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Authors

Deverel, Steven J.
Leighton, David A.
Finlay, Mark R.

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Processes Affecting Agricultural Drainwater Quality and Organic Carbon Loads in California's Sacramento-San Joaquin Delta

Steven J. Deverel*

David A. Leighton

Mark R. Finlay

Hydrofocus, Inc.

*Corresponding author: sdeverel@hydrofocus.com

ABSTRACT

From 2000 to 2003 we quantified drain flow, drain- and ground-water chemistry and hydrogeologic conditions on Twitchell Island in the Sacramento-San Joaquin Delta. The primary objective was to quantify processes affecting organic carbon concentrations and loads in agricultural drainage water. We collected physical and chemical data in southern and northern areas: TN and TS, respectively. Corn grew in both areas during the spring and summer. The peat soils in the TN area are more decomposed than those in the TS area. Results elucidate processes affecting drain flow and concentrations under varying hydrologic conditions. During May through November, ground-water flows from the permanently saturated zone to drainage ditches, and the resulting average drainage-water quality and dissolved organic carbon (DOC) concentration was similar to the groundwater; the median DOC loads in the TN and TS study areas ranged from 9 to 27 g C/ha-day. The major ion chemistry and stable isotope data confirmed that groundwater was the primary source of drainflow. In contrast, during December through April the drainwater is supplied from the shallow, variably saturated soil-zone. The DOC concentrations, major-ion chemistry

and stable isotope data indicate the shallow-zone water is partially evaporated and oxidized. Higher flows and DOC concentrations during these months result in higher median DOC loads, which ranged from 84 to 280 g C/ha-day.

During December through April, increasing groundwater levels in the shallow peat layers and mobilization of organic carbon result in high drain flow and increased trihalomethane precursor concentrations and loads. On a per mass DOC basis, drain water collected during high flow periods is less likely to form THMs than during low flow periods. However, the high flows and subsequent high concentrations contribute to substantially higher trihalomethane precursor and DOC loads.

KEYWORDS

agricultural drainage, organic carbon, drinking water quality, disinfection byproducts, organic soils

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INTRODUCTION

The Sacramento–San Joaquin Delta is the hub of California’s water supply system. Drinking water for over 22 million Californians flows through the Delta channels from water-rich northern California to water-poor southern California. Dissolved organic carbon (DOC) concentrations in Delta export waters can be problematically high due to potential formation of disinfection byproducts (DBPs) such as trihalomethanes (THMs) during the drinking water treatment process. Amy et al. (1990) estimated that agricultural drainage from Delta island organic soils contribute 20% of the THM formation potential (THMFP) at Delta export pumps. Understanding the factors and processes contributing to DOC and THMFP on Delta islands is pivotal to developing management strategies to minimize the THMFP in exported drinking water.

For over a century, subsidence of organic soils has led to an increasing need for subsurface drainage on Delta islands and tracts. Aerobic oxidation of organic carbon, the primary cause of subsidence (Deverel and Rojstaczer 1996), began in the late 1800s as the nutrient-rich soils were cleared and dewatered for agriculture. Since then, island elevations have decreased to as much as 9 m below sea level and are protected from flooding by over 1,800 km of man-made levees. Networks of ditches collect and transport irrigation recharge and levee seepage to pumps that discharge to adjacent channels. As the organic soils oxidize and disappear, farmers deepen drainage ditches to maintain an unsaturated root zone. By decreasing the land mass supporting levees, subsidence also contributes to levee instability, failure, and water supply vulnerability (Procopovitch 1985).

Delta organic deposits formed during the last 7,000 years under wetland conditions (Atwater et al. 1977; Atwater 1980, 1982). Plant material decayed and accumulated under anaerobic conditions as sea level increased (Shlemon and Begg 1975). Thicknesses of

organic deposits increase from east to west. Organic deposit thickness ranges from less than 1 m on the eastern, southern, and northern margins of the Delta to over 10 m in the western Delta (Deverel 1998). Agricultural drainage increases microbial oxidation of organic carbon, which results in land subsidence rates of less than 1 to over 3 centimeters per year (Deverel and Rojstaczer 1996; Rojstaczer and Deverel 1995; Deverel 1998).

Previous investigations elucidated some factors affecting DOC and THMFP in soil water, groundwater, and drainage water. Fujii et al. (1998) reported on the concentrations and nature of DOC in relation to THMFP on Twitchell Island. Their work illustrated the influence of organic soil conditions and decomposition on DOC and THMFP. Aromatic compounds that are generally considered the primary THM precursors were higher in the deeper, saturated, anoxic deposits relative to the shallow, variably saturated, oxidized deposits. Fleck et al. (2004) evaluated the effects of soil chemical and management differences among different areas on Twitchell Island. They found higher DOC concentrations associated with more recently cultivated and higher organic-matter soils.

In a study of carbon fluxes on three Delta islands (Jersey, Sherman and Orwood Tract), Deverel and Rojstaczer (1996) reported the highest DOC concentrations in drainage water from poorly drained Jersey Island. The Jersey Island DOC was predominantly acidic and hydrophilic. In contrast, DOC concentrations were lower and DOC was more hydrophobic on two well-drained islands. California Department of Water Resources (DWR) (1997) data consistently shows the highest DOC concentrations in Delta channels during high flows in winter and early spring. Also, Deverel and Rojstaczer (1996) showed high drainage DOC concentrations and loads associated with groundwater level highs in winter and early spring. Heretofore, DOC and THMFP loads and processes affecting loads on Delta agricultural lands and in managed wetlands for subsidence reversal have not been sufficiently quantified.

DOC from soil organic matter is a mixture of organic compounds whose reactivity to form DBPs depends on land- and water-management practices and biogeochemical, hydrologic, and soil forming processes.

Previous studies indicated that the aromatic portion of DOC contains the major precursors of THMs (Rook 1976; Rook 1977; Reckow et al. 1990; Croue et al. 1984; Wu et al. 2000). Fujii et al. (1998) showed that increasing specific ultraviolet absorbance—the amount of ultraviolet light absorbed by a sample per unit weight of dissolved organic carbon—corresponds to increasing aromaticity. However, the relationships among DOC, specific ultraviolet absorbance (SUVA), and THMFP for Delta drainage samples are not predictive even though significantly correlated within specific regions (DWR 1994).

Continuing subsidence will increase seepage onto Delta islands and increase the need for drainage. Together with Delta water supply and water quality concerns, these issues necessitate a better understanding of processes affecting DOC and THMFP in Delta channel water as related to agricultural drainage.

This study attempted to answer two questions:

1. What are the per area DOC and THMFP loads for agricultural drainage?
2. What are the primary hydrologic and geochemical processes affecting these loads and concentrations?

We focused data-collection efforts in two areas on Twitchell Island (Figure 1); the northwestern area (TN) (wells 19 through 25) which includes the area studied by Fujii and others (1998), and the southeastern area (TS) (wells 3 through 12 and the NHC wells). These areas have different water management practices and soil characteristics (Fleck et al. 2004). During 2000 to 2003, we collected physical data for drain flow, groundwater levels, and aquifer parameters. We collected and analyzed water samples from wells and drainage ditches for inorganic and organic constituents. We integrated and analyzed the data to develop a conceptual model for processes resulting in the observed temporal and spatial variability in DOC and THMFP loads.

METHODS

Well Construction and Hydrologic Data

Using a hollow stem auger, we installed 22 monitoring-well clusters on Twitchell Island (Figure 1). Two to

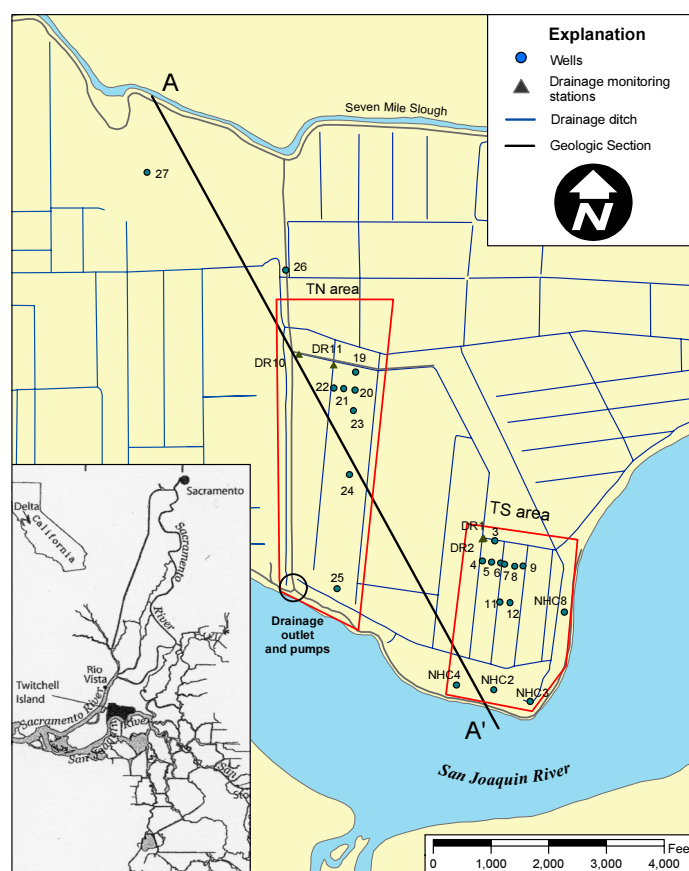


Figure 1. Study area location and site features

four wells were installed per cluster to depths of 0.3 to 10 meters below land surface. At selected sites we collected core samples and visually determined the texture and nature of the borehole materials. In each borehole we placed 5.08-cm diameter, flush threaded, schedule 40, polyvinyl chloride pipe and stainless steel 0.0508-cm slotted well screens. The annular space between the borehole wall and well casing was filled with clean #2-12 Lonestar sand to a depth of 30 - 60 cm above the well screen. The remaining annular space was filled with bentonite grout or cement. After well completion, we developed the wells using surge block and bailer until water from the well was clear. We employed USGS methods (USGS 1997) to measure water levels in all wells approximately every four weeks; we utilized transducers and data recorders to continuously record water levels in selected wells at intervals varying from 15-minute to twice daily.

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In four locations (DR1, DR2, DR10, and DR11 in [Figure 1](#)), we established drain flow monitoring stations as follows. We installed V-notch weirs and staff gages at each location and utilized pressure transducers and recorders to record drain stage changes at 15 minute intervals. At biweekly to monthly intervals, we measured flow at the weirs by either measuring the time to fill a bucket of known volume or by measuring velocity and flow cross sectional area. We developed and used a flow-stage relationship for each weir to estimate daily flow. We also measured drain flow at the main discharge point for the entire island using a McCrometer propeller flow meter installed in both of two island discharge pipes at the drainage outlet and pump location shown on [Figure 1](#).

Chemical Data Collection

At biweekly to monthly intervals, we collected drain-water samples and measured electrical conductivity (EC), pH, temperature, and dissolved oxygen (DO) at the weirs and island discharge outlet. We collected groundwater samples and field measured groundwater EC, pH, temperature, oxidation-reduction potential (Eh), and DO in all wells; some wells were sampled on several different occasions. Sample analytes included dissolved organic carbon (DOC), ultraviolet absorbance (UVA), trihalomethane formation potential (THMFP), major ions (calcium, magnesium, potassium, sodium, chloride, sulfate, bicarbonate), and stable isotopes of oxygen and hydrogen (oxygen-18 and deuterium). Sampling methodology was conducted as follows.

All meters were calibrated at each sampling site using standards within 10% of the measured values and maintained at the temperature of the water to be sampled. For Eh, we checked meters and platinum electrodes with Zobell's solution (Nordstrom 1977). We calibrated and checked the YSI, platinum DO electrode, and meter in a moisture saturated air chamber at the same temperature as the water to be sampled and using a zero-oxygen solution.

We used a peristaltic pump to collect well-water samples. Each well had dedicated Teflon tubing that connected to silicon tubing on the peristaltic pumps. All wells were purged prior to sampling by pumping at

least three well-casing volumes or until the well dewatered. We used a flow-through chamber to measure Eh, pH, EC, and DO during well development, and these parameters were allowed to stabilize within 10% prior to sample collection. If the well dewatered, we waited for the well to recover and then measured field parameters and collected samples. We determined bicarbonate concentrations in the field on unfiltered samples using incremental titration with dilute sulfuric acid and a calibrated pH meter.

