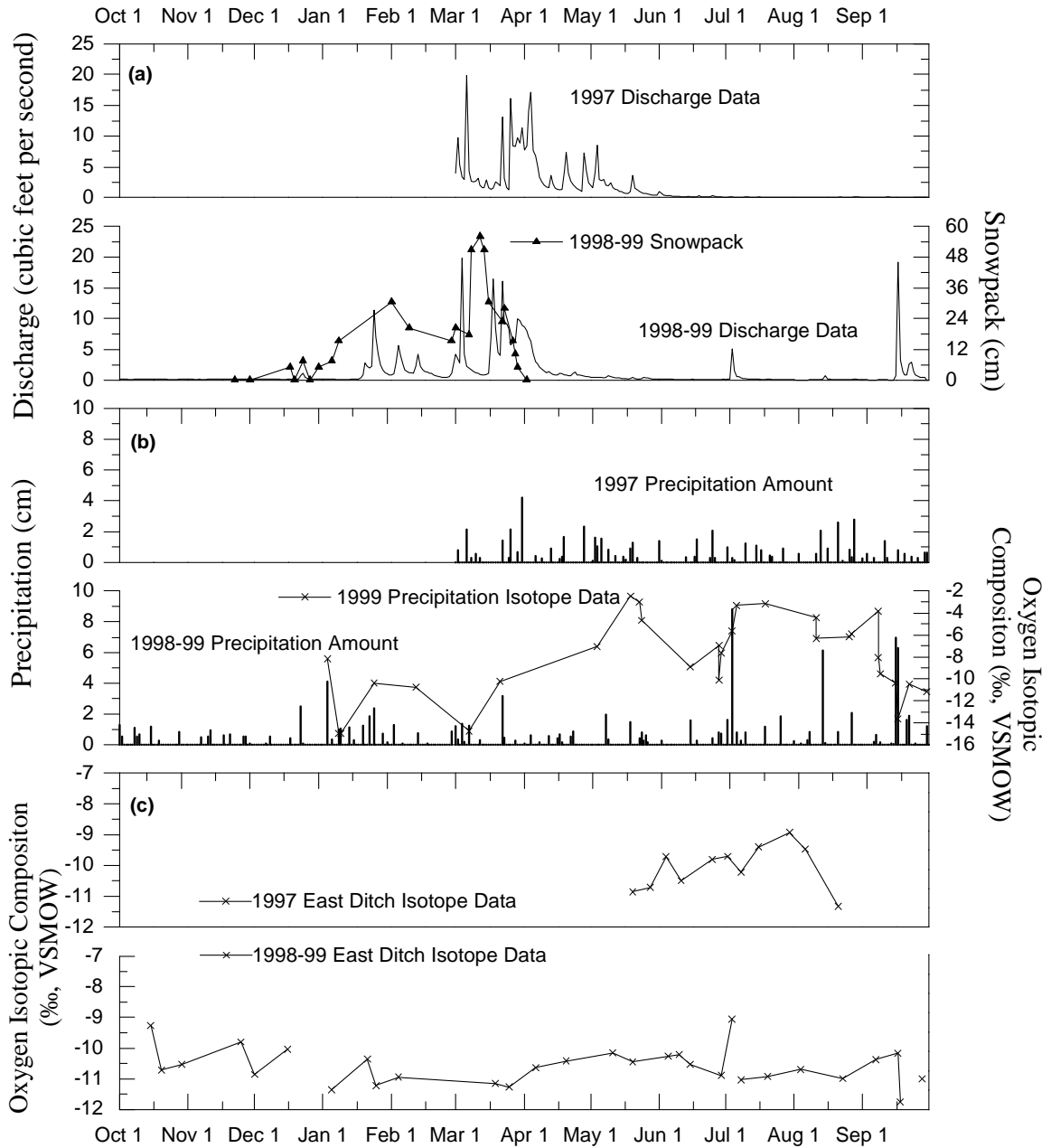
Appendix B-10 (a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999. **(c)** Water table elevation and oxygen isotopic composition of water samples from well 14, May to September, 1997, and October, 1998 to October, 1999.



