



CALIFORNIA URBAN WATER AGENCIES

May 8, 2001

R37A
(copy)

Delta

Joe Karkoski
Central Valley Regional Board
3443 Routier Road, Suite A
Sacramento, CA 95827-3003

Re: Water Quality Information – Regional Board notice of February 21, 2001

Dear Mr. Karkoski:

Thank you for the opportunity to submit information to support the CWA 303(d) and 305(b) submittals to USEPA in 2002.

California Urban Water Agencies (CUWA) is a non-profit corporation formed in 1990 with a mission to provide a forum for combining the expertise and resources of its member agencies to study and promote the need for a reliable, high quality water supply for the state's current and future urban water needs. The organization is headquartered in Sacramento, California from where its various research and water management studies and efforts are coordinated with its eleven member agencies which directly and indirectly serve over two-thirds of the state's population. Resources of the member agencies are pooled to study technical water management issues of common interest and to develop common understanding and consensus solutions among the urban community to meet California's water resource needs.

At this time CUWA is not submitting specific new data developed by this organization. However, we wish to call your attention to two reports by others that are germane to the 303(d) and 305(b) submittals and to your development of a drinking water policy for the Delta. Both reports were published subsequent to July of 1997. They are:

1997 Compendium of Water Quality Investigations in the Sacramento River Watershed, Sacramento-San Joaquin Delta, and San Francisco Bay Area, published by the Municipal Water Quality Investigation Program of the Department of Water Resources published in August of 1998.

Dissolved Organic Carbon concentrations and Compositions, and Trihalomethane Formation Potentials in Waters from Agricultural Peat Soils, Sacramento-San Joaquin Delta, California: Implications for Drinking-Water Quality. USGS and California Department of Water Resources (Water Resources Investigations Report 98-4147).

We may have additional comments between now and the May 15 submittal deadline, but we want to assure that the two referenced documents are in the record of the several proceedings.

Thank you for considering our comments. Please contact me at the letterhead address/phone number if you have any questions.

Sincerely,

A handwritten signature in cursive script that reads "Walt Pettit".

Walt Pettit
Executive Director

cc: Elaine Archibald
Water Quality Committee



Dissolved Organic Carbon Concentrations and Compositions, and Trihalomethane Formation Potentials in Waters from Agricultural Peat Soils, Sacramento-San Joaquin Delta, California: Implications for Drinking-Water Quality



Water-Resources Investigations Report 98-4147

**Prepared in cooperation with the
CALIFORNIA DEPARTMENT OF WATER RESOURCES**

**U.S. Department of the Interior
U.S. Geological Survey**

Dissolved Organic Carbon Concentrations and Compositions, and Trihalomethane Formation Potentials in Waters from Agricultural Peat Soils, Sacramento-San Joaquin Delta, California: Implications for Drinking-Water Quality

By Roger Fujii, Anthony J. Ranalli, George R. Aiken, and Brian A. Bergamaschi

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Water-Resources Investigations Report 98-4147

Prepared in cooperation with the
California Department of Water Resources

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Sacramento, California
1998



U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary



U.S. GEOLOGICAL SURVEY
Thomas J. Casadevall, Acting, Director

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CONVERSION FACTORS, ABBREVIATIONS, and VERTICAL DATUM

Multiply	By	To obtain
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
square foot (ft ²)	0.09290	square meter (m ²)
gallon (gal)	3.785	liter (l)

ABBREVIATIONS OF MEASUREMENT

L = liter

L/mg-cm = liter per milligram-centimeter

MCL = maximum contaminant level

μg/L = microgram per liter

μg/mg = microgram per milligram

μm = micrometer

μM = micromolars

μM/mM = micromolar per millimolar

μS/cm = microsiemen per centimeter

mg = milligram

mg/L = milligram per liter

min = minute

mL = milliliter

mV = millivolt

M = molar, or mole per liter

nm = nanometer

N = normality, or equivalent per liter

ppm = part per million

VERTICAL DATUM

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$$

USE OF DUAL UNITS

Dual units of measurement are reported for measurements of ultraviolet absorbance and specific conductance. Ultraviolet absorbance is measured as absorbance of light of a specific wave length (254 nanometers) by water over a distance or length, the convention being per centimeter (metric units). Similarly, specific conductance is measured as the electrical conductance of water over a distance or length, the convention also being per centimeter. All other length measurements, such as distance below land surface, are reported in feet and inches.

Dissolved Organic Carbon Concentrations and Compositions, and Trihalomethane Formation Potentials in Waters from Agricultural Peat Soils, Sacramento-San Joaquin Delta, California: Implications for Drinking-Water Quality

By Roger Fujii, Anthony J. Ranalli, George R. Aiken, and Brian A. Bergamaschi

ABSTRACT

Water exported from the Sacramento-San Joaquin River delta (Delta) is an important drinking-water source for more than 20 million people in California. At times, this water contains elevated concentrations of dissolved organic carbon and bromide, and exceeds the U.S. Environmental Protection Agency's maximum contaminant level for trihalomethanes of 0.100 milligrams per liter if chlorinated for drinking water. About 20 to 50 percent of the trihalomethane precursors to Delta waters originates from drainage water from peat soils on Delta islands. This report elucidates some of the factors and processes controlling and affecting the concentration and quality of dissolved organic carbon released from peat soils and relates the propensity of dissolved organic carbon to form trihalomethanes to its chemical composition.

Soil water was sampled from near-surface, oxidized, well-decomposed peat soil (upper soil zone) and deeper, reduced, fibrous peat soil (lower soil zone) from one agricultural field in the west central Delta over 1 year. Concentrations of dissolved organic carbon in the upper soil zone were highly variable, with median concentrations ranging from 46.4 to 83.2 milligrams per liter. Concentrations of dissolved organic carbon in samples from the lower soil zone were much less variable and generally slightly higher than samples from

the upper soil zone, with median concentrations ranging from 49.3 to 82.3 milligrams per liter.

The dissolved organic carbon from the lower soil zone had significantly higher aromaticity (as measured by specific ultraviolet absorbance) and contained significantly greater amounts of aromatic humic substances (as measured by XAD resin fractionation and carbon-13 nuclear magnetic resonance analysis of XAD isolates) than the dissolved organic carbon from the upper soil zone. These results support the conclusion that more aromatic forms of dissolved organic carbon are produced under anaerobic conditions compared to aerobic conditions.

Dissolved organic carbon concentration, trihalomethane formation potential, and ultraviolet absorbance were all highly correlated, showing that trihalomethane precursors increased with increasing dissolved organic carbon and ultraviolet absorbance for whole water samples. Contrary to the generally accepted conceptual model for trihalomethane formation that assumes that aromatic forms of carbon are primary precursors to trihalomethanes, results from this study indicate that dissolved organic carbon aromaticity appears unrelated to trihalomethane formation on a carbon-normalized basis. Thus, dissolved organic carbon aromaticity alone cannot fully explain or predict trihalomethane precursor content, and further investigation of aromatic and nonaromatic

forms of carbon will be needed to better identify trihalomethane precursors.

INTRODUCTION

The Sacramento-San Joaquin River Delta (fig. 1), hereafter referred to as the Delta, supplies drinking water to more than 20 million people in California. Delta waters contain elevated concentrations of dissolved organic carbon (DOC) and bromide (Br) and can, at times, exceed the U.S. Environmental Protection Agency's (USEPA's) maximum contaminant level (MCL) for trihalomethanes (THMs) of 0.100 milligrams per liter (mg/L) (U.S. Environmental Protection Agency, 1994) if chlorinated for drinking water (Amy and others, 1990; California Department of Water Resources, 1994a). This constraint will become more stringent when stage one of the Disinfectant-Disinfection Byproducts rule is implemented (originally scheduled for June 1998), under which the MCL for THMs will be decreased to 0.080 mg/L (Pontius, 1991; Means and Krasner, 1993).

Drainage water from Delta islands is estimated to contribute from 20 to 50 percent of the DOC contributing to the formation of THMs (THM precursors) in water samples collected at the H.O. Banks pumping plant (Amy and others, 1990; California Department of Water Resources, 1990). The H.O. Banks pumping plant is one of the primary diversion points from the Delta for drinking-water supply. The release of DOC from organic peat soils is believed to be the primary source of the DOC and THM precursors to the island drainage water from Delta islands (Amy and others, 1990; California Department of Water Resources, 1994a), although other carbon sources, such as recent crop residue and microbial biomass, also contribute to DOC releases. Island drainage water is pumped over the levees and into the channel waters of the Delta.