In the field, we pressure filtered samples for analysis of DOC, THMFP, UVA, DOC fractionation, and major ions through three sequential filters in a 142 mm-diameter stainless steel filter plate/holder; 1.4 and 0.75 micrometer glass fiber filters overlying a 0.45 micrometer cellulose nitrate filter. Prior to sample filtration, we thoroughly rinsed all sampling apparatus and tubing with deionized water and pumped two liters of deionized, carbon free water and 0.5 liter of sample water through the filters. Prior to filling, all bottles were rinsed three times with sample water. We collected unfiltered samples in polyethylene bottles for analysis of oxygen-18 and deuterium and bicarbonate, and we collected filtered samples for major-ion analysis. For DOC, THMFP, UVA, and DOC fractionation we collected the samples in glass amber bottles. To collect POC samples, we pressure filtered a known volume of sample water through 0.45 micrometer pre-ashed glass fiber filters. The samples were stored no more than seven days at 4°C prior to organic carbon and UVA analysis.

Laboratory Methods

Organic Carbon

Samples were analyzed for DOC, UVA₂₅₄, THMFP, and for DOC fractionation and isolation at the U.S. Geological Survey Laboratories in Sacramento, California. The samples were analyzed for total DOC using a Shimadzu TOC-5000A total organic carbon analyzer (Bird et al. 2003). Ultraviolet (UV) absorbance at 254 nanometers (nm) (UV₂₅₄) was analyzed using a spectrophotometer (Model UV/Vis Lambda 3B, Perkin-Elmer). From the measured data, carbon quality was assessed using specific ultra-violet absorbance (SUVA, L mg C⁻¹ cm⁻¹), calculated by

normalizing UV_{254} to DOC (UV_{254}/DOC). Higher SUVA values generally reflect a higher aromatic content of the DOC (Fujii et al. 1998). THM formation potential (THMFP) was measured using a modified version of EPA Method 502.2 (Fram et al. 2002). Specific THMFP [STHMFP in millimoles per mole (mmol/mol)] was calculated by normalizing THMFP to DOC on a molar basis (Fram et al. 2002).

For selected samples, DOC was fractionated into five operationally defined categories: hydrophobic acids (HPOA), hydrophobic neutrals (HPON), transphilic acids (TPIA), hydrophilic neutrals (HPIN), and hydrophilic acids (HPIA). This fractionation was accomplished using XAD-8 and XAD-4 resin. A detailed description of the physical and chemical properties of these resins and the operationally defined fractions are given by Aiken and others (1992).

The HPOA and TPIA fractions constitute the majority of organic carbon in fresh waters. Aiken and others (1992) define HPOA as that portion of the DOC that sorbs on a column of XAD-8 resin at pH 2 under conditions where the capacity factor (k') for the column is 50 (defined as the grams of solute on resin per gram of solute in column void volume), and is eluted at pH 13. This fraction can contain aliphatic carboxylic acids of five to nine carbons, one- and two-ring aromatic carboxylic acids, one- and two-ring phenols, and aquatic humic substances. TPIA is defined as that portion of the DOC contained in the XAD-8 resin effluent at pH 2 that sorbs on a column of XAD-4 resin under conditions where k' is 50 for the column, and is eluted at pH 13. This fraction can contain polyfunctional organic acids and aliphatic acids with five or fewer C atoms.

A detailed description of the XAD resin fractionation and isolation procedure is reported by Fujii et al. (1998). The fractionation of the samples onto the XAD-8 and XAD-4 resins allows for calculation of the mass of each operationally defined category (fraction), expressed as the percent of the original total DOC mass for a particular sample. The percent of each DOC fraction was calculated as the mass for a particular fraction divided by the total mass of DOC multiplied by 100.

Inorganic and Isotope Analyses and Groundwater Age Dating

Weck Laboratories in City of Industry, California, and Sequoia Laboratories of Sacramento, California utilized EPA methods 200.7 and 300 to determine calcium, magnesium, potassium, sodium, chloride, and sulfate concentrations in filtered samples. Oxygen-18 and deuterium in unfiltered samples were analyzed by the University of Arizona Department of Geosciences Isotope Laboratory using mass spectrometry methods described in Epstein and Mayeda (1953) and Kendall and Coplen (1985).

In three monitoring wells, we collected samples for tritium/helium-3 age dating as directed by the University of Miami Rosenstiel School of Marine and Atmospheric Sciences Noble Gas Laboratory (Top, Zafer 2002). We also collected drain-water and San Joaquin River samples for tritium analysis. We collected unfiltered water samples for tritium analysis in 1-L plastic bottles. The University of Miami Rosenstiel School of Marine and Atmospheric Sciences Noble Gas Laboratory determined tritium concentration in the samples by radioactive counting. Tritium concentrations are expressed in tritium units (TU), where 1 TU is equal to 1 tritium atom in 1018 hydrogen atoms. The reporting limit is 0.4 TU.

We collected unfiltered samples for He isotope analysis in 0.95-cm diameter copper tubes that were sealed at each end with clamps. The copper tubes were attached to the discharge line from a positive displacement pump (Grundfos Rediflow) and the tubes were sealed while pumping groundwater through the tubes to prevent atmospheric contamination. We prevented potential contamination by observing for and eliminating bubbles in a section of clear tubing on the discharge end of the copper tubing. Helium isotope ratios and concentrations were analyzed by mass spectrometry (Solomon et al. 1992) at the University of Miami Rosenstiel School of Marine and Atmospheric Sciences Noble Gas Laboratory.

RESULTS

Hydrogeologic Framework

Geologic logs recorded during drilling and well installation on Twitchell Island and in the San Joaquin

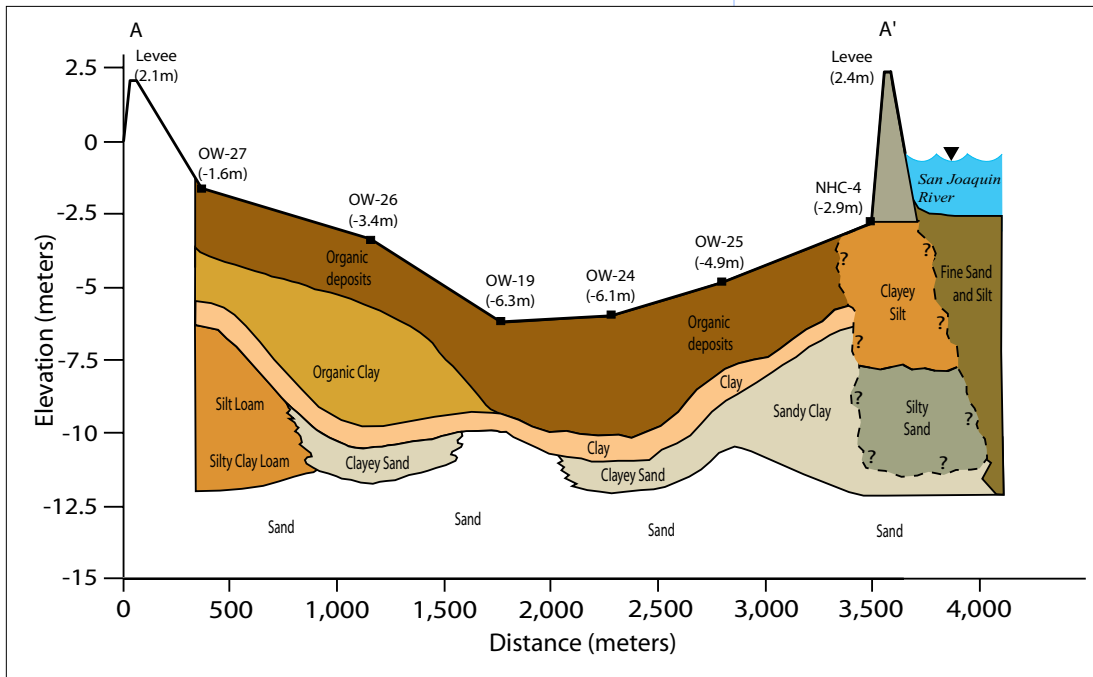


Figure 2. Geologic section A-A' as shown in Figure 1.

River illustrate Holocene depositional history (Figure 2). Three to five meters of organic deposits, accumulated during the last 7,000 years (Atwater 1980), overlie mineral deposits of varied texture deposited during the last glacial period. We observed an approximately 15-cm thick chemically reduced blue clay layer below the organic deposits. Coarser materials of primarily Sierran origin underlie the clay. Tugel (1993) described the Twitchell Island soils as Rindge mucky silt loam (Euic thermic Typic medisaprists) formed from wetland vegetation with minor amounts of alluvium. Previous researchers have reported the carbon composition of Twitchell Island soils. Fujii et al. (1998) reported that the northern (TN) island soils ranged from 18.3 to 27.7 % carbon, and Fleck et al. (2004) reported that the TN and southern (TS) island soils ranged from about 18 to 24% and 20 to 28% carbon, respectively.

Groundwater originating from the San Joaquin River flows towards the island center. Beneath the island, groundwater flows upward within the organic deposits and underlying sand, clayey sand, and sandy clay towards the drainage ditches. Groundwater ages for two water samples from wells in the deposits underly-

ing the peat located 549 and 1,097 m from the midpoint of the San Joaquin River were 16.6 and 36.5 years, and correspond to groundwater velocities of 33 and 30 m/yr, respectively. Since the mineral aquifer is confined beneath the island, the San Joaquin River is the only significant recharge source for groundwater sampled by the wells.

We also collected water samples to determine the tritium levels in drainage water, San Joaquin River water, and a 3-m well

screened in the organic deposits located at cluster site 3 in the TS area. The estimated groundwater age of the July 2003 TS well 3 sample was 17.8 years and the tritium concentration was 5.41 TU. The July and August 2000 DR1 drain sample tritium concentrations were 4.3 and 4.37 TU, respectively. July and August 2000 San Joaquin River samples had 3.64 and 3.99 TU, respectively.

Figure 3 shows typical hydrographs for monitoring wells. Island groundwater levels and drain flow respond to winter rains and increasing San Joaquin River stage. The four hydrographs illustrate the variation in island groundwater hydraulic response. Groundwater levels in wells consistently show upward vertical hydraulic gradients, and water levels in wells screened in the underlying mineral aquifer are consistently close to or above land surface. However, groundwater levels in the organic deposits closest to the levee in the NHC wells showed vertical downward gradients. In the TN and TS areas, water levels in wells screened in the organic deposits are near or above land surface during the winter, and decrease to over 1 m below land surface during summer.

In the TS area, well cluster 3 is located next to drainage ditch DR1. The water levels in the 2- and 3-m wells at

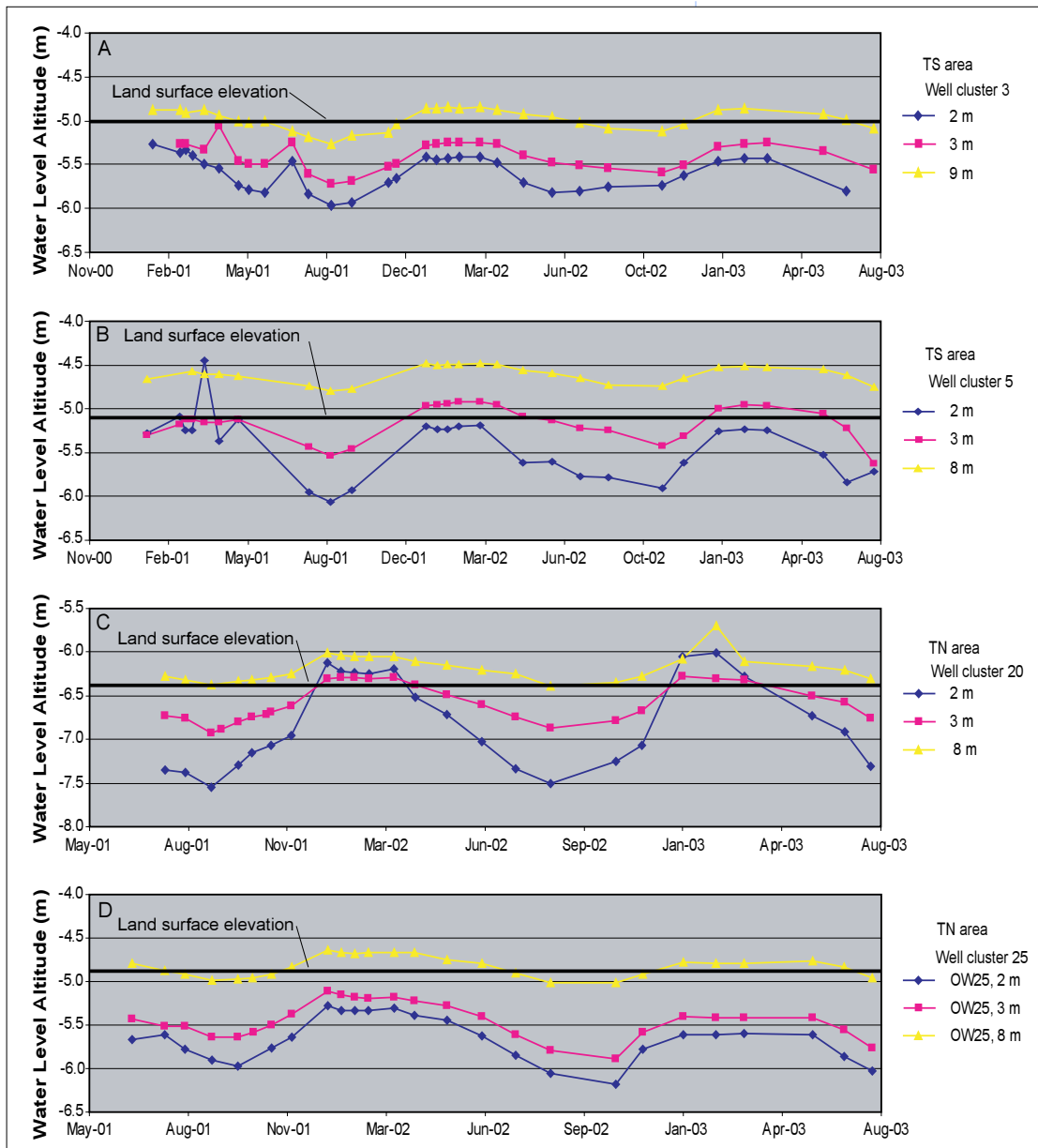


Figure 3. Water level elevation in selected wells.