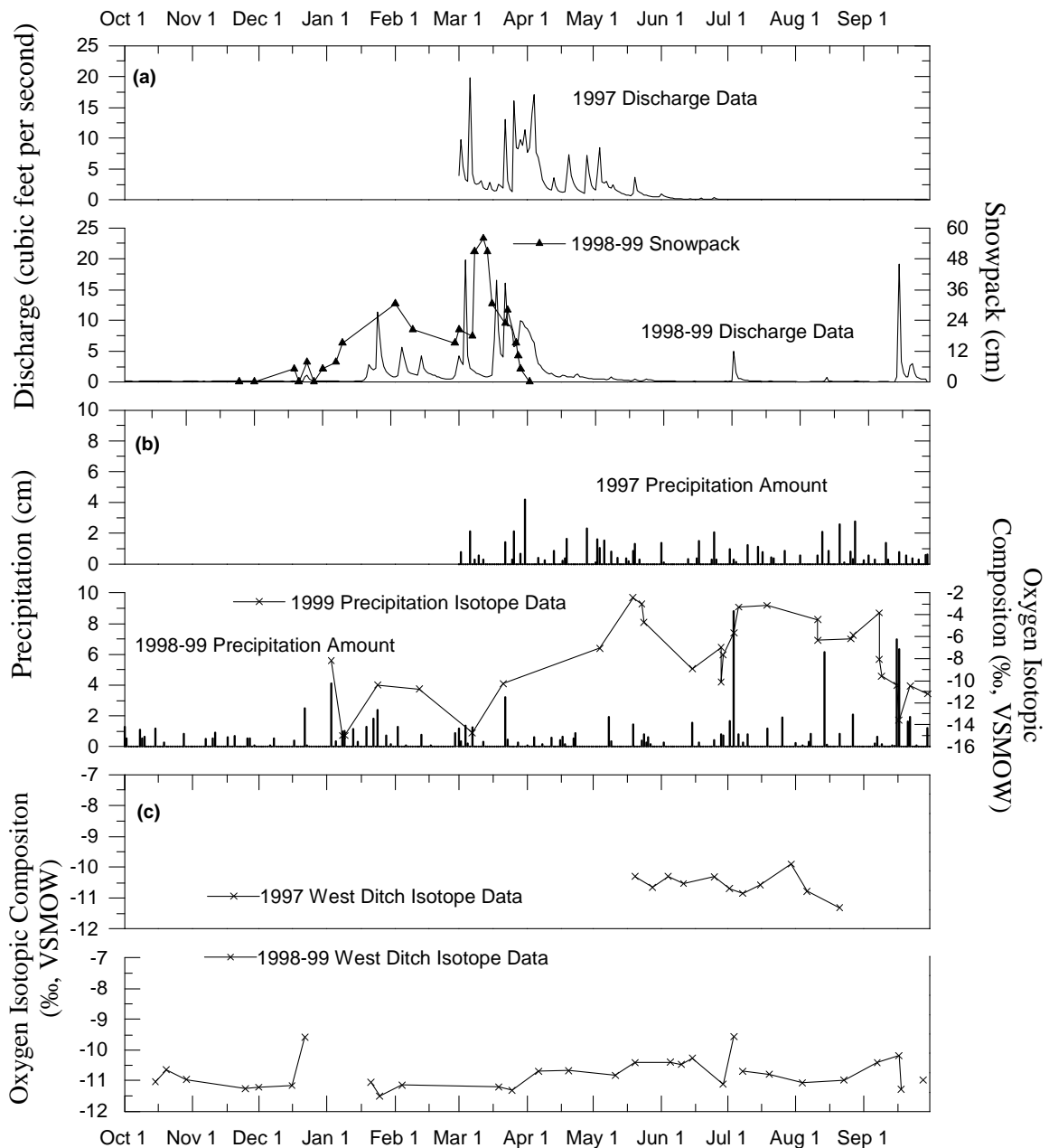
Appendix B-11(a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999. **(c)** Oxygen isotopic composition of water samples from CC9A, May to September, 1997, and CC13, October, 1998 to October, 1999.