Organic soils in the Delta developed primarily from the accumulation of decaying plant material in this once tidal wetland during the last 10,000 years (Atwater and others, 1977; Atwater, 1980). Decomposition of the organic material by bacteria, fungi, and other organisms has contributed to the formation of the peat soils present on Delta islands, up to 60 feet (ft) deep in some areas (California Department of Water Resources, 1993). By the mid-1800's, settlers began

farming the rich organic soils of the Delta, and, by 1869, extensive levee systems were built around Sherman and Twitchell Islands (California Department of Water Resources, 1993) to allow for the expansion of agriculture. Reclamation of Delta islands for agricultural purposes continued into the 1920's, and agriculture accounts for about 70 percent of the current land-use in the Delta (Templin and Cherry, 1997).

Reclamation of Delta islands by the construction of levees and the dewatering of soils for agricultural production has increased the exposure of organic soils to oxygen, resulting in subsidence of the land. Microbial oxidation of the peat soils is the predominant process that contributes to the loss of land-surface elevation in the Delta (Rojstaczer and Deverel, 1993, 1995; Deverel and Rojstaczer, 1996; Deverel and others, 1998); parts of the Delta are more than 20 ft below sea level (California Department of Water Resources, 1993). The resulting large difference between Delta channel water levels and island land-surface elevation increases hydraulic pressures on levees, increasing the probability of levee failure and also requiring the pumping of large volumes of drainage water off the islands to maintain ground-water levels below crop root zones.

Ground-water levels under the Twitchell Island agricultural field studied for this report are maintained at about 3 ft below land surface under nonflooded and nonirrigated conditions, resulting in a vertical oxygen gradient within the soil profile—aerobic at the surface, transitioning to anaerobic below the water table. Under these contrasting redox conditions, microbial decomposition of the soil organic matter (SOM) differs. Under aerobic conditions, microorganisms decompose SOM at much faster rates, with carbon dioxide (CO₂) and water (H₂O) as their metabolic end products. Under anaerobic conditions, bacterial decomposition rates of SOM are much slower and result in reduced compounds such as gaseous nitrogen (N₂), hydrogen sulfide (H₂S), and methane (CH₄) [depending on the availability of oxidized forms of nitrogen (N), sulfur (S), and carbon (C) as terminal electron acceptors] as their metabolic end products (Stevenson, 1985, 1994; Tate, 1987). Under both redox conditions, decomposition of SOM releases carbon that is potentially available to the aqueous phase. These contrasting decomposition pathways result in two soil layers that grade from one to the other. The surface and

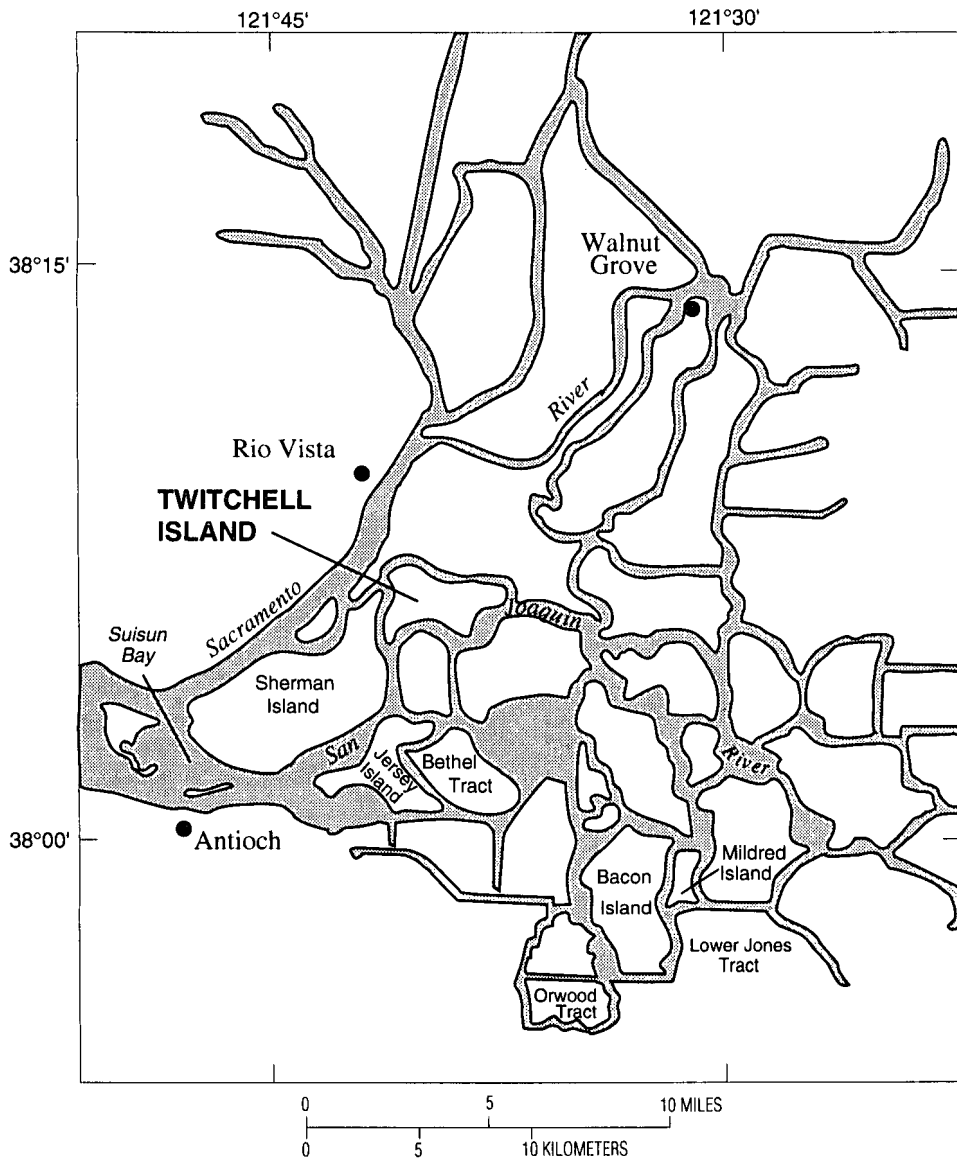


Figure 1. Location of the study area, Twitchell Island, Sacramento-San Joaquin Delta, California.