well cluster 3 are consistently below land surface. Monitoring well cluster 5 in the TS area is located over 50 m from a drainage ditch, and water levels in the 2- and 3-m deep wells at well cluster 5 rise to within a few centimeters of and to above land surface. The maximum depth of the unsaturated zone is 1 m or less. In the TN area, water levels at well cluster 20 show a slightly larger maximum unsaturated depth of about

1.2 m. During winter, water levels increased in the 2- and 3-m deep wells located at well cluster 20, and we measured a downward hydraulic gradient. Well cluster 20 is one of a few well clusters that showed vertically downward gradients, which reflects winter flooding that occurs at this location of the island.

In the TN area, water levels in the 3-m deep wells generally reflect deeper groundwater depths and greater drainage ditch efficiency. For all TS clusters, water levels in the 3-m wells were within 0.5 m of land surface. In contrast, water levels in the TN area were greater than 0.6 m below land surface. The wetter and more recently cultivated TS area has resulted in less decomposed soils with higher organic carbon contents (Fleck et al. 2004).

Drain Flow

Drain flow at the four monitoring locations (Figure 1) ranged generally from less than 0.1 m³/min during late spring, summer, and fall to over 0.5 m³/min during winter and early spring (Figure 4). Maximum drain flow generally corresponds to maximum groundwater levels during the winter. Beginning with November and December precipitation, groundwater levels and hydraulic gradients to the drainage ditches increase. Drain flow increases during winter, with peak flows generally corresponding to winter precipitation (Figure 4). Drain flow generally

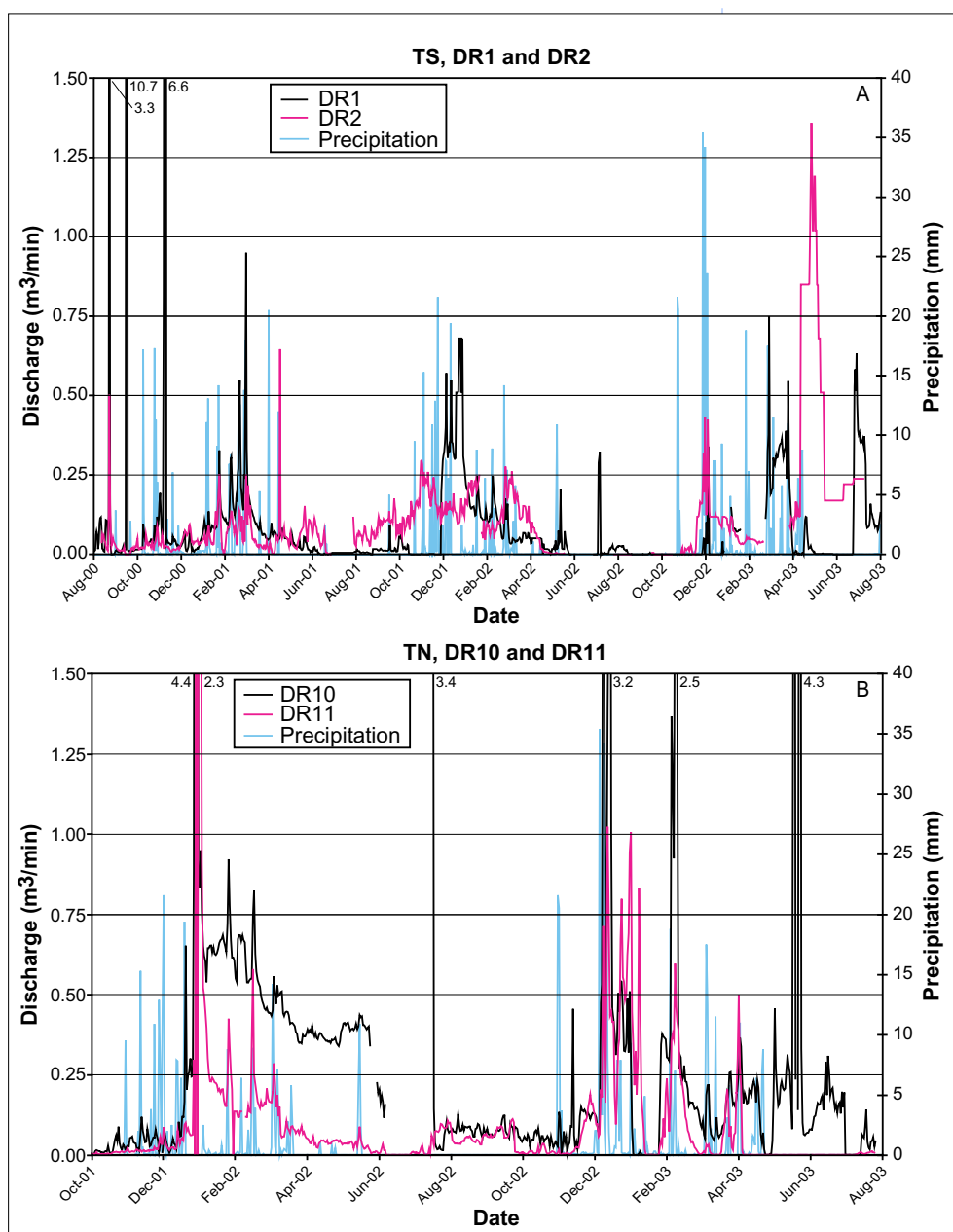


Figure 4. Measured discharge and precipitation at sites DR1, DR2, DR10, and DR11.

decreased in April and May. Peak flows during late spring through fall generally corresponded to irrigation activities. Due to rainfall in April and May 2003, we measured higher drain flow during April-June 2003 relative to 2001 and 2002. Also, maintenance personnel deepened drainage ditches DR1 and DR2 during April 2003, which caused the increased flows

in these drains relative to previous years. Based on the observed seasonal drain-flow patterns, we separated December-April drainage ditch water quality samples from May-November samples. We obtained precipitation data from the California Irrigation Management System station on Twitchell Island.

Chemistry and Loads

Concentrations of organic and inorganic chemical constituents in drainage water samples vary temporally. Figure 5 shows the variation in DOC, THMF, STHMF, SUVA, DO, and EC for DR1, DR2, DR10, and DR11. In general, during winter flow conditions, DOC, THMF, EC, and DO increased with increasing drain flow, whereas SUVA and STHMF decreased with increasing drain flow.

Specifically for DR1 and DR2 (Figures 5A and 5B) we measured maximum DOC and THMF concentrations over 50 mg/L and 3,000 $\mu\text{g/L}$, respectively during December-April 2001, 2002, and 2003. Because of land surface alterations, there was surface water runoff to DR2 that probably diluted DOC concentrations during winter 2002 - 2003. For DR10 and DR11 (Figures 5G and 5H), DOC and THMF concentrations were consistently lower than DR1 and DR2 and less temporally variable.

We measured maximum DOC (over 25 mg/L) and THMF (over 2,000 $\mu\text{g/L}$) concentrations in samples collected in winter 2001-2002.

For all drain monitoring stations, STHMF increased from less than 10 mmol/mol during December-April to greater than 10 mmol/mol during May-November (Figures 5D and 5J). SUVA increased from about 0.04 to 0.06 during December-April to greater than 0.06 during May-November (Figure 5C and 5I). EC and DO consistently increased to maximum values during December-April.

TS, DR1 and DR2

TN, DR10 and DR11

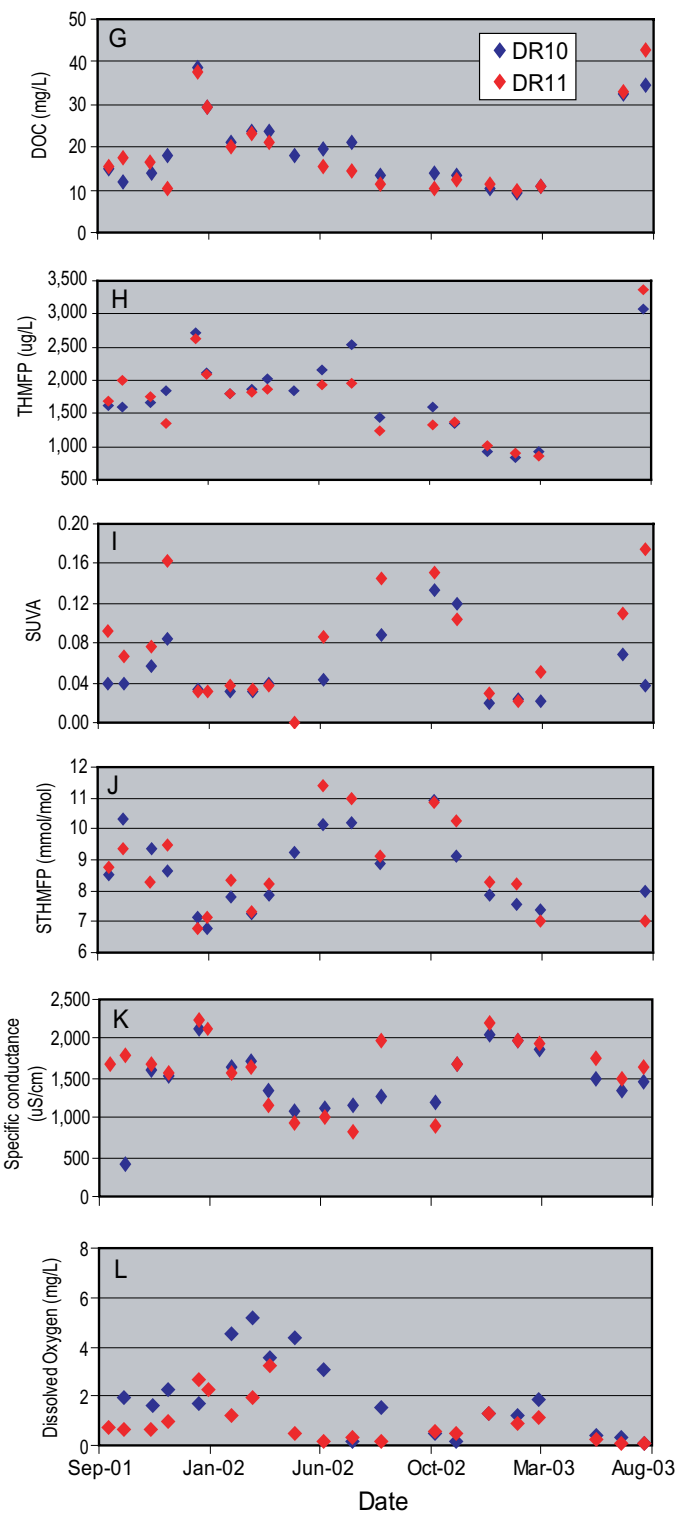
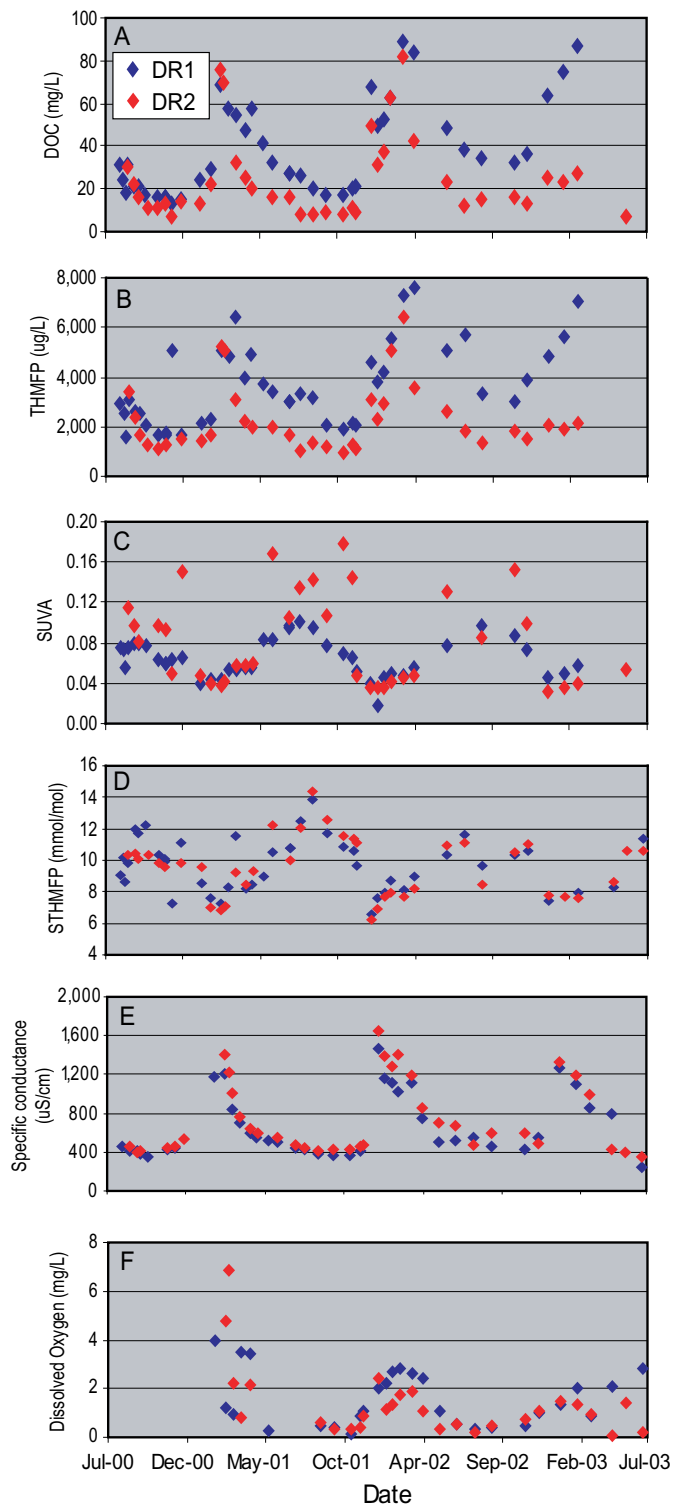