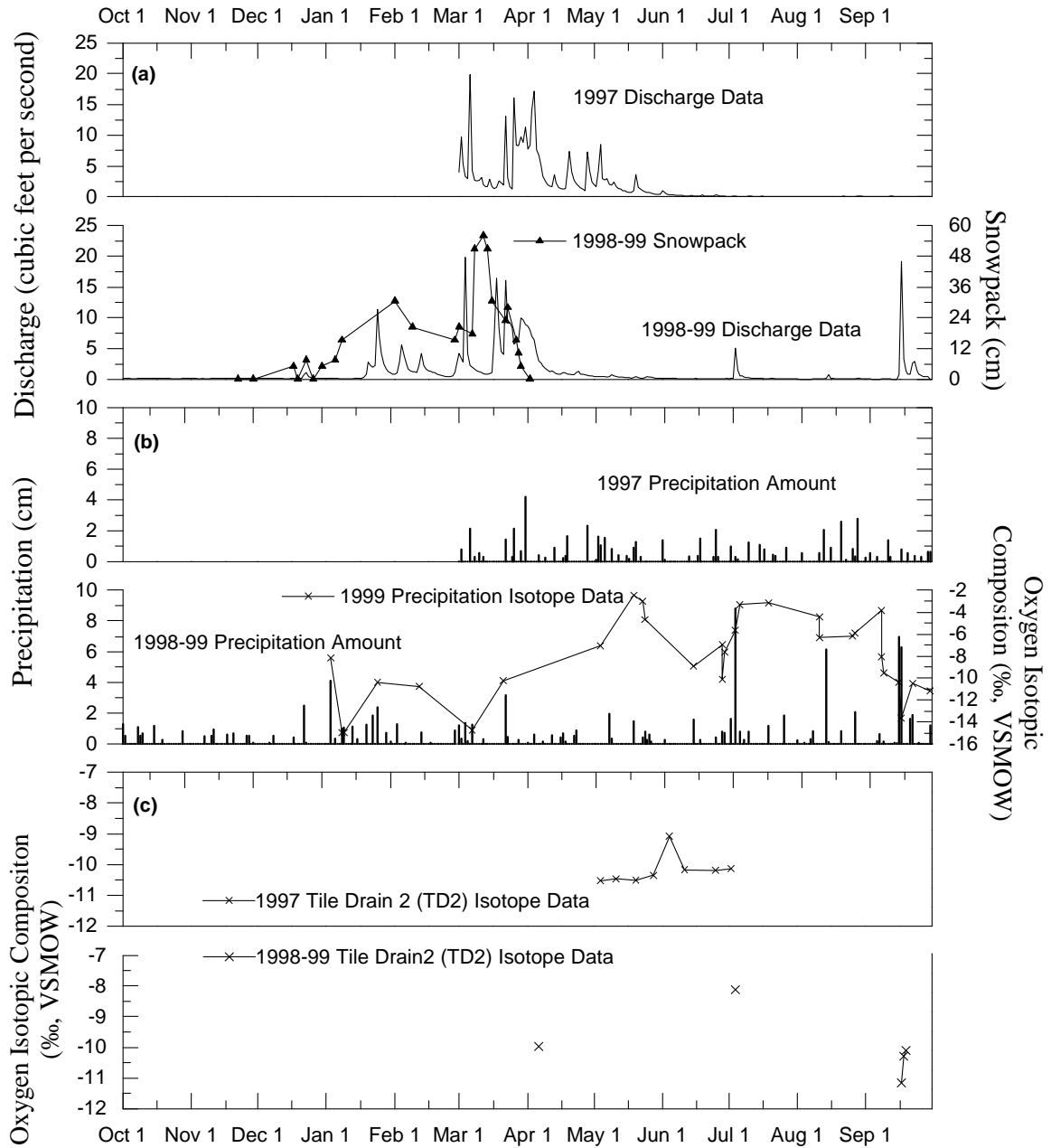
Appendix B-12 (a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999. **(c)** Oxygen isotopic composition of water samples from CC14, May to September, 1997, and October, 1998 to October, 1999.