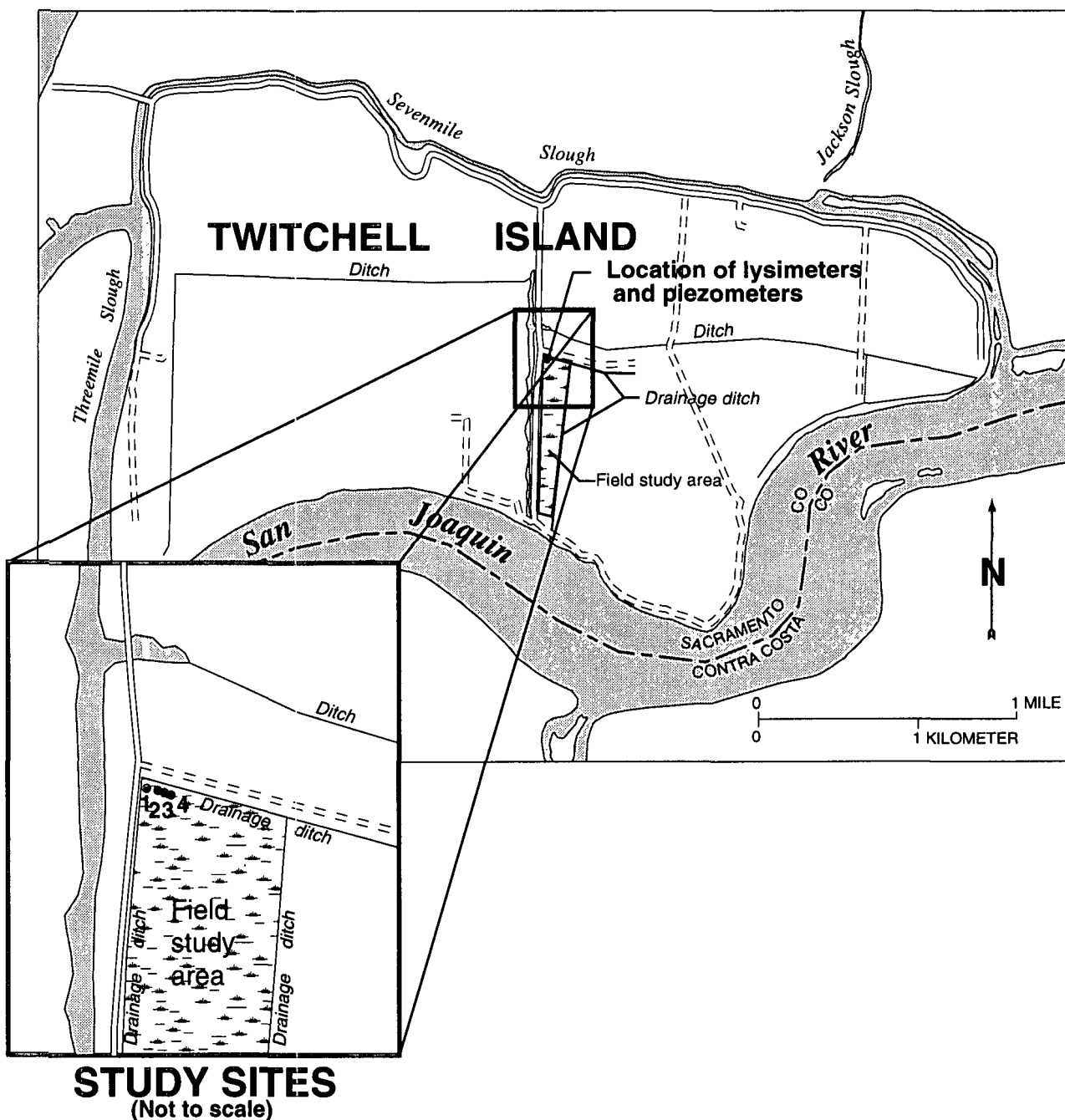


Figure 2. Location of the lysimeters and piezometers in the agricultural field study site, Twitchell Island, California.

near-surface soils form an oxidized, well-decomposed, organic soil layer. Below the water table, deeper than about 4 ft below land surface, is a reduced, fibrous peat soil layer that is much less decomposed. The chemical characteristics of the different organic compounds released to the aqueous phase under these different redox conditions are discussed in detail in the

Composition and Reactivity of Dissolved Organic Carbon section of this report.

Organic matter derived from different sources (for example, historically accumulated peat and recent agricultural inputs) and affected by different processes (for example, decomposition under varying redox conditions) has distinctive chemical characteristics

associated with those materials and processes. The DOC released from SOM is a complex, heterogeneous mixture of a multitude of organic compounds whose chemical characteristics and reactivity are the result of all of the factors (organic matter sources, land-use practices, hydrology, and so forth) and biogeochemical processes (microbial decomposition, redox reactions, sorption to solids, and so forth) affecting DOC within the system (Aiken and Cotsaris, 1995). Throughout the Delta, these factors and processes vary spatially, and the DOC produced varies in composition and reactivity. Thus, not all DOC in drainage water is the same, and not all organic compounds react in the same way or to the same degree. This underlying premise must be considered when assessing the origin of THM precursors in the Delta.

The primary focus of this study was to evaluate the concentration and composition of DOC released from the soil and in drainage water from one agricultural field on Twitchell Island in the Delta (fig. 2) and to relate the DOC composition to its propensity to form THMs.

The purpose of this report is to transfer information and understanding of the results of the DOC/THM drainage-water study to the cooperator and other water-resource managers. The report focuses on data and interpretation of the more salient aspects of the DOC/THM drainage-water study, and many of the details regarding methods and additional data are in the appendices. Appendix A reports sample collection methods and the analytical results from the DWR Bryte Laboratory. The DOC, ultraviolet absorbance (UVA) at 254 nanometers (nm), specific UVA (SUVA or UVA/DOC), and analytical methods for samples analyzed by the U.S. Geological Survey (USGS) are presented in appendix B. Appendix C describes the methods and results of the DOC fractionation and isolation techniques using XAD resins. The methods and data for THM formation potential of selected whole-water samples and DOC isolates (fractionated using XAD resins) analyzed by the USGS are presented in appendix D. Appendix E presents methods and results of liquid-state carbon-13 nuclear magnetic resonance (^{13}C -NMR) analyses of selected XAD fractionation isolates, solid-state ^{13}C -NMR analyses of selected DOC isolates, and preliminary analysis of two soil samples by solid-state ^{13}C -NMR. Appendix F presents DOC, SUVA, and other water-quality data for three wetland-habitat test ponds.

This study was done by the USGS in cooperation with the California Department of Water Resources

(DWR) Municipal Water Quality Investigation Program and is part of the USGS National Drinking Water Initiative.

DESCRIPTION OF STUDY SITE AND STUDY DESIGN

One agricultural field on Twitchell Island in the west-central Delta (fig. 2) was chosen for the study. Corn was grown in the field during 1996 as well as during the previous several years. Corn is one of the predominant crops grown in the Delta, and the field was chosen to represent a typical land-use practice in the Delta. Soil at the site is classified as a Rindge muck, with oxidized, well-decomposed peat dominating from the surface to about 2 ft below land surface, and reduced, fibrous peat dominating below about 3.5 to 4 ft. Soils at the site contain high concentrations of SOM. Concentrations of soil organic carbon (soil organic matter is approximately equivalent to twice the soil organic carbon concentrations) at sites where lysimeter and piezometer samplers were installed (described in the following paragraph) ranged from 18.3 to 27.7 percent carbon for near-surface soils (0.5 to 1.5 ft below land surface), from 25.2 to 36.9 percent carbon for soils from 4.5 to 6.0 ft below land surface, and from 24.3 to 38.6 percent carbon from 6.0 to 7.0 ft below land surface. In November 1995, after the irrigation season and before the winter rains, the water table was about 3.0 to 3.5 ft below land surface.

Three pairs of stainless steel lysimeters and piezometers were installed at the northwestern end of the field (fig. 2), spaced about 40 to 80 ft apart. The lysimeters were installed from 0.5 to 1.5 ft below land surface to sample soil water influenced by the oxidized, well-decomposed peat soil layer (upper soil zone, USZ) (fig. 3). The piezometers were installed from 4.5 to 6.5 ft below land surface to sample ground water associated with the reduced, fibrous peat soil layer (lower soil zone, LSZ). Placement of the lysimeters and piezometers was designed to sample DOC released from soils influenced mainly by aerobic and anaerobic soil microbial decomposition processes, respectively. The samplers were installed parallel to and about 50 ft south of the ditch that drains the field, and their placement was intended to capture water draining from the field to the ditch.

Four pairs of lysimeters and piezometers were initially installed in the field. During installation of the lysimeter and piezometer at site 3, water was filling the

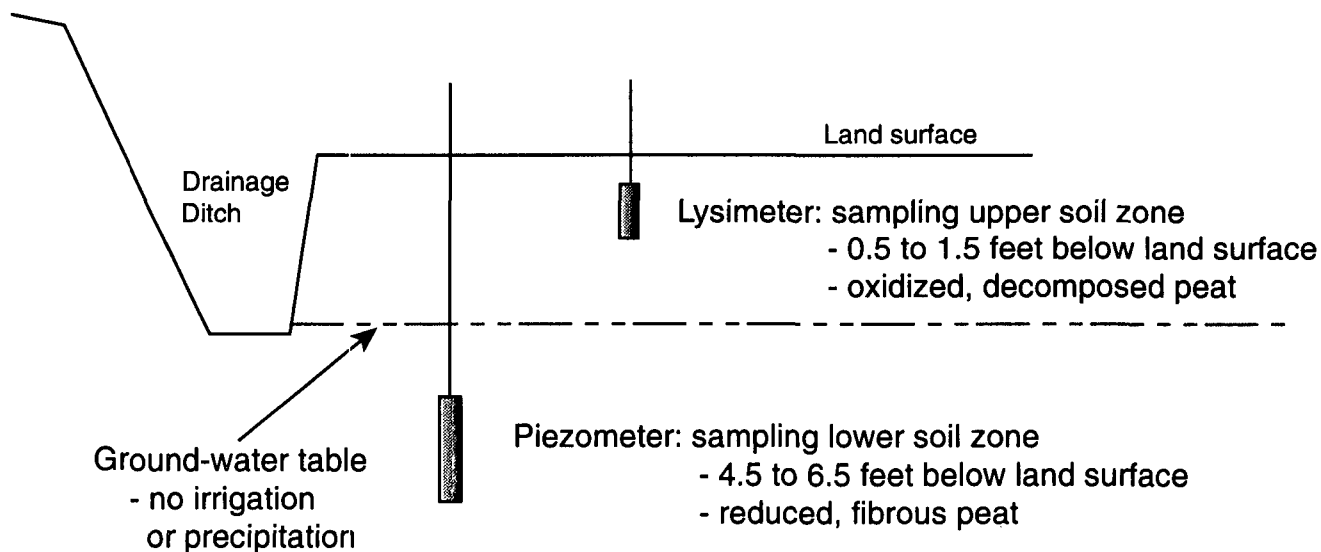


Figure 3. Typical installation of lysimeter and piezometer pairs for sampling soil water from the upper and lower soil zones, Twitchell Island, California.