Figure 5. Concentrations of DOC, THMF_P, SUVA, STHMF_P, specific conductance, and dissolved oxygen in drain water.

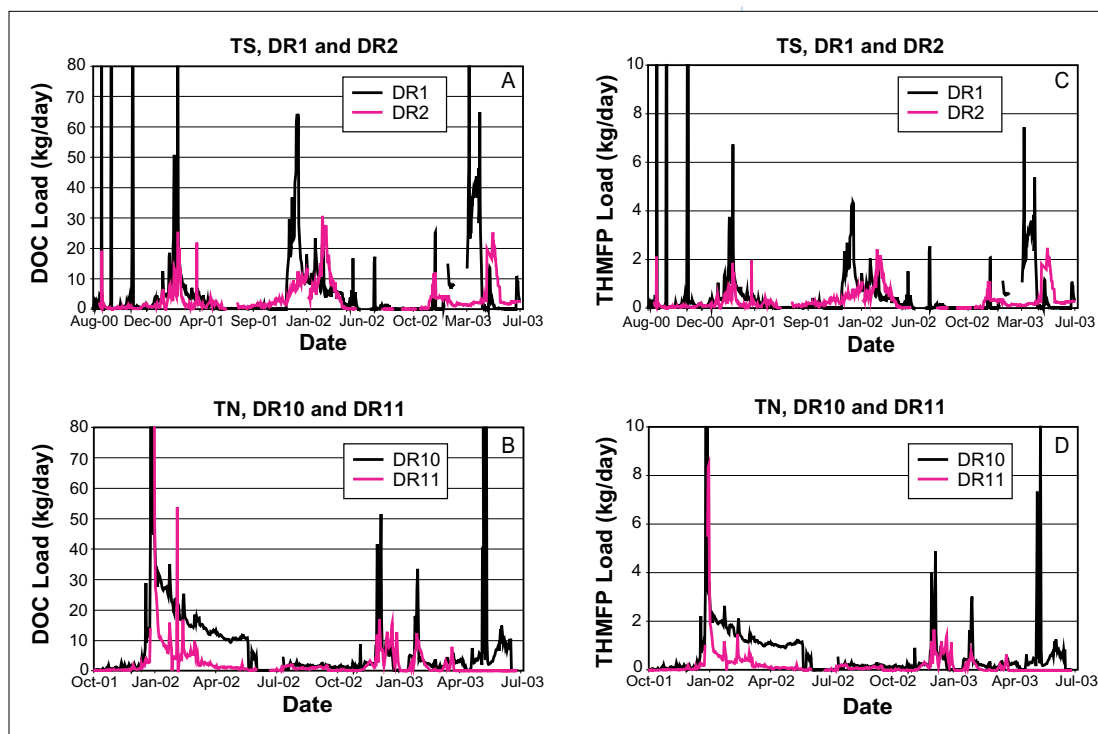


Figure 6. DOC and THMFP loads at sides DR1, DR2, DR10, and DR11.

Using concentrations and daily flow values shown in Figures 4 and 5, we estimated DOC and THMFP loads for all drainage ditches (Figure 6). For all drain monitoring, May–November DOC and THMFP loads are generally less than 20 and 2 kg/day, respectively. Exceptions include summer irrigation events. Higher DOC and THMFP concentrations and higher flows occurred during December–April 2000–2001, 2001–2002, and 2002–2003 resulting in peak loads exceeding 100 and 1 kg/day, respectively.

Table 1 shows the median and range for daily per hectare loads for the May–November and December–April periods. For all loads, we divided the total load by the contributing area to the drainage ditches to estimate the per hectare load. Median DOC, POC, and THMFP loads are consistently lower for the May–November period relative to the December–April period for TS and TN areas and for the entire island. For DOC, TOC, and THMFP, areal variations in loads appear primarily due to variations in DOC and THMFP concentrations as per-area drain flows were generally similar (except for TN-DR10). Annual average per

hectare flows were 0.005, 0.002, 0.007, and 0.006 m³/min-ha for TS, TN-DR10, TN-DR11, and the entire island, respectively.

Particulate organic carbon loads were lower for the May–November samples relative to the December–April samples, but the median percentage of the total carbon was greater during May–November, except for DR11. The higher POC percentage during May–November is probably due to the oxidation of ferrous iron to ferric iron, and subsequent precipitation of iron oxides in the drainage ditch where the water was

exposed to atmospheric oxygen. The relatively greater chemically reducing nature of the samples during this time probably results in higher ferrous iron concentrations. We observed iron-oxide precipitates during sampling, which probably co-precipitated organic carbon upon oxidation to ferric iron in the drainage ditch, accounting for the higher POC percentages during this period.

We also estimated loads for the entire island (1,423 ha). The entire-island loads are not directly comparable with loads in Table 1 due to different measurement frequencies and technique. Specifically, discharge from the island main drain occurs through two discharge pipes. In each pipe, a McCrometer propeller-type meter measures instantaneous flow and registers cumulative flows. When collecting samples from the main drain, we recorded the cumulative volume pumped from the island since the previous sampling and estimated the load by multiplying the cumulative volume times the concentration. Due to malfunctions in one of the meters during 2002, we estimated loads 12 times during fall 2001, winter 2002, and summer 2002 through spring 2003. Median DOC and THMFP loads for the December–April period were 566 (inner quartile range was 330 to 925 g/ha-day) and 54 g/ha-day (inner

Table 1. Median and inner quartile range for daily DOC, POC, TOC, and THMFP loads and median percent POC.

DOC g/ha-day			
	TS (DR1 and 2)	TN - DR10	TN-DR11
Dec-April Median Q1-Q3	260 104 - 646	84 26 - 187	115 39 - 266
May-Nov Median Q1-Q3	27 4 - 58	15 5 - 36	9 0-32
POC g/ha-day			
	TS (DR1 and 2)	TN - DR10	TN-DR11
Dec-April Median Q1-Q3	16 10 - 38	11 5 - 36	41 9 - 84
May-Nov Median Q1-Q3	0.8 0 - 8	4 0.7 - 11	2 0 - 16
Median % POC			
	TS (DR1 and 2)	TN - DR10	TN-DR11
Dec-April	4	11	44
May-Nov	13	17	20
TOC g/ha-day			
	TS (DR1 and 2)	TN - DR10	TN-DR11
Dec-April Median Q1-Q3	433 119 - 770	98 29 - 289	94 0 - 282
May-Nov Median Q1-Q3	6 0 - 55	24 8 - 66	10 0 - 56
THMFP g/ha-day			
	TS (DR1 and 2)	TN - DR10	TN-DR11
Dec-April Median Q1-Q3	23 9 - 50	0.02 0.01 - 2.7	10 3 - 21
May-Nov Median Q1-Q3	4 0.4 - 7	1.6 0.6 - 3.3	1 4 - 61

quartile range was 31 to 75 g/ha-day), respectively. For the May-November period, median DOC and THMFP loads were 180 (inner quartile range was 149 to 269 g/ha-day) and 20 g/ha-day (inner quartile range was 17 to 25 g/ha-day), respectively. These values are generally higher than those measured at DR1, DR2, DR10, and DR11.

However, the higher values do not indicate that the individual drains were not representative of processes on the island. First, the different frequency of entire island flow measurements and sample collection prevented direct comparison. Second, the processes affecting entire-island drain flows and loads are different. The island drainage pumps discharged water continuously from the island from the main drainage ditch, which collected drainage water from the extensive network of smaller drainage ditches from individual fields. There was not always measurable flow in individual drainage ditches, which resulted in periodic zero flow and loads for DR1, DR2, DR10, and DR11. Drain flow in these ditches is controlled by the cycling of the drainage discharge pumps. Because the main drain loads reflect continuous gathering of drain flow from all the feeder ditches, a greater sampling and measurement frequency would be required for direct comparison of per hectare loads. We expect that our measured loads in DR1, DR2, DR10, and DR11 are representative as we studied drainage ditches located in the highest organic matter soils on the island (Tugel 1993) where farming practices were similar to those for the entire island.

Chemical Relations for Drainage and Groundwater

Temporal variability in agricultural drainage ditch concentrations of organic and inorganic constituents primarily reflect varying groundwater flow conditions and sources of carbon from different subsurface zones. Groundwater from different depths seasonally flows to drainage ditches in different proportions. Chemical and physical data indicate two primary sources of subsurface flow to drainage ditches. During December-April, substantial drain flow originates from within 1.5 m of land surface where oxidized and well decomposed organic soils predominate. During May-November, drain flow is predominantly from permanently saturated, moderately to undecomposed, and anoxic organic deposits.

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Organic Chemistry

Figure 5 shows different DOC, THMFP, STHMFP, and SUVA values for the December-April and May-November drain samples. Similar to Fujii et al. (1998), THMFP concentrations were significantly and highly correlated with DOC concentrations (Figure 7). Figure 7 illustrates the relatively low DOC and THMFP concentrations associated with the TN area relative to the TS area. The correlation explains 96% of the variance in THMFP concentrations.