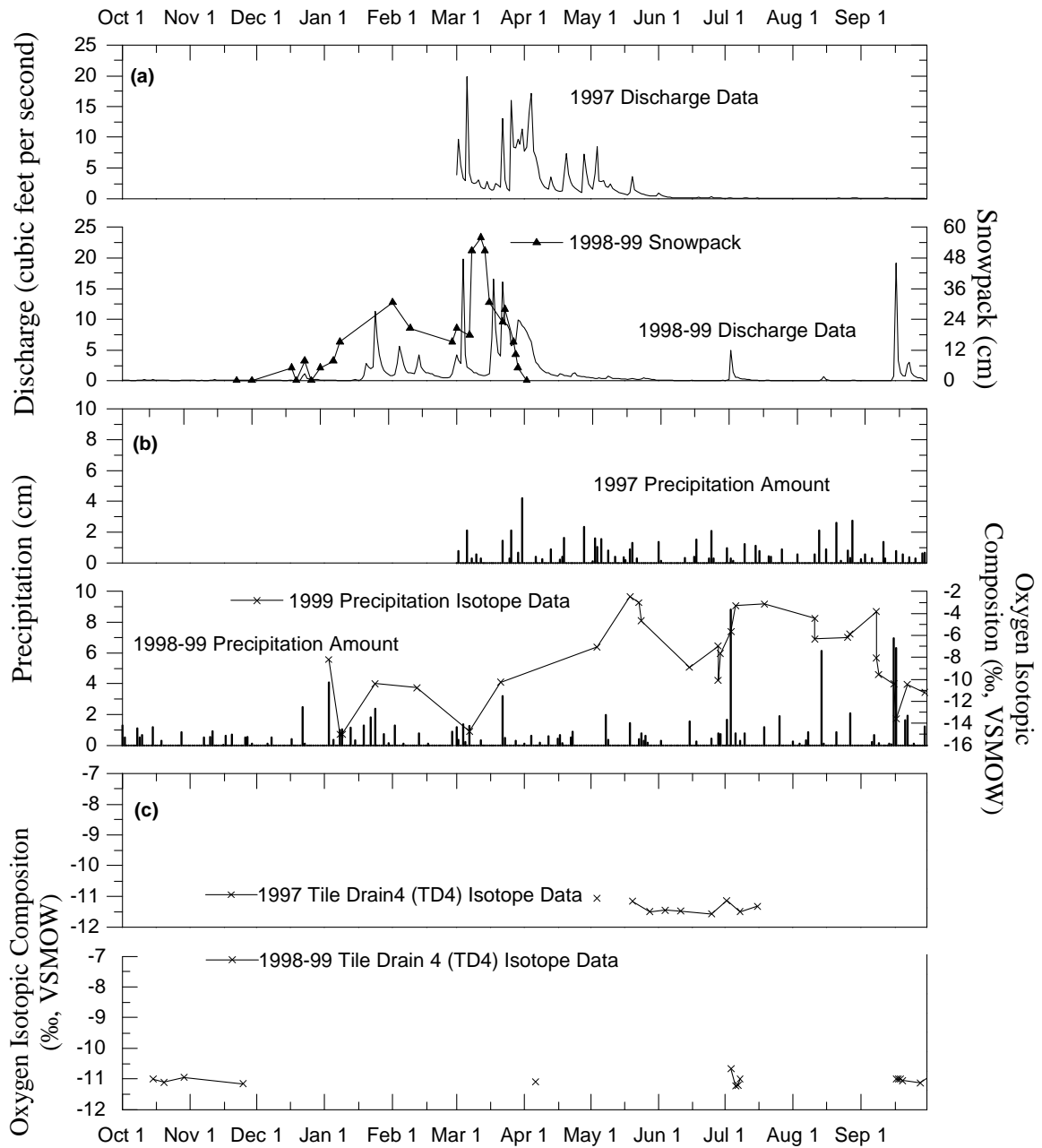
Appendix B-13 (a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999. **(c)** Oxygen isotopic composition of water samples from the east ditch, May to September, 1997, and October, 1998 to October, 1999.