borehole from an opening about 2 ft below land surface. It appeared that this represented a direct connection from the ditch draining the field to the borehole, either a channel in the peat or a rodent hole. Water-quality results from Lysimeter 3 and Piezometer 3 supported this observation. The results indicated that the quality (DOC and specific conductance) of water sampled at this site was considerably different from the other three sites and was similar to the quality of water in the drainage ditch. It was concluded that soil water sampled at site 3 was being significantly influenced by water originating from the drainage ditch and did not represent water that was influenced mainly by surrounding peat. Therefore, sampling from this site was discontinued and results for Lysimeter 3 and Piezometer 3 are not included in this report.

Lack of available water in the unsaturated zone for much of the year greatly hindered using the lysimeters to sample soil water in the USZ. Although lysimeters are designed to sample unsaturated soil, obtaining sufficient water for all the analyses was difficult, except when the field was intentionally flooded in February 1996. Even during the period when the field was irrigated, sample volumes obtained from the lysimeters were small, which limited the types of analyses done. In contrast, piezometers, which were installed below the water table, supplied ample water for analyses.

Hydrologic Framework for Study Design

A simplified conceptual hydrologic model (fig. 4) provides the framework for interpreting the DOC data for the agricultural field. The study began after the field was intentionally flooded (fig. 4a) in February 1996. The ditch draining the field was plugged, and water from the ditch overflowed into the field, flooding the field to about 3 ft above land surface in the area where the lysimeters and piezometers were located. The drainage ditch supplies water to the field for winter flooding and receives drainage from the field and from fields to the east. Because of the multiple roles of the ditch, the water flooding the field was from a combination of sources: irrigation water siphoned from the San Joaquin River, precipitation accumulating in the ditch and falling directly on the field, and water originating from fields to the east that contribute water to the ditch.

Prior to flooding, precipitation during late December 1995 and early January 1996 began saturating the soils and leaching accumulated salts and DOC toward the water table and laterally toward the drainage ditch. When intentional flooding began (fig. 4a), most water probably moved downward, saturating the soil and releasing carbon from the soil, thereby increasing interstitial DOC concentrations in the USZ and LSZ with time.

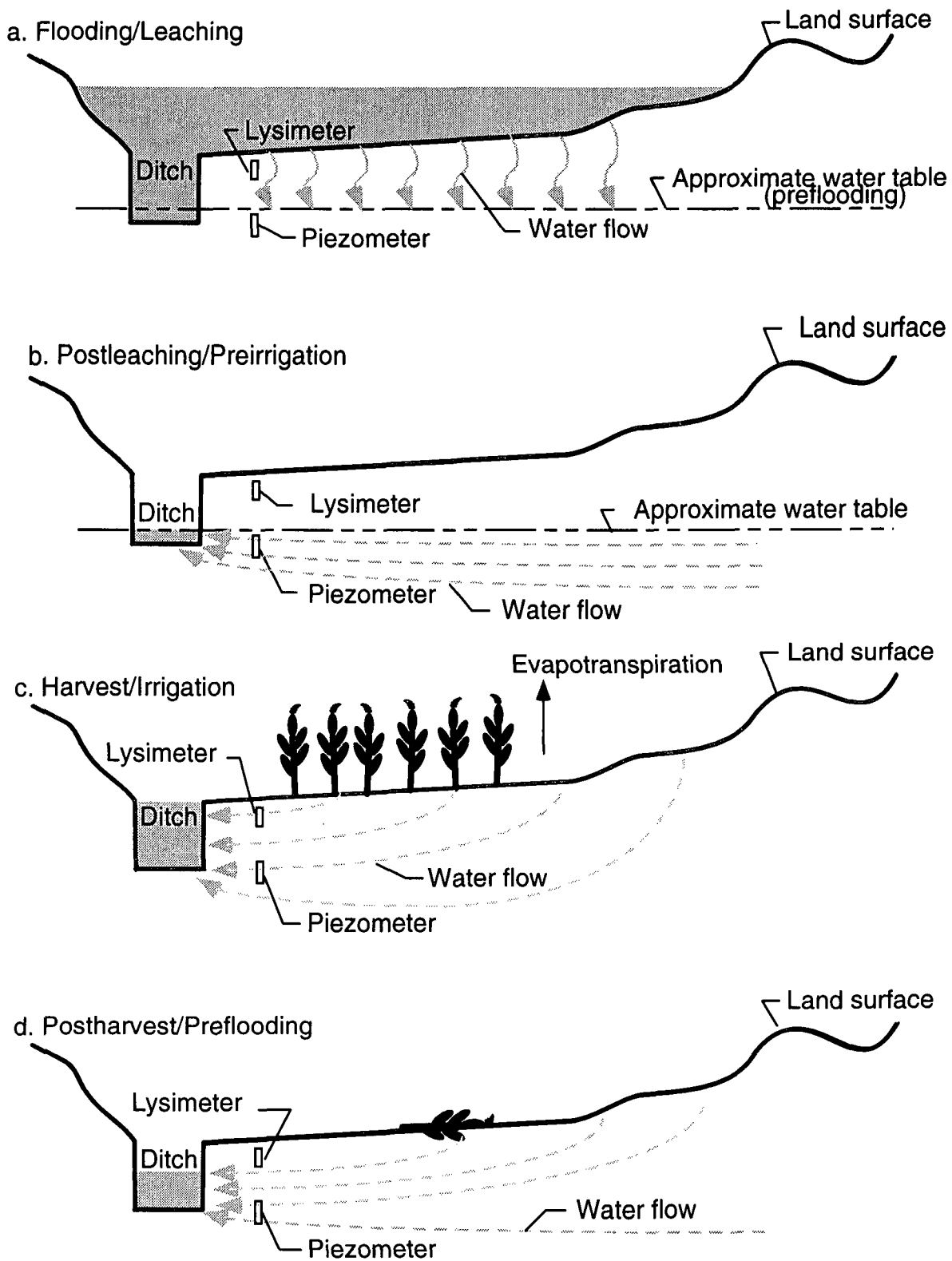


Figure 4. Simplified conceptual hydrologic model of the field studied, Twitchell Island, California.