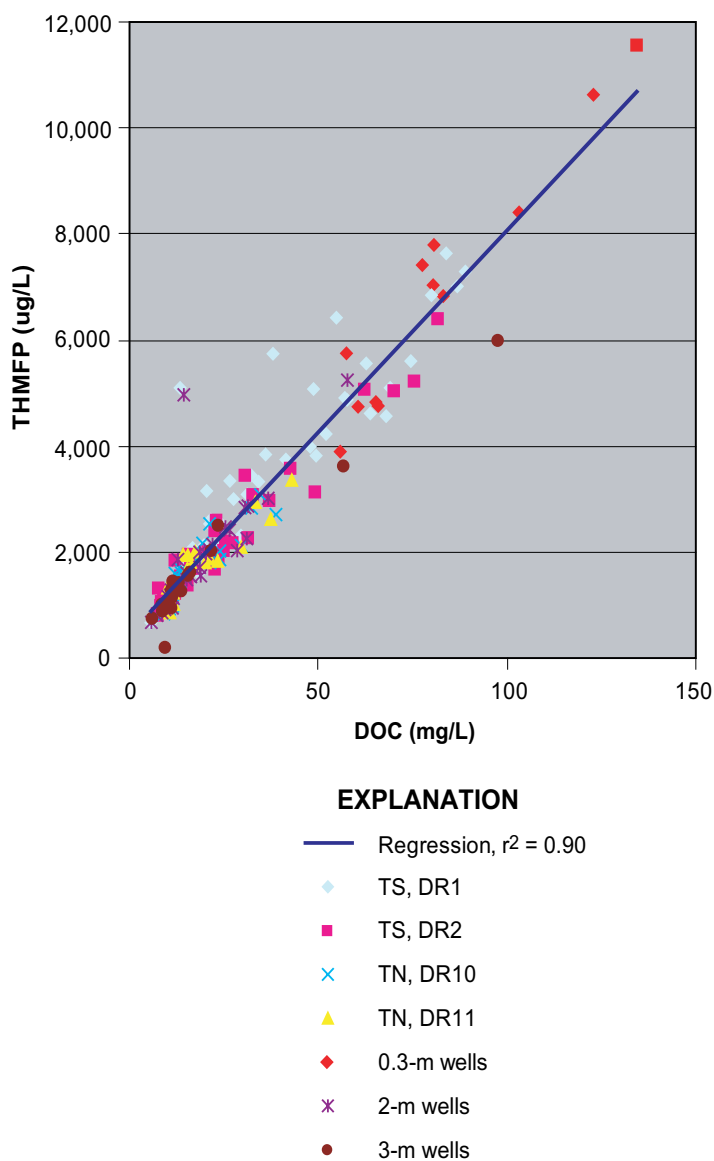
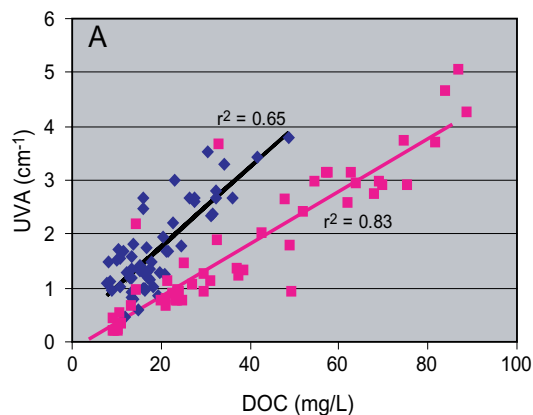
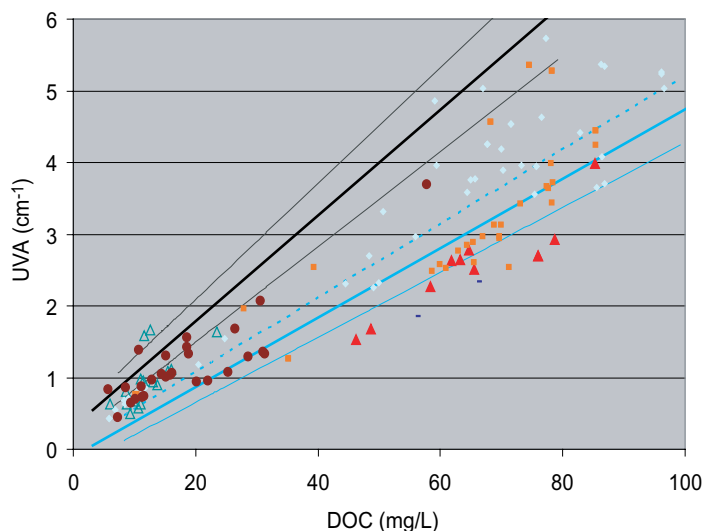


Figure 7. Relationship between DOC and THMFP concentrations indrainwater and groundwater samples



EXPLANATION

- ◆ Drains, May - November
- Drains, Dec - April
- May-Nov regression
- Dec - April regression



EXPLANATION

- △ 3-m wells
- 0.3-m wells
- ▲ Fujii et al, lysimeters
- Fujii et al piezometers, May - Nov
- Fujii et al, piezometers, Dec - April
- May - Nov drain regression
- Dec - April drain regression
- 2-m wells
- May-November regression confidence interval

Figure 8. Seasonal relationship between DOC concentrations and UVA in (A) drainwater samples and (B) drainwater and groundwater samples.

The quality of DOC as represented by UVA and the propensity to form THMs varies spatially and temporally. Figure 8 shows the different UVA-DOC relationship for the two drainage periods. For drain-water DOC, UVA is greater for the May-November samples relative to the December-April samples (Figure 8A). Figures 8B show different DOC-UVA relations for groundwater samples collected from different depths. Specifically, Fujii et al. (1998) lysimeter data and December-April piezometer samples and our 0.3-m well samples generally plot with the December-April drain water samples. The May-November Fujii et al. (1998) piezometer samples and some of our 0.3-m well samples show a UVA - DOC relation intermediate between the drain period relations. In contrast, points representing our 2- and 3-m monitoring-well samples generally plot close to the May-November drainage samples.

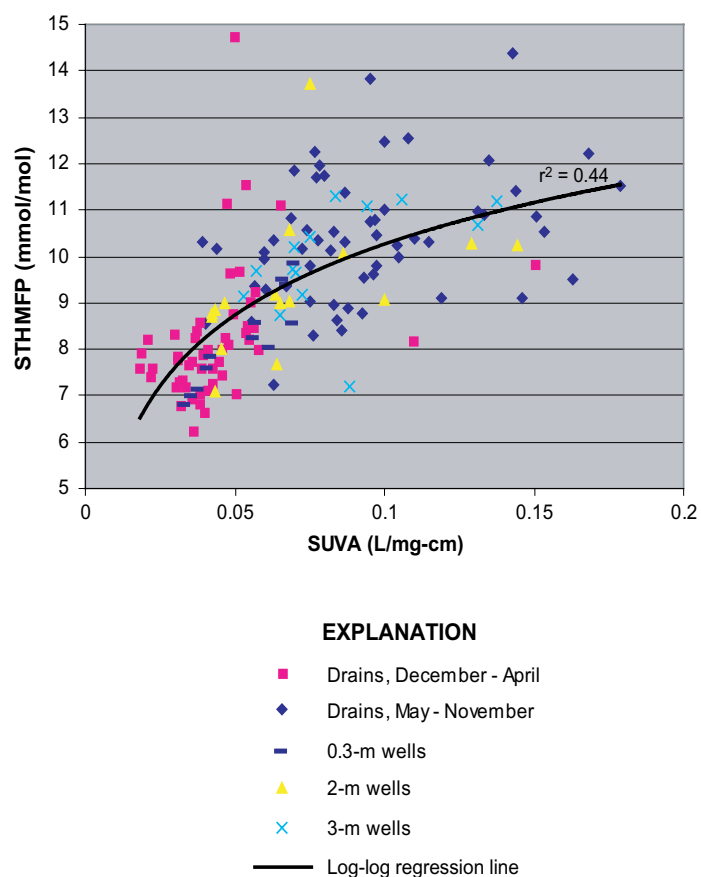


Figure 9. Relation of STHMFP to SUVA for drainwater and groundwater samples.

The Fujii et al. (1998) piezometers were all within 30 m of the drainage ditch near DR10 (Figure 1) and collected a seasonally-variable mixture of shallow and deep groundwater discharge to the drainage ditch. Similarly, values for the 2-m monitoring wells with higher DOC concentrations plot with December-April drain samples. These wells (wells 19, 20, 21, and 22 in the TN area) are located closer to drainage ditches and the center of the island, where groundwater is influenced to a greater degree by shallow, more decomposed organic matter. Similarly, three points representing the 3-m wells that plot close to the drain regression, were collected close to drains or near the center of the island (wells 19 and 20 in the TN area and well 6 in the TS area).

The STHMFP-SUVA relation (Figure 9) shows the log-log regression relation for drain and well samples collected in the two areas. May-November drain samples and most 2- and 3-m well samples have a greater propensity for THM formation relative to December-April drain and 0.3-m well samples. This log-log relation explains 44% of the variance for STHMFP. Greater UV absorbance per mg of DOC corresponds to higher THMs per mole of DOC. This indicates generally greater propensity to form THM for samples primarily originating from deep, anaerobic, and less decomposed organic materials. Consistently, the results of the Mann-Whitney Confidence Interval Test for a comparison of the December-April and May-November drain samples show significantly higher median STHMFP (10.33 mmol/mol) for 64 May-November samples relative to the 52 December-April samples (median = 7.87 mmol/mol).

Fractionation data provides additional information about DOC composition. The primary DOC components are hydrophobic acids (HPOA), hydrophilic acids (HPIA), and transphilic acids (TPIA). For all samples, HPOA is the dominant fraction, accounting for 40% or more of the DOC. The Kruskal-Wallis test for all HPOA results indicated significant ($p = .001$) differences among sample location and time. Figure 10 shows boxplots for the different sample locations and time for HPOA, HPIA, and TPIA. Further statistical comparisons using the Kruskal-Wallis test indicate that HPOA percentages are as follows: May-November drain samples were significantly greater than December-April drain samples and May-November drain samples were

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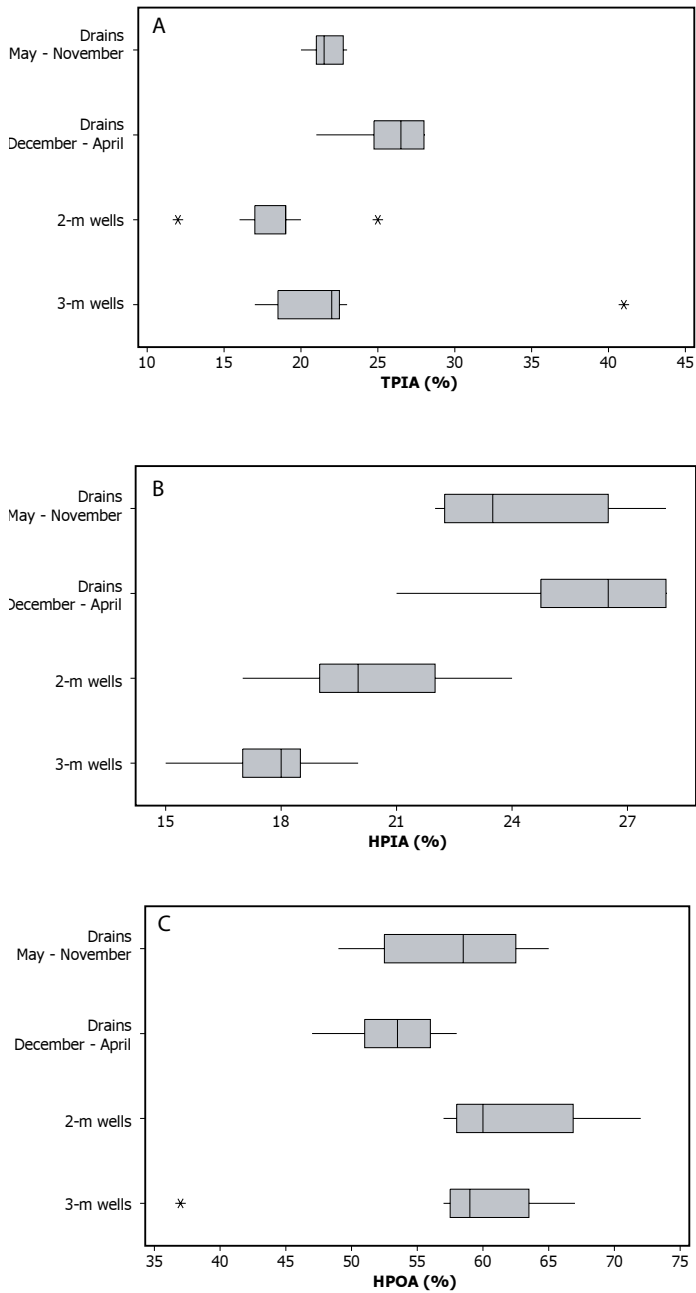


Figure 10. Boxplots of TPIA (A), HPIA (B), and HPOA (C) for groundwater and drainwater samples. Shaded box represents the inner quartile range, vertical line in the shaded box is the median and horizontal lines extending from the shaded box represent the range of the data. Asterisks represent outliers.

not significantly different from samples from 2-m and 3-m wells. December-April samples were significantly less than 2-m and 3-m well samples.