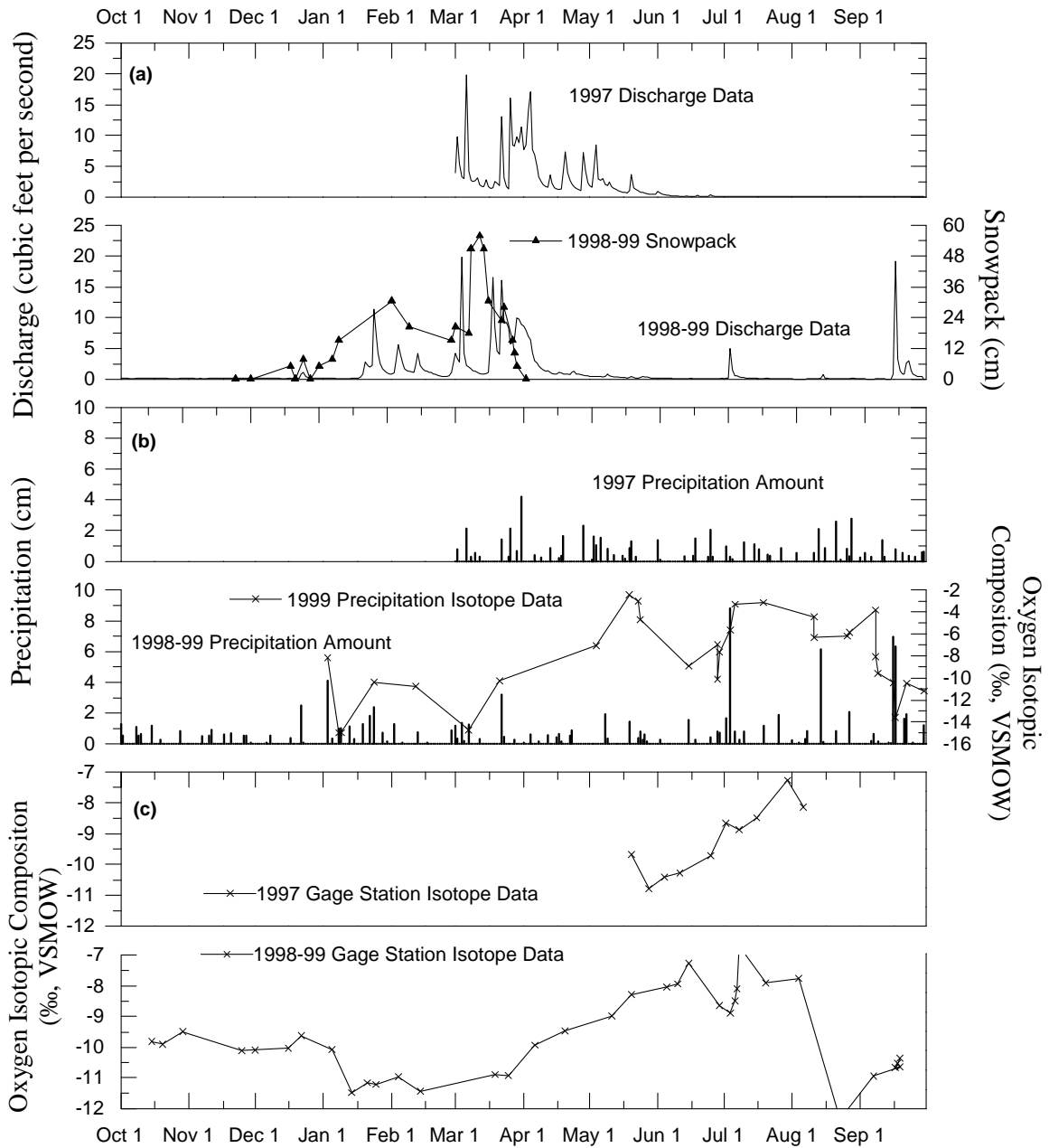
Appendix B-14 (a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999. **(c)** Oxygen isotopic composition of water samples from the west ditch, May to September, 1997, and October, 1998 to October, 1999.



Appendix B-15 (a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999. **(c)** Oxygen isotopic composition of water samples from TD2, May to July, 1997, and October, 1998 to October, 1999.



Appendix B-16 (a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999. **(c)** Oxygen isotopic composition of water samples from TD4, May to July, 1997, and October, 1998 to October, 1999.



Appendix B-17 (a) Streamflow discharge at the outlet of the Canajoharie Creek, March to October, 1997, and October, 1998 to October, 1999, and snowpack depth, November, 1998 to April, 1999. **(b)** Precipitation amounts, March to October, 1997, and October, 1998 to October, 1999, and oxygen isotopic composition of precipitation samples collected at the University at Albany, January to October, 1999. **(c)** Oxygen isotopic composition of water samples from the Streamflow gaging station, May to September, 1997, and October, 1998 to October, 1999.