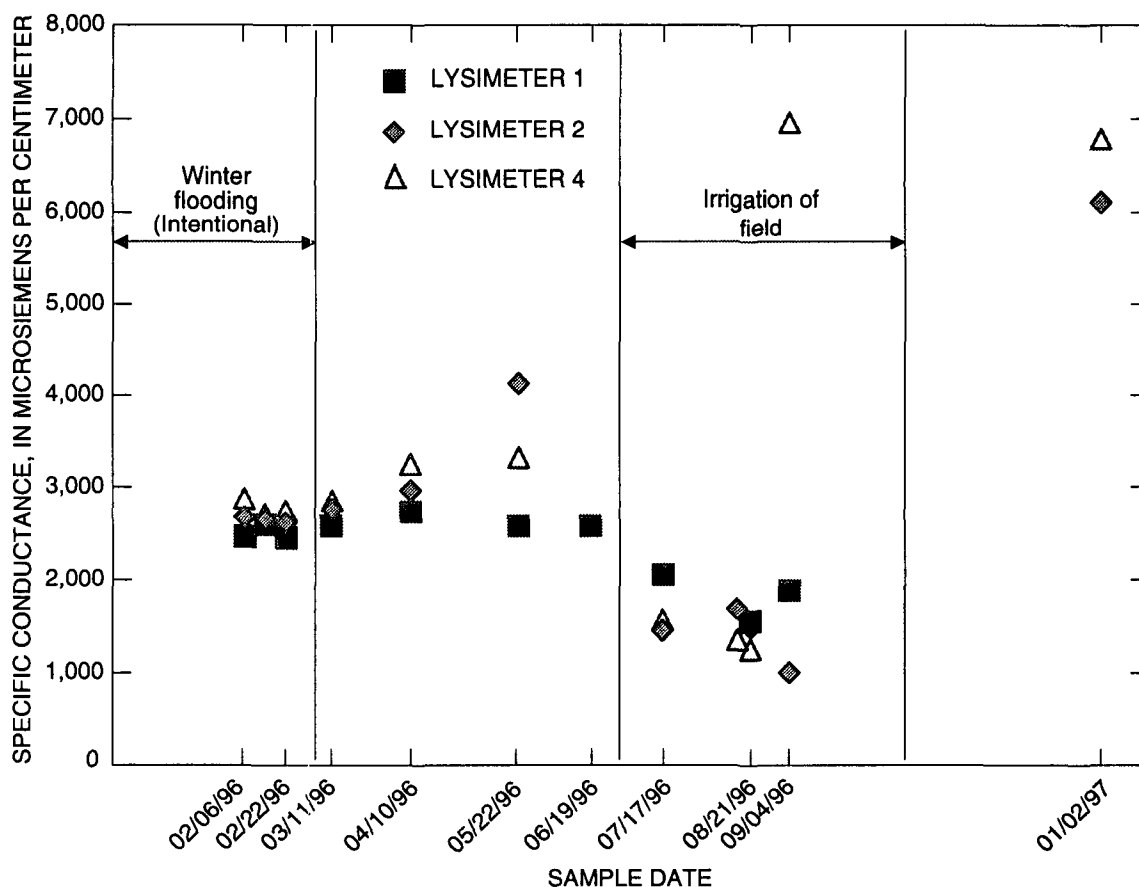


Figure 5. Specific conductance of lysimeter samples, December 1995–January 1997, Twitchell Island, California.

The field was drained in March after 1 month of flooding. During this period, water transported DOC from the field to the ditch (fig. 4b). Following draining, the field was plowed and corn was planted in June. The crop was first irrigated in mid-July, after which irrigation water was applied at various intervals until September 5. After the field was drained and during the cropping/irrigation period (fig. 4c), the near-surface soil went through periods of wetting and drying, resulting in considerable variations in soil moisture. Under conditions of variable soil moisture and relatively high temperatures, it was assumed that microbial activity varied, and reached periods of maximum activity in surface and near-surface soils, which most likely released large amounts of available carbon.

Corn was harvested in mid-October and the field was left fallow (fig. 4d). In the near-surface soils, microbial activity continued to release available carbon from the peat soil, and evaporation increased the levels of soil salinity during this period. Small amounts of precipitation occurred in early December 1996 and

large amounts occurred at the end of December and in early January 1997, which caused flooding throughout northern California and the Delta. Final sampling of the field took place in early January. Near-surface soil salinity was high at this time, with specific conductance values as high as 6,780 microsiemens per centimeter ($\mu\text{S}/\text{cm}$) (fig. 5), reflecting dissolution of accumulated salts.

Sampling and Analytical Approach

Lysimeters, piezometers, and the ditch draining the field were sampled monthly to assess the DOC released from the two soil zones and the drainage from the field. In addition, samples were collected weekly during the intentional flooding period, from the beginning of February to the beginning of March. Samples were analyzed for DOC and UVA by the USGS using the methods described in appendix B. Specific conductance and pH of water samples were measured in the

field. Samples for which enough water was available also were analyzed for DOC, UVA, Br, trihalomethane formation potential (THMFP), major cations [calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K)], and major anions [chloride (Cl) and sulfate (SO₄)] by the DWR Bryte Laboratory (California Department of Water Resources, 1994b).

In August, additional analyses were added to better assess redox conditions and THMFP. Flow-through chamber measurements of dissolved oxygen (DO), pH, and platinum-electrode redox potential (Pt-electrode Eh) were made on the piezometer samples. Ground water was pumped through the airtight, flow-through chamber (fitted with DO, Pt-electrode, and pH probes) from the bottom to exclude any air, thus permitting measurement of these parameters while minimizing the influence of atmospheric gases.

For seven of the samplings, additional water samples were collected to characterize the DOC in more detail (DOC fractionation and analysis of isolated fractions). These samplings included the beginning and end of the intentional flooding period (February 6 and March 11, 1996), after flooding but before irrigation (June 19, 1996), at the beginning and in the middle of the irrigation period (July 17 and August 4, 1996), before the winter rains (November 13, 1996), and during winter rains but before flooding (January 2, 1997). We hypothesized that these periods would provide critical information regarding DOC quality for periods when drainage water production and DOC loads would be greatest and when microbial generation of available carbon in soils would be important.

During previous studies in the Delta, DOC, UVA, and THMFP were measured in an attempt to develop relations to predict or estimate THMFP. SUVA (UVA/DOC) is a spectroscopic measurement that estimates the molecular, aromatic structure of the bulk DOC, normalized to carbon, in a water sample; the aromatic part of DOC is believed to contain the major precursors of THMs (Rook, 1976, 1977; Reckow and others, 1990). However, simple linear correlations among DOC, SUVA, and THMFP (on a molar basis) for drainage and channel waters from throughout the Delta have not resulted in useful predictive relations, even though some correlations were significant for specific regions or units in the Delta (California Department of Water Resources, 1994a). These results indicate that the nature and character of the DOC resulting from drainage in different parts of the Delta vary, influenced by differing conditions throughout the

Delta. Sources of carbon (peat vs. recent vegetation) and the relative amounts of organic and mineral soils present in the different regions are important factors that cause the differences in DOC quality and quantity. These factors contribute to the lack of correlation on a regional scale among DOC, SUVA, and THMFP in drainage and channel waters.

The general approach in this study was to examine the chemical variability of the DOC released from the two soil zones and in the drainage ditch over the course of a year for one agricultural field and to relate the chemical character of the DOC to its propensity to form THMs. This approach should help discern the effects of redox conditions and land- and water-management practices on DOC quantity, quality, and reactivity with respect to the formation of THMs. In addition to measuring DOC, UVA, and THMFP of the whole-water samples, DOC for seven selected samples (described previously) were fractionated and isolated using XAD-8 and XAD-4 resins. Amberlite XAD resins are nonionic macroporous copolymers with large surface areas that have been used by many investigators to sorb organic acids such as humic substances (Aiken, 1985). This method divides the DOC into operationally defined organic acid fractions extracted by XAD-8 and XAD-4 resins (fig. 6) (Aiken and others, 1992) and provides valuable information about the types of organic constituents present in the bulk sample.

The part of the DOC extracted by the XAD-8 resin and eluted with base [0.1 molar (*M*) sodium hydroxide (NaOH)] represents the hydrophobic acid (HPOA) fraction that can contain aliphatic carboxylic acids of five to nine carbons, one- and two-ring aromatic carboxylic acids, one- and two-ring phenols, and other humic substances (Aiken and others, 1992). This fraction contains humic and fulvic acids that contain the more aromatic compounds and are considered the primary reactive component of DOC contributing to the formation of THMs and other disinfection byproducts (DBPs) (Amy and others, 1990; Reckow and others, 1990; Owen and others, 1993). The part of DOC extracted by the XAD-4 resin and eluted with base (0.1 *M* NaOH) represents the hydrophilic acid (HPIA) fraction that contains polyfunctional organic acids and aliphatic acids with five or fewer carbon atoms (Aiken and others, 1992). This fraction contains fewer aromatic compounds; therefore, it should contain relatively fewer THM and DBP precursors compared to the HPOA fraction.