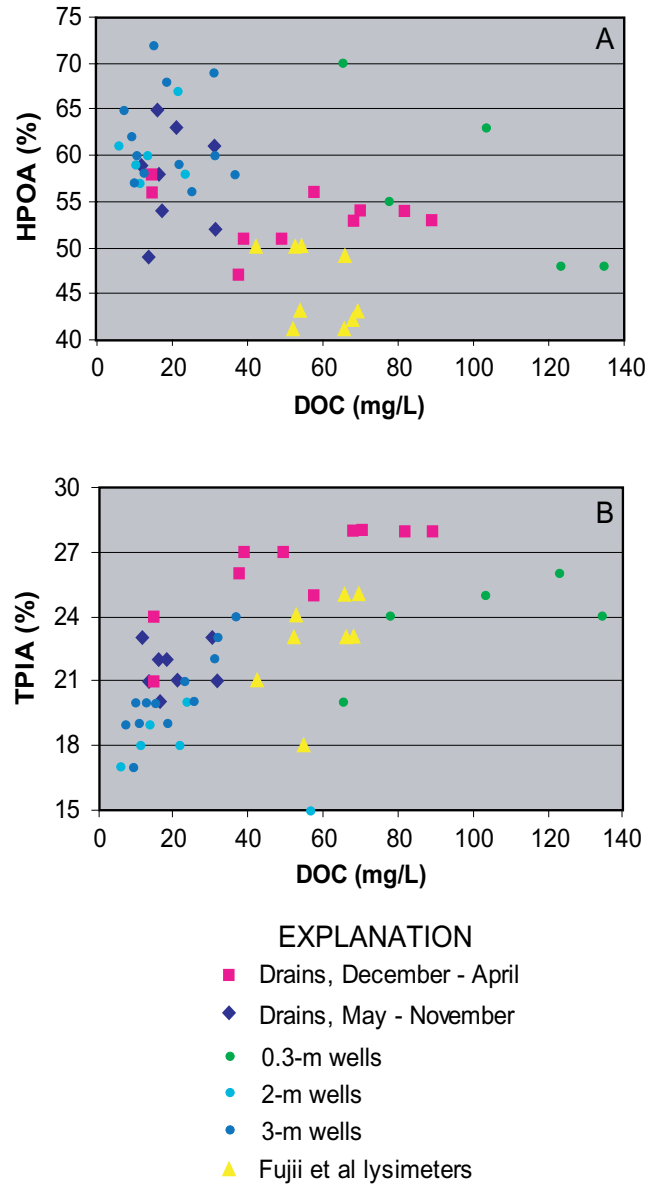


Figure 11. Relationship between DOC and HPOA (A) and DOC and TPIA (B).

The TPIA and HPIA fractions accounted for most of the remainder of the DOC. Kruskal-Wallis testing for locations and seasonal drain samples for TPIA percentage also resulted in significant differences; December-April drain samples were greater than May-November drain samples, which were greater than samples from the 2-m and 3-m wells. Samples from the different well depths were not significantly differ-

ent. HPIA percentages were also significantly different among locations and seasonally for drain samples. May–November and December–April drain samples were not significantly different but drain samples were greater than 2-m wells which were greater than 3-m wells. For the December–April drain samples, fractionation varied with DOC concentrations; higher DOC generally corresponded to lower HPOA fractions and higher TPIA fractions (Figure 11). For comparison, we plotted fractionation results for lysimeters from Fujii et al. (1998) which are generally consistent.

High DOC values for December–April drain samples and the 0.3-m wells also correspond to low pH values. The higher measured pH values for drain samples relative to well samples are probably the result of CO₂ outgassing in the drain. We measured significantly (at alpha = 0.05 using the Mann–Whitney comparison test) lower pH values in 56 December–April drain samples (median = 6.16) relative to 81 May–November drain samples (median = 6.58). Low pH (median = 5.5) in 0.3-m well samples in the variably saturated zone indicate an influence of water from this zone on December–April drain samples. Median pH for 2- and 3-m wells were 6.19 and 6.31, respectively. We measured San Joaquin River water pH values between 7.5 and 7.8.

Inorganic Chemistry

Piper diagrams (Hem 1985) (Figure 12) further illustrate spatial and temporal differences among samples. The San Joaquin River is the primary source of island groundwater through irrigation recharge and seepage through the levee. San Joaquin River samples showed sodium dominance and anion dominance varied from bicarbonate to chloride. San Joaquin River water composition varied with salinity. Calcium, magnesium, and bicarbonate percentages increased with decreasing salinity. The salinity (total dissolved solids) of San Joaquin River samples collected in 2000 ranged from 120 mg/L in winter to 483 mg/L in late fall.

Figures 12 A and B show the major ion composition of the TN and TS drain and groundwater samples, piezometer and lysimeter samples collected by Fujii et al. (1998), and San Joaquin River samples. The May–November TS and TN drain samples are predominantly sodium chloride but with lower or zero sulfate per-

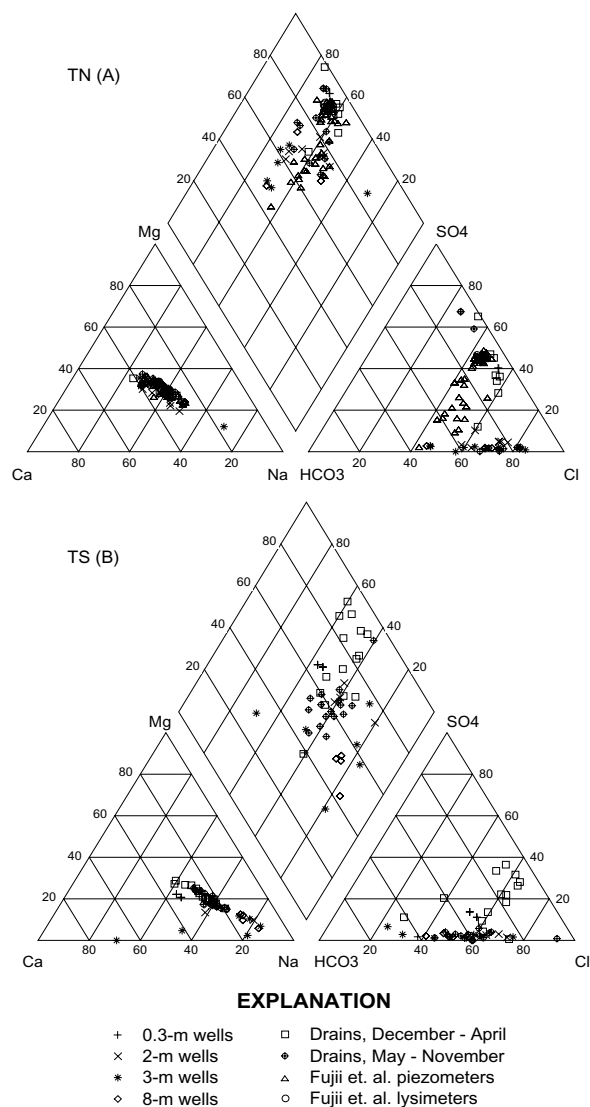


Figure 12A-B Piper diagrams for drainwater and groundwater samples from field TN (A) and field TS (B).

centages relative to San Joaquin River samples (Figure 12A and B). All 2-, 3-, and 8-m well samples show a similar absence of sulfate. In contrast, December–April drain samples, Fujii et al. (1998) lysimeter and piezometer samples, and our 0.3-m well samples show increasing sulfate, calcium, and magnesium percentages with increasing salinity.

In the deep organic and underlying mineral horizons, which are the primary sources of May–November drainwater, anaerobic conditions result in sulfate reduction in groundwater (Deverel et al. 1986). We measured

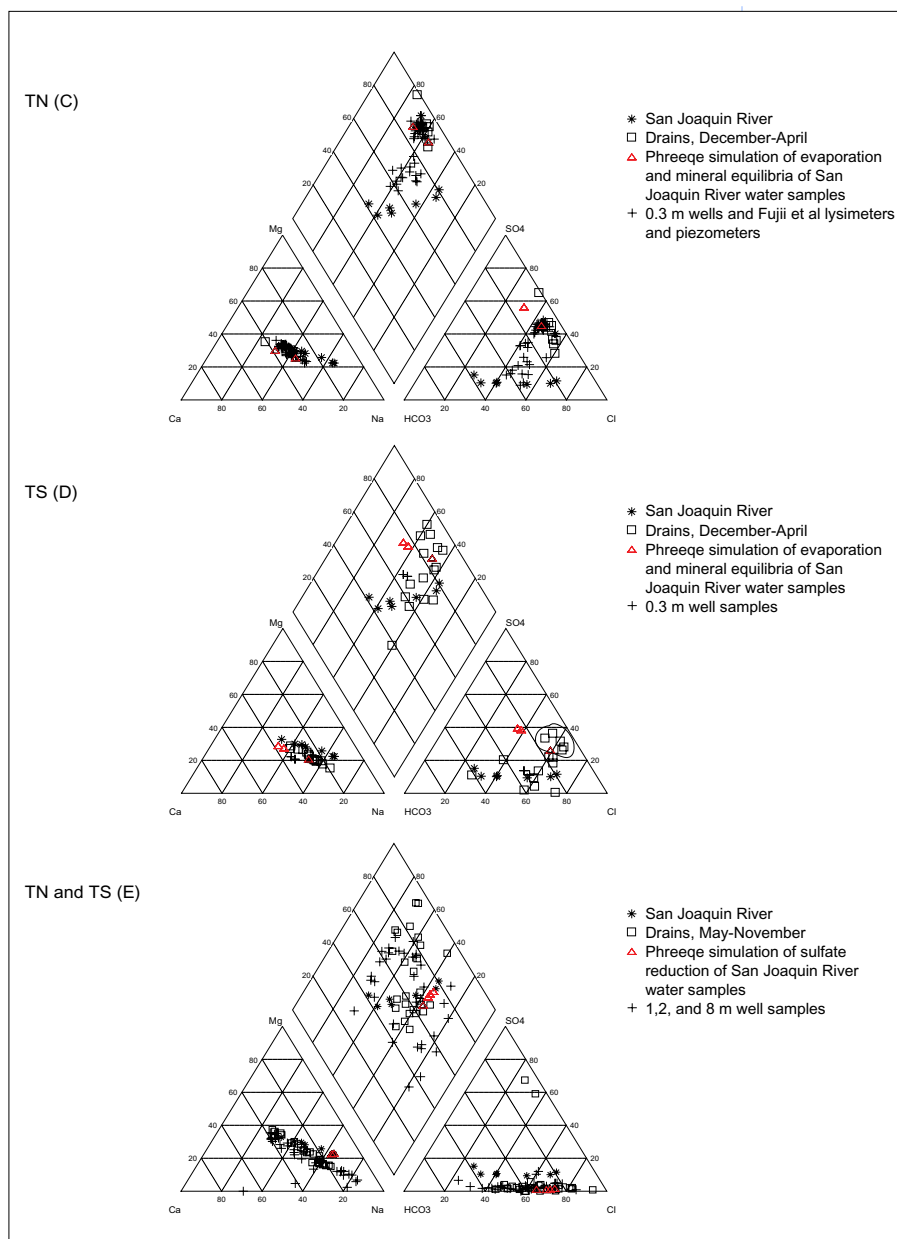


Figure 12C-E (cont'd) Piper diagrams for drainwater and groundwater samples from field TN (C), field TS (D), and TN and TS fields (E)

low dissolved oxygen in drain samples during this time period (Figure 5) and non detectable dissolved oxygen in 2-, 3-, and 8-m well samples. Eh values for these well samples ranged from -383 to 89 (median = -69) mV. The only positive value was for the 2-m well at well cluster 3 next to the drainage ditch at DR1 in the TS area

(Figure 1). Removing this value, the median Eh value was -74.

Results of stable isotope analysis indicate partial evaporation as a cause of varying salinity and major ion composition for drain and groundwater samples. Figure 13 shows that most of the points representing drain and well samples plot on a line having a slope of 6, indicating partial evaporation (Gat and Gonfiantini 1981). Figure 13 indicates that the source of the partially evaporated drain and well water is San Joaquin River water. Isotopic enrichment as represented by $\delta^{18}\text{O}$ is significantly correlated with specific conductance. For all well and drain samples, $\delta^{18}\text{O}$ explains 43% of the variance in the logarithms of specific conductance. Separating the TN and TS samples, $\delta^{18}\text{O}$ explains 72% and 54% of the variance in logarithms of specific conductance, respectively. Increasing specific conductance corresponds to a shift towards higher sulfate concentrations (Figure 12). High DOC concentrations are also significantly correlated with isotopic enrichment. Variations in $\delta^{18}\text{O}$ explain 38% of the DOC variance for drain and well samples. Removing the two highest DOC values for 0.3-m wells in the TS area resulted in 49% variance.

Figure 13 shows that December-April drain samples are partially evaporated and more isotopically enriched than May-November samples. Among groundwater samples, 0.3-m samples showed the greatest isotopic enrichment. Selected samples from 2-m wells also showed significant enrichment. We collected these samples from 2-m wells located close to the center of the island at well clusters 19, 20, and 22 in the TN area. Well clusters 19 and 22 are within 6 m of drainage ditches DR10 and DR11, respectively. Well cluster 20 is located within 100 m of a drainage ditch (Figure 1). The remaining 2- and 3-m well samples and all 8-m well samples were isotopically similar to San Joaquin River water and showed no indication of evaporative enrichment.

We attempted to understand the observed sample inorganic chemistry using geochemical modeling. We used the geochemical model PHREEQE (Parkhurst et al. 1980) to simulate the observed sample chemistry represented in Figure 12. Specifically, we used PHREEQE to simulate the probable processes resulting in high salinity and sulfate concentrations in the samples from the 0.3-m wells and December–April drain samples. Since San Joaquin River water is the primary source of irrigation recharge and appears to be the source of partially evaporated drain and well samples (Figure 13), we hypothesized that partial evaporation of river water is the primary process resulting in the measured concentrations in these wells. Simulation of 70 to 80 % evaporation of San Joaquin River water resulted in chemical composition similar to the evaporated 0.3-m wells and December–April drain samples in the TN and TS areas (Figures 12C and D) when sources of calcium, magnesium and sulfate were simulated (we simulated the presence of calcite, dolomite, and gypsum). Figures 12C and D indicate that the shallow groundwater and drainwater samples represent mixing of San Joaquin River water and San Joaquin River water, subject to evaporation with addition of calcium, magnesium and sulfate. However, thermodynamic equilibrium calculations show that drain and groundwater samples are undersaturated with calcite, dolomite, and gypsum indicating that these minerals are probably not sources of calcium, magnesium, and sulfate.

Consistently, the range of values for PHREEQE-simulated total dissolved solids (TDS) concentrations of the evaporated San Joaquin River water generally agree with measured values. For the TN area, the average of drain and well samples shown on Figure 12C was 1,461 mg/L. The average TDS for PHREEQE-simulated evaporated and mineral-equilibrated San Joaquin River samples shown in Figure 12C was 1,706 mg/L. For the TS area, TDS values for April–December drain samples ranged from 302 to 1,053 mg/L; the average was 675 mg/L. The average value for the drain samples represented by points circled on Figure 12D was 768 mg/L. The circled points on Figure 12D represent samples collected in January, February, and March when the highest salinity waters were being flushed from the variably saturated zone. The average of evaporated San Joaquin River water simulated by PHREEQE was 860 mg/L (Figure 12D).

Because sources of calcium, magnesium, and sulfate were required to simulate the composition of well and drain samples, yet no apparent inorganic source of these ions is present in the soils, we hypothesize that the oxidation of organic soil contributes calcium, magnesium, and sulfate to solution which upon evaporation can result in measured concentrations. Specifically, the literature indicates that peat sulfur, calcium, and magnesium contents range from less than 0.1% to several percent (e.g. Shotyk 1988; Cameron et al. 1989).

We used literature values for sulfur content to elucidate the potential contribution of organic soil oxidation to shallow groundwater salinity. Rojstaczer and Deverel (1993, 1995) indicated that present-day subsidence rates in organic soils with similar organic carbon contents to those on Twitchell are about 3 cm/year. Using a subsidence rate of 3 cm/year and assuming 1% sulfur, oxidation of this volume of organic soil results in liberation of about 1,500 kg/ha-yr

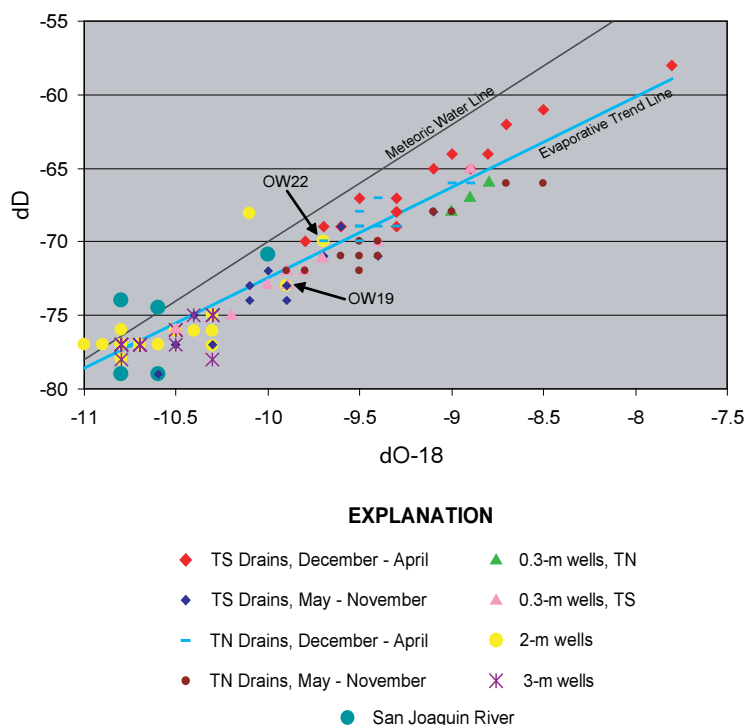


Figure 13. Relationship between Delta deuterium and Delta oxygen -18 for drainwater and groundwater samples.

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of sulfur. Dissolution by 30 cm of irrigation or precipitation recharge results in 500 mg/L sulfate. Using 0.5% for the organic soil sulfur content results in 250 mg/L. These concentrations can increase with evaporation. For comparison, the mean sulfate concentration for 42 samples from our 0.3-m wells and drains sampled during December-April and Fujii et al. (1998) lysimeters was 374 mg/L. In contrast, the average sulfate concentration for seven San Joaquin River samples was 18 mg/L. Five-fold concentration (80% evaporation) of San Joaquin River water results in an average sulfate concentration of 90 mg/L, substantially lower than the measured average.

Our results are generally consistent with Meyer and Carlton (1975) who oxidized a Delta organic soil with hydrogen peroxide and analyzed the chemical composition. They identified sulfur as the primary anionic constituent but they assumed a large portion would precipitate with heavy metals released (iron, manganese, copper, and zinc). They did not provide data or calculations but estimated oxidative release 115 to 630 kg of soluble salts per hectare per year. Their numbers are probably conservative, as oxidation of sulfur to sulfate under observed shallow zone aerobic conditions would exclude precipitation with metals.

Groundwater-level data show that San Joaquin River water moves laterally onto the island and upward from mineral deposits connected to the San Joaquin River. Along the groundwater flow path from the San Joaquin River to island groundwater, chemically reducing conditions cause sulfate reduction. Bicarbonate concentrations also increase which is probably due to sulfate reduction (Deverel et al. 1986). Using PHREEQE, we specified Eh values from wells screened in the mineral aquifer underlying the organic deposits and simulated sulfate reduction. This resulted in modeled compositions similar to those measured in samples collected from the deep wells and drains during May - November (Figure 12E).

DISCUSSION

Chemical and physical data illustrate the relationship of hydrologic conditions, groundwater flow and agricultural drain flow, chemistry, and carbon loads.

Figure 14. summarizes our conceptual model of physi-

cal and chemical processes affecting drain flow, chemistry, and loads. Groundwater flows from the San Joaquin River onto the island primarily via underlying mineral deposits. San Joaquin River water is also the source of irrigation water. During low flow conditions in May-November (Figure 14B), drainwater DOC and THMFP concentrations and SUVA and fractionation results are consistent with deep groundwater flow to drainage ditches from chemically reduced permanently saturated deposits (as represented by 2-, 3-, and 8-m wells). Also, inorganic chemical and stable isotopic drainwater composition is similar to that of groundwater represented by most 2- and 3-m wells and Fujii et al. (1998) piezometer samples. (Fujii et al. (1998) collected samples from piezometers and lysimeters within 30 m of drainage ditch DR10. Piezometers were 1.4 to 2 m deep and lysimeters were 0.15 to 0.46 m deep.) Specifically, these samples had no dissolved oxygen, low Eh values (median for our samples was -74 mV), low or absent sulfate, and stable oxygen and hydrogen isotope composition similar to deep groundwater and San Joaquin River water.

Groundwater age dating and tritium analysis of drain water samples support our conceptual model. The well cluster 3 (TS area) 3-m well sample (adjacent to drainage ditch DR1) age of 17.8 years (tritium concentration of 5.41 TU) reflects probable mixing of recent (within the last decade) recharge and upward flowing older (36.5 years, 4.51 TU) groundwater represented by the nearby well cluster 5, 8-m well sample. Since the drainage ditch collected groundwater during the July and August 2000 samplings, the similarity of the drainage ditch tritium values of 4.30 and 4.37 TU to the well cluster 5-8 m well sample indicates that the drainage water is probably substantially influenced by water that recharged prior to 1982.

During high flow conditions in December-April (Figure 14c), groundwater flowing from variably saturated organic soils dominates drain-water chemistry. Drainwater DOC and THMFP concentrations and SUVA and fractionation results are consistent with shallow groundwater flow in the variably saturated zone (as represented by Fujii et al. (1998) lysimeters and 0.3-m wells) to drainage ditches from chemically oxidized soils. Also, drainwater inorganic chemical and stable isotopic composition during December-April is similar

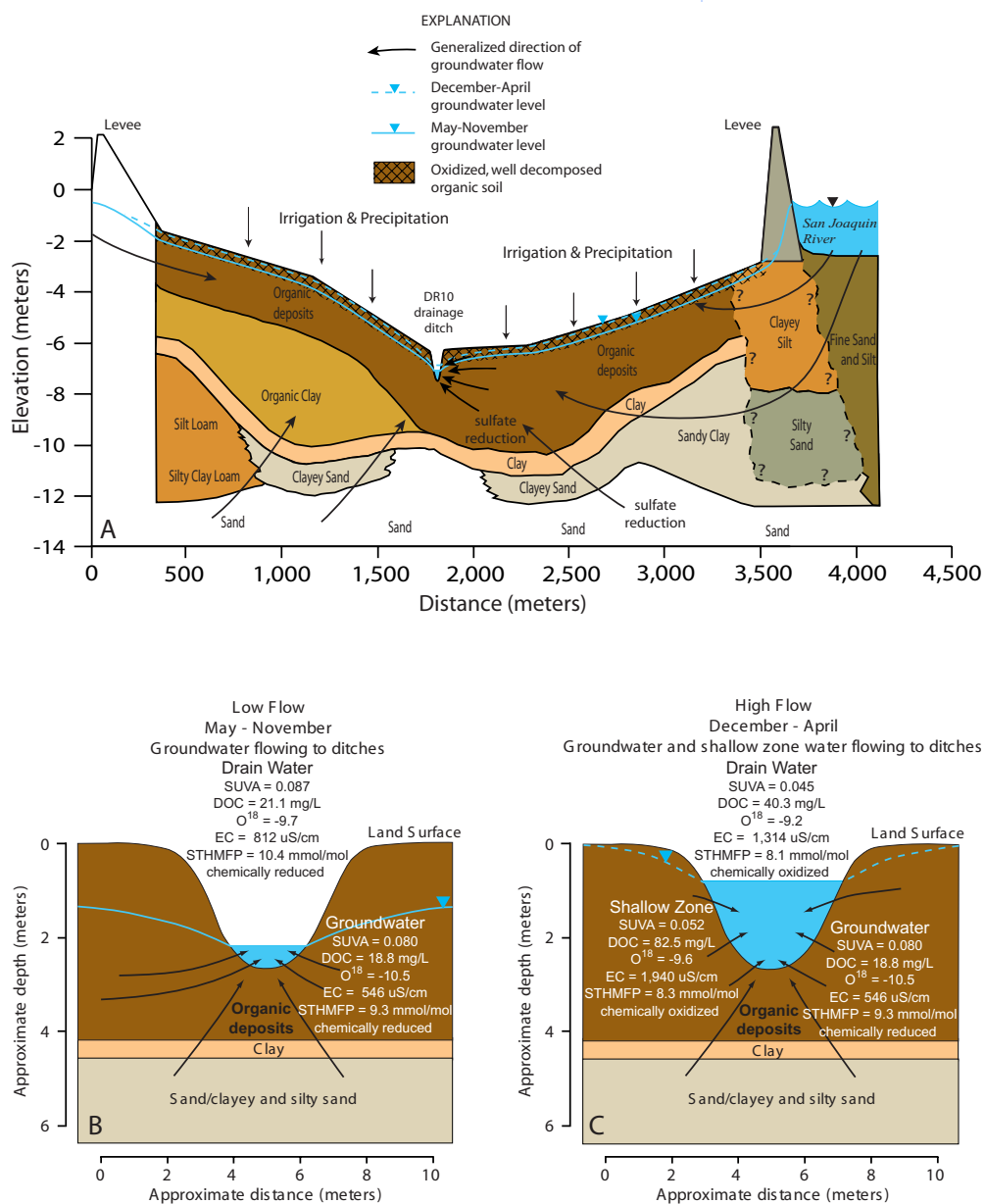


Figure 14. Water flows from the San Joaquin River towards the island center and drainage ditches (A). During May-November, groundwater is the primary source of drain flow (B). During December-April, shallow-zone flow predominates drain flow (C).

to shallow groundwater; dissolved oxygen and sulfate was present and stable oxygen and hydrogen isotope composition was similar to water in the variably saturated zone, which probably is partially evaporated San Joaquin River water. The generally higher measured hydraulic conductivity of this zone facilitates transport to drainage ditches and explains the apparently pre-

dominant chemical influence of the shallow zone.