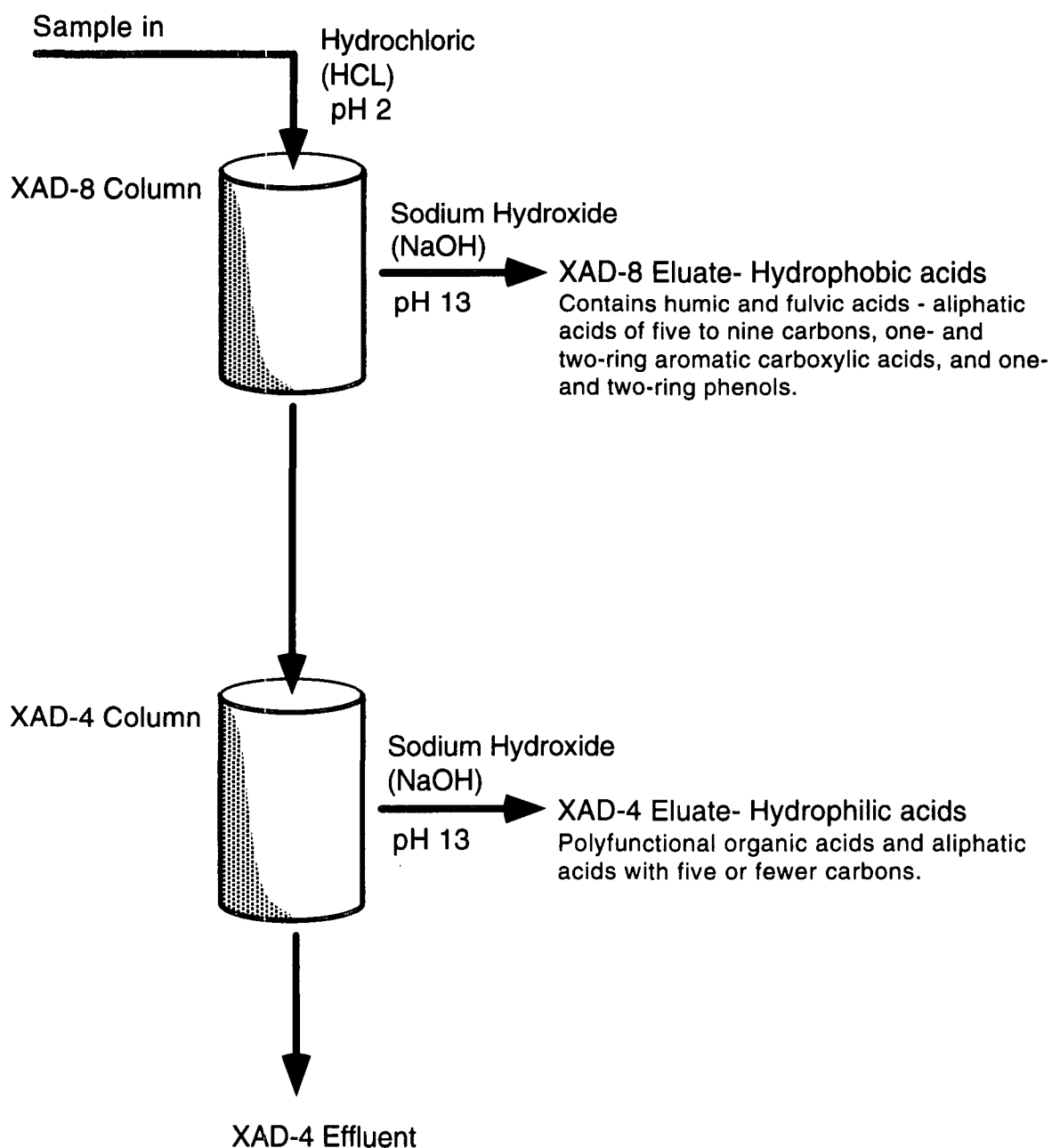


Figure 6. XAD isolation procedure, Twitchell Island, California.

The DOC was further characterized by examining selected isolates in more detail. The SUVA of HPOA and HPIA isolates provided an initial evaluation of their aromaticity. The THMFPs of the isolates provided a direct assessment of the relative contributions of the HPOA and HPIA fractions to the whole-water THMFP. Liquid- and solid-state ^{13}C -NMR analyses provided a quantitative and qualitative assessment of

structural and functional group composition of the isolates, and this information--in particular the aromatic carbon content--was used to further assess (on a relative basis) the probable THM precursors contained in each fraction.

Statistical comparisons of differences between lysimeter and piezometer DOC, SUVA, THMFP, specific trihalomethane formation potential (STHMFP),

and HPOA and HPIA related parameters used the non-parametric Mann-Whitney test for population medians (Helsel and Hirsch, 1992).

DISSOLVED ORGANIC CARBON CONCENTRATION

Interpretation of the DOC data is in the context of the simplified, conceptual, hydrologic model discussed previously and depicted in figure 4. These interpretations are conceptual and somewhat speculative because of the lack of hydrologic information necessary to determine water flow and transport of DOC within this hydrologic system.

Upper Soil Zone

The lysimeters sampled interstitial water from the USZ (0.5 to 1.5 ft below land surface), where the peat soil is usually oxidized, well decomposed, and usually unsaturated with respect to soil moisture

(except during winter precipitation and flooding and summer irrigation). Distribution of DOC concentrations for the lysimeter samples from February 2, 1996, through January 2, 1997, are plotted in figure 7. For samples collected while the field was intentionally flooded (February 6, 14, and 22), DOC concentrations consistently increased, with median DOC concentrations increasing from 51.9 to 61.0 mg/L. These slight increases reflect the release of available carbon from the soil to the aqueous phase under flooded conditions.

After the field was drained (March 1), lysimeter DOC concentrations increased during March, April, and May, with the median DOC concentration for replicate samples reaching 73.9 mg/L in May (fig. 7). During this period (post-leaching/pre-irrigation) (fig. 4b), the soils became drier and temperatures increased, creating conditions conducive to increased microbial activity and the release of DOC. Results of previous studies of gaseous CO₂ fluxes from peat soils (indicative of microbial activity) on Twitchell Island indicate that fluxes increased with increasing temperature, and the highest fluxes occurred at soil moisture content

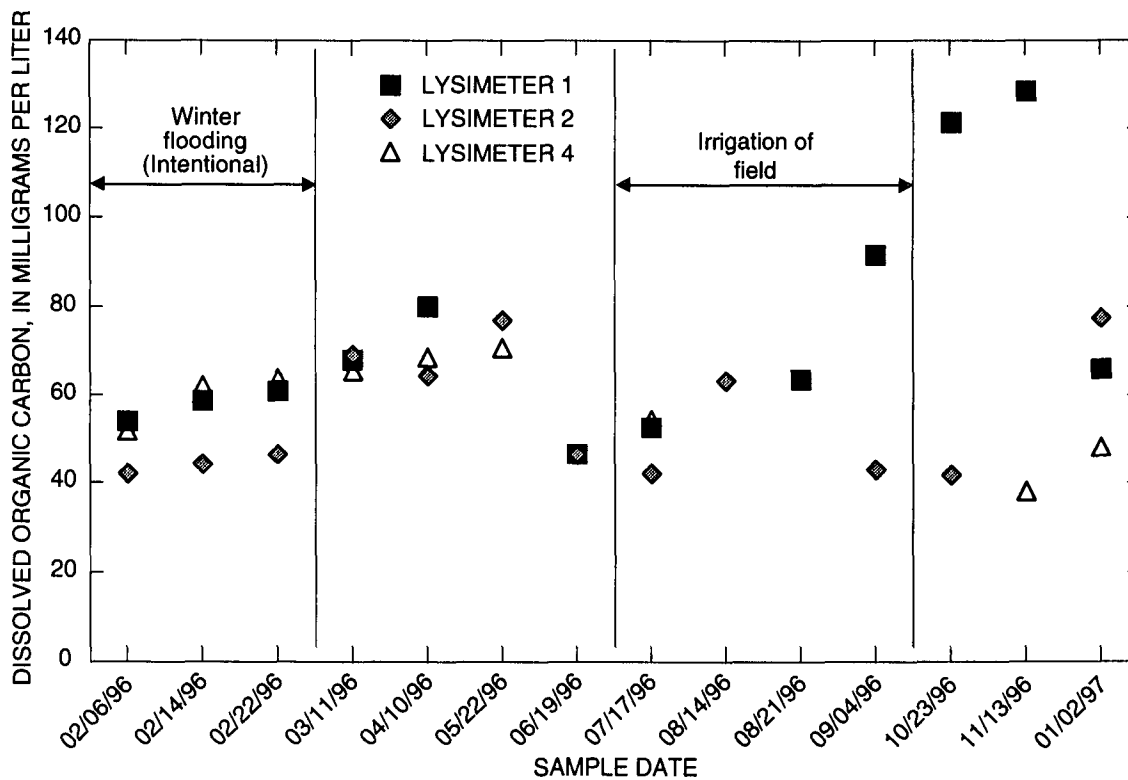


Figure 7. Dissolved organic carbon concentrations for lysimeter samples, February 1996–January 1997, Twitchell Island, California.

ranging from about 20 to 30 percent on a volume basis (Deverel and others, 1998). A decrease in soil moisture in June may have resulted in near-surface conditions dry enough (<20 percent by volume) to decrease microbial activity, thereby decreasing available DOC in the USZ.

The first irrigation of the field began on July 13. This field was irrigated using "spud ditches," a common method for irrigation in the Delta. Spud ditches are temporary ditches that are trenched approximately 1-ft wide and 2- to 3-ft deep and run parallel to the length of the field and perpendicular to the ditch draining the field. Water was siphoned from the San Joaquin River into the ditches that convey irrigation water to the southern end of the field where the spud ditches were filled. Water in the spud ditches took about 3 days to reach the drainage ditch at the north end of the field, during which time water flowed laterally from the spud ditches and increased the moisture content of the near-surface soil. The DOC concentrations in the USZ for the July 17 sampling (median DOC of 52.7 mg/L) increased slightly compared to the June sampling (median DOC of 46.4 mg/L) (fig. 7), probably reflecting the initial wetting of the soil and the release of DOC.

Between July 13, when irrigation of the field began, and September 5, when irrigation for the season ended, there were four irrigation periods that resulted in varying degrees of water saturation of the near-surface soils. Decreases in specific conductance of the lysimeter samples during the irrigation period reflect the dilution of soil salinity by the applied irrigation water (fig. 5). The variable moisture content of the near-surface soils caused difficulties in obtaining samples from lysimeters, resulting in the collection of DOC samples from only one lysimeter during both the August 14 and August 21 samplings (fig. 7).

Spatial variability in soil moisture and soil organic matter seems to have contributed to large differences in DOC concentrations between lysimeter samples on each of the samplings in September, October, and November (fig. 7). For each of these sampling dates, only two lysimeters produced enough water for DOC measurements, and the differences between the lysimeter DOC concentrations were large. Lysimeter 1 DOC concentrations increased during this period from 91.7 to a maximum of 128 mg/L, the highest concentration of DOC detected during this study. In contrast, lysimeter 2 yielded DOC concentrations of 42.9 and 41.7 mg/L for the September and October samplings,

and lysimeter 4 had a concentration of only 38.1 mg/L in November. These large differences most likely reflect the variability in soil moisture between sites while the field was drying (irrigation was terminated on September 5). Lysimeter 1 is located at the lowest point in the field (the northwest corner), and almost always had the wettest soil conditions. These relatively wet conditions during this period undoubtedly created soil-moisture conditions that favored increased microbial activity and contributed to the much higher DOC concentrations observed for lysimeter 1.

Considerable amounts of precipitation fell during the month of December 1996 and the beginning of January 1997 resulting in flooding throughout the Delta and northern California. Concentrations of DOC in the lysimeter samples (January 2, 1997; fig. 7) were much less variable, most likely reflecting the mixing of near-surface soil water and the torrential rains that occurred just prior to and during the sampling.

Lower Soil Zone

The piezometers allowed sampling of ground water from the LSZ (4.5 to 6.5 ft below land surface) where the peat soil usually is reduced and fibrous (less decomposed). Analysis of redox parameters did not begin until August 1996 during the irrigation period. Available DO data for piezometers indicate low concentrations of DO; the highest concentration was 0.38 mg/L (fig. 8). These low DO concentrations generally indicate anaerobic, reduced conditions. Actual ground-water DO concentrations probably were lower because small amounts of oxygen contamination, caused by oxygen diffusion through tubing and around probe fittings, can affect readings at these low DO levels. Redox potential data also indicate anoxic conditions, with Eh values ranging from about 88 to 310 millivolts (mV) (fig. 9). Although many factors complicate the accuracy of Pt-electrode Eh measurements (for example, relative rates of electron transfer reactions at the electrode surface), the range of these measurements is far below the value (800 mV at pH 7) where depletion of oxygen (O₂) in soils is expected (Bohn and others, 1985). Thus, both DO and redox potential data clearly indicate that the LSZ contained anaerobic and relatively reduced ground water.

Although median DOC concentrations were similar for many piezometer samples (fig. 10) and lysimeter samples (fig. 7) for the same sampling dates, the nonparametric Mann-Whitney test for population

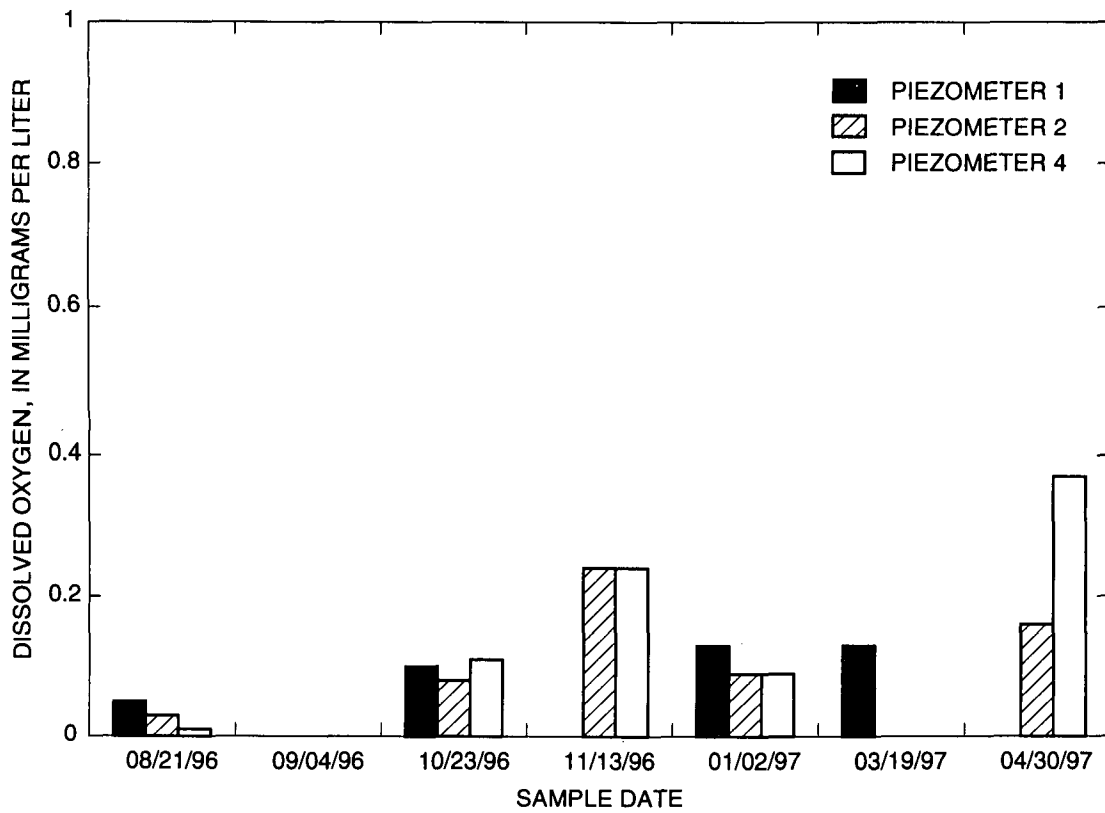


Figure 8. Dissolved oxygen concentrations for piezometer samples, August 1996–April 1997, Twitchell Island, California.