Drainage organic carbon and THMFP loads vary seasonally and areally. Relatively high DOC concentrations and THMFP from oxidized shallow soils and high groundwater levels result in large drain flows and loads during December-April relative to the May-November period (Figures 3 and 4). Median total organic carbon (POC + DOC) and THMFP loads during December through April were four to over 70 times higher than during May-November (Table 1). POC represented 4 to 44 % of the total organic carbon load. Median DOC loads for the northern area (9 to 115 g/ha-day) were lower than the southern area loads (27 to 260 g/ha-day) primarily due to lower drain-water DOC concentrations. This is consistent with lower soil organic carbon content in the TN area (Fleck et al. 2004).

Our measured DOC loads are generally consistent with other measured agricultural drainage loads in the Delta (Table 2) although there is substantial spatial and temporal variability. With the exception of Jersey Island, Table 2 shows that average May-November load estimates are generally less than December-April loads and are consistent with our estimates. The Jersey Island drainage system was poorly maintained during the Deverel and Rojstaczer (1996) study, and the study field flooded during the winter and slowly drained during the spring and early sum-

May-November load estimates are generally less than December-April loads and are consistent with our estimates. The Jersey Island drainage system was poorly maintained during the Deverel and Rojstaczer (1996) study, and the study field flooded during the winter and slowly drained during the spring and early sum-

Table 2. Comparison of average agricultural drainage DOC load estimates for Delta islands.¹

Island	May-November loads (g C/ha-d)	December-April loads (g C/ha-d)	Source
Jersey Island (fallow)	Average = 3,020 Range = 1,800 - 4,100		Deverel and Rojstaczer (1996)
Orwood Tract (aparagus)	Average = 19.8 Range = 1.3 - 24	Average = 114 Range = 95 - 133	Deverel and Rojstaczer (1996)
Sherman Island (winter grains and fallow)	Average = 15.3 Range = 0.20 - 52		Deverel and Rojstaczer (1996)
Twitchell Island 1995 - 1996 (Predominantly corn with other field and row crops)	Average = 180 Range = 44 - 397	Average = 1,424 Range = 192 - 3,095	Templin and Cherry (1997) and Department of Water Resources Municipal Water Quality Investigations Program
This study (Predominantly corn)	Averages for: TS = 102 TN (DR10) = 48 TN (DR11) = 19 Entire Island = 198	Averages for: TS = 431 TN (DR10) = 138 TN (DR11) = 240 Entire Island = 615	Range of averages for entire island and TN and TS areas

¹ Averages were compared due to the small number of measurements reported in Deverel and Rojstaczer (1996).

mer. This resulted in the reported high loads. In contrast, Deverel and Rojstaczer (1996) reported average DOC loads ranging from 1.3 to 133 g/ha-day for well drained Orwood Tract and Sherman Island. Our May-November load estimates for the entire island are consistent with data collected at the main island drainage pump station on Twitchell Island in 1995 (Table 2) (180 versus 198 g/ha-day).

However, our average load estimate for the entire island for December-April is less than for the load measured in 1995 (1,424 versus 616 g/ha-day). This is probably the result of wetter conditions in 1995. California Department of Water Resources classified water year (WY) 1995 as a wet year in the San Joaquin Basin. Our data were for WY 2001, 2002, and 2003 which were classified as dry, dry, and below normal, respectively, in the San Joaquin Basin (<http://cdec.water.ca.gov/cgi-progs/iodir/WSIHIST>). As evidenced by our data, increased groundwater levels due to increased recharge and higher river stage lead to higher drain flows, concentrations, and loads. The

evidence points to higher December-April loads associated with a wetter year. DiGiorgio et al. (2006) reported an average load from Staten Island of 31 g/Ha-day for measurements from October 2005 through August 2006. Although data for May-November and December-April periods were not provided in their poster, they stated that 66% of the total organic carbon load occurred

during the rainy season and 33% occurred during the irrigation season.

Agricultural drainage loads are generally lower than wetland drainage loads. Using groundwater chemical data and a groundwater flow model, Burow et al. (2005) estimated subsurface DOC loads from a non-tidal constructed wetland on Twitchell Island as 1,233 to 3,671 g/ha-day. Fleck et al. (2007) reported an annual average load of 2,566 g/ha-day.

These load data point to hydrologic, land, and water management effects, and sources of organic carbon to drainage ditches. Our data and data from Burow et al. (2005), Fleck et al. (2007), and Deverel and Rojstaczer (1996) indicate that land-management practices and hydrologic conditions that result in high groundwater levels increase DOC loads 3 to over 100 times relative to late spring, summer, and fall agricultural drainage loads. Questions remain about the long-term effects of permanent flooding on DOC and THMFP loads. Laboratory data for soil cores (USGS written communication 2003) indicate that continued water movement though shallow, oxidized organic soils under permanently flooded conditions will result in decreased drain-water DOC and THMFP concentrations over time.

Specifically, San Joaquin River water flowed through undisturbed cores collected from the Twitchell TS area. The cores were maintained saturated. Dissolved organic carbon concentrations in the column effluent decreased to a few mg/L above levels in the influent water. These data indicate that under permanently flooded conditions in which drainage-ditch water levels are maintained similarly to present-day conditions (about 1 meter below land surface), DOC concentrations will decrease over time.

Temporal variation and drain-water chemistry concomitant with increased groundwater levels and drain flow indicate two primary sources of groundwater flow to drainage ditches. Figure 5 shows that high DOC and THMFP concentrations during December-April and high groundwater levels and drain flows are associated with high dissolved oxygen, salinity, and low SUVA levels relative to May-November. The depth distribution of DOC concentrations and quality, environmental factors (redox, moisture content, etc.), and biogeochemical processes affecting carbon in the organic deposits determine concentrations and loads. High DOC and THMFP concentrations associated with shallow, oxidized, and aerobic soil layers contribute to high drainage concentrations and loads when groundwater levels rise to near land surface and drain flows are high during the winter and early spring (Figure 6).

Figure 8 illustrates a spatially variable DOC-UVA relation for drainage and groundwater samples; May-November drain samples and 2- and 3-m groundwater samples (and Fujii et al. 1998) May-November piezometer samples) have higher UVA values per mg DOC (SUVA) relative to December-April drain samples and shallow subsurface (Fujii et al. 1998) piezometer and our shallowest 0.3-m well) samples. THMFP increases logarithmically with increasing SUVA (Figure 9) and the log-log SUVA-STHMFP relation explains 44% of the variance in STHMFP.

These DOC, UVA, and THMFP data generally indicate that greater sample aromaticity corresponds to greater propensity to form THMs for samples primarily originating from anaerobic and less decomposed organic deposits. Specifically, samples collected from the 2-m and 3-m wells and from drainage ditches during May-November had greater THM formation potential and

greater UVA values per mass of DOC than those collected from shallower wells, lysimeters, and piezometers and drainage ditches during December-April. Rook (1977) and Reckow et al. (1990) indicated that formation of THMs results from the reaction of chlorine with aromatic rings in humic substances. SUVA is an indicator of DOC aromaticity (Fujii et al. 1998). Shallow groundwater, a primary source of drain water during December-April, has less propensity to form THMs, and the DOC has less aromaticity than the deeper groundwater that is the primary source of drain water during May-November.

DOC fractionation further elucidates processes affecting spatial and temporal variability in DOC, SUVA, and THMFP. HPOA, the primary component of DOC, generally decreased with increasing sample DOC concentrations (Figure 11). Fujii et al. (1998) showed that SUVA values of HPOA fractions were significantly higher than for the HPIA or TPIA fractions, indicating greater aromaticity of the HPOA fraction. Consistently, the HPOA fraction for samples collected during this study was highest in the 2- and 3-m well samples and May-November drain samples (Figure 10). These samples are associated with the deep, less decomposed, anaerobic organic materials. The HPOA fraction, aliphatic carboxylic acids of five to nine carbons, one- and two-ring aromatic carboxylic acids, one- and two-ring phenols, and aquatic humic substances probably comprise a large portion of the DOC for these samples. In contrast, lower HPOA fractions and thus lower aromaticity are associated with December-April drain samples and the Fujii et al. (1998) lysimeter samples from the variably saturated zone.

The TPIA DOC fraction generally increases with DOC (Figure 11B), indicating that polyfunctional organic acids and aliphatic acids with five or fewer C atoms represent more of the DOC at higher concentrations in groundwater in the shallow, variably saturated zone. Drain samples collected during December-April and from 0.3-m wells and lysimeters (Fujii et al. 1978) consistently have the highest TPIA fractions whereas 2- and 3-m well samples and May-November drain samples have the lowest TPIA fractions. Samples with high TPIA fractions have a lower, per mole carbon propensity to form THMs. Major ion chemistry (Figure 12) and stable isotope data (Figure 13) further eluci-

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date processes affecting groundwater flow to drainage ditches. The major-ion chemistry and stable isotope composition of May–November drain samples and 2- and 3-meter well samples is similar to San Joaquin River samples except for the general absence of sulfate due to sulfate reduction. In contrast, the December–April drain samples and 0.3-m well samples show isotopic evidence of partial evaporation which resulted in increased salinity and sulfate concentrations. High sulfate concentrations relative to San Joaquin River water appear to result from oxidation of organic soils.

SUMMARY AND CONCLUSIONS

The results of our investigation on Twitchell Island illustrate the chemical and physical processes affecting drain flow and organic carbon in Delta agricultural drain water. Analysis of chemical and physical data led to the development of a conceptual model that describes temporally variable groundwater flow to drainage ditches (Figure 14). Our primary conclusions follow. Groundwater flow to drainage ditches affects drain water chemistry primarily under two regimes: high drain flow during December–April and low drain flow during May–November. During high flow, high DOC and more saline groundwater from the shallow, variably saturated zone dominates drain flow. During low flow, drain flow has low DOC concentrations and is less saline due to groundwater flowing from the chemically reduced permanently saturated zone.

During low flow (Figure 14B), groundwater in deep (below 1 m) organic deposits flows to drainage ditches. Also, drain water and deep groundwater chemical compositions were generally similar. Drainwater DOC was about 21 mg/L and had a relatively high per mole DOC propensity to form THMs. The median STHMFP was 10.4 mmol/mol. Drain water and groundwater were chemically reducing. Consistent with the literature and as indicated by the DOC fractionation and UVA data, these May–November samples were relatively high in aromatic and long-chained carbon compounds (HPOA fraction).

During high flow (Figure 14C), groundwater in shallow, variably saturated, organic deposits flowed to drainage ditches during periods of high groundwater levels. Drainwater and shallow groundwater were

chemically similar; average drainwater DOC was about 40 mg/L and had relatively low per mole DOC propensity to form THMs. The median STHMFP was 7.87 mmol/mol. Larger amounts of DOC in samples collected from the chemically oxidized, variably saturated zone and December–April drain samples had a relatively higher proportion of short chained (five or fewer carbons) polyfunctional organic and aliphatic acids (TPIA fraction).

Drainage organic carbon and THMFP loads varied seasonally and areally. Median DOC loads for the northern area (9 to 115 g/ha-day) were lower than southern area (27 to 260 g/ha-day), primarily due to lower drain-water DOC concentrations which were reflective of lower soil organic carbon content. December through April drainage DOC loads were 3 to over nine times higher than during May–November for all locations. Median drainage THMFP loads for the northern area (0.02 to 10 g/ha-day) were lower than the southern area (4 to 23 g/ha-day) primarily due to lower drain-water DOC and THMFP concentrations. POC represented 4 to 44% of the total organic carbon load.

Inorganic chemical and hydrogen and oxygen isotope data and groundwater age dating helped to confirm our conceptual understanding of the groundwater–drainage system. Deep groundwater and May–November drainage chemical composition was similar to San Joaquin River water chemistry except for sulfate reduction which occurs in deep groundwater. December–April drainage and shallow groundwater samples show evidence of partial evaporation and increased salinity, and the major ion chemistry for groundwater and drainage samples are similar. Age dating and tritium concentrations also support our conceptual model for groundwater flowing to drains.

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