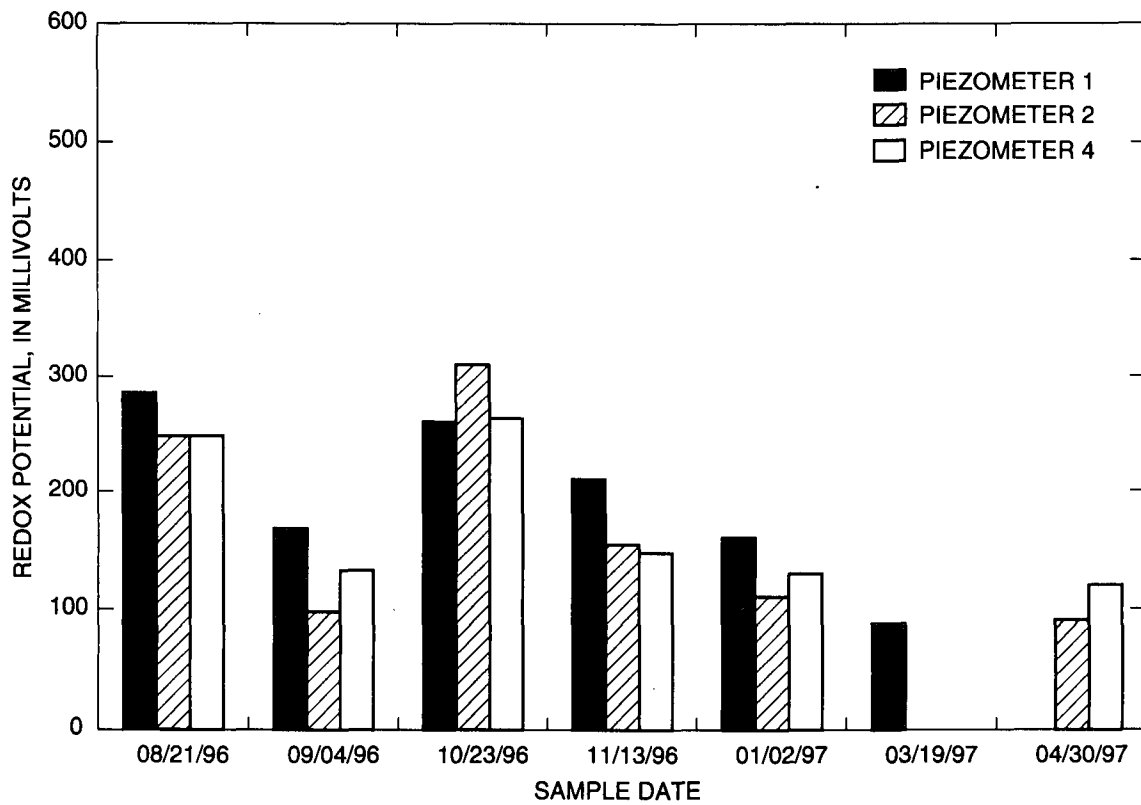


Figure 9. Redox potential measurements for piezometer samples, August 1996–April 1997, Twitchell Island, California.

medians (Helsel and Hirsch, 1992) indicated that median DOC concentrations in the LSZ (piezometer samples) (fig. 10) were significantly higher ($\alpha=0.05$) than those in the USZ (lysimeter samples) (fig. 7). These differences are apparent for periods when the field was intentionally flooded (February) until the field was irrigated (July) and for the winter sampling in January 1997 (figs. 7 and 10). The piezometers were installed to sample mainly ground water, but the ground-water table fluctuated, and the water quality varied in response to water management and flow in the field. Concentrations of DOC in samples from the piezometer during the intentional flooding period indicated a slight increase for piezometer samples from February 6-14 (fig. 10). After the field was drained (March 1), median DOC concentrations in the LSZ increased for the March, April, and May samplings to a high of 82.0 mg/L in May (fig. 10). During this period, the soils above the water table were becoming less saturated, and microbial decomposition of SOM may have contributed additional carbon to the ground water.

After irrigation began (July 13), DOC concentrations in piezometer samples reached their lowest median concentration of 49.3 mg/L on July 17 (fig. 10). Subsurface irrigation through spud ditches apparently allowed water low in DOC (2 mg/L) to rapidly migrate downward through the highly permeable peat soils (J.L. Meyer and A.B. Carlton, University of California, written commun., 1975; Delta organic soil salinity and nutrient status study: Report of laboratory analyses, progress report by the University of California Agricultural Extension to the California Department of Water Resources) and to dilute the ambient ground-water DOC concentrations. The effect of dilution on specific conductance also is apparent in the piezometer samples taken during and after the irrigation period (fig. 11).

For the remainder of the irrigation season (irrigation ceased on September 5) and through the October sampling, DOC concentrations in piezometer samples were variable (fig. 10), reflecting a combination of irrigation-influenced processes. In most cases, median DOC concentrations in lysimeter samples exceeded median DOC concentrations in piezometer samples. In

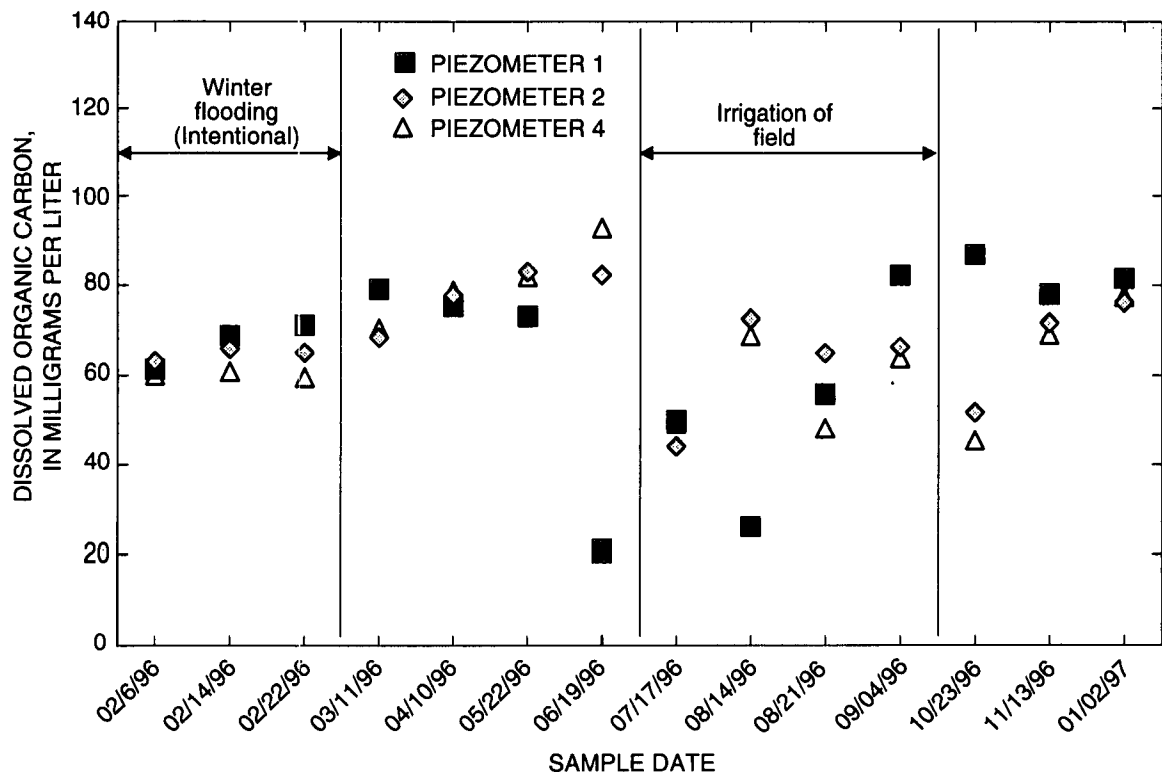


Figure 10. Dissolved organic carbon concentrations for piezometer samples, February 1996–January 1997, Twitchell Island, California.

the short term, application of irrigation water with low DOC concentrations tends to decrease DOC in the soil zone, thus influencing the piezometer samples, as discussed previously. During the longer term irrigation period, irrigation cycles cause wetting and drying of soils above the water table thus creating variable conditions for microbial decomposition of SOM and the release and transport of available carbon. These complex hydrologic and microbially related processes both act to produce the high variability in DOC concentrations observed during this period.

In contrast, piezometer samples collected during November and January were much less variable (fig. 10). This decreased variability in DOC following the irrigation season probably reflects the lack of irrigation-induced alternating wetting and drying cycles and the associated effect on DOC concentrations.

Water flux and DOC transport data would have aided interpretation of DOC concentration trends in the USZ and LSZ and allowed estimates of DOC loading

to the drainage ditch. This, however, was beyond the scope of this investigation.

Drainage Ditch

Concentrations of DOC in all samples from the drainage ditch ranged from 9.8 to 54.9 mg/L (fig. 12) and were always lower than the median concentrations for either the lysimeter or the piezometer samples (figs. 7 and 10). These results reflect the various sources of water to the ditch: drainage from the study field, drainage from fields east of the study site, water siphoned from the San Joaquin River, precipitation, and water from the main drainage canal on the island that can back up when pumping from the island is shut down. This combination of sources to the ditch complicate the interpretation of the origin of DOC concentrations in the ditch and make it extremely difficult to estimate the contributions of DOC from the two soil zones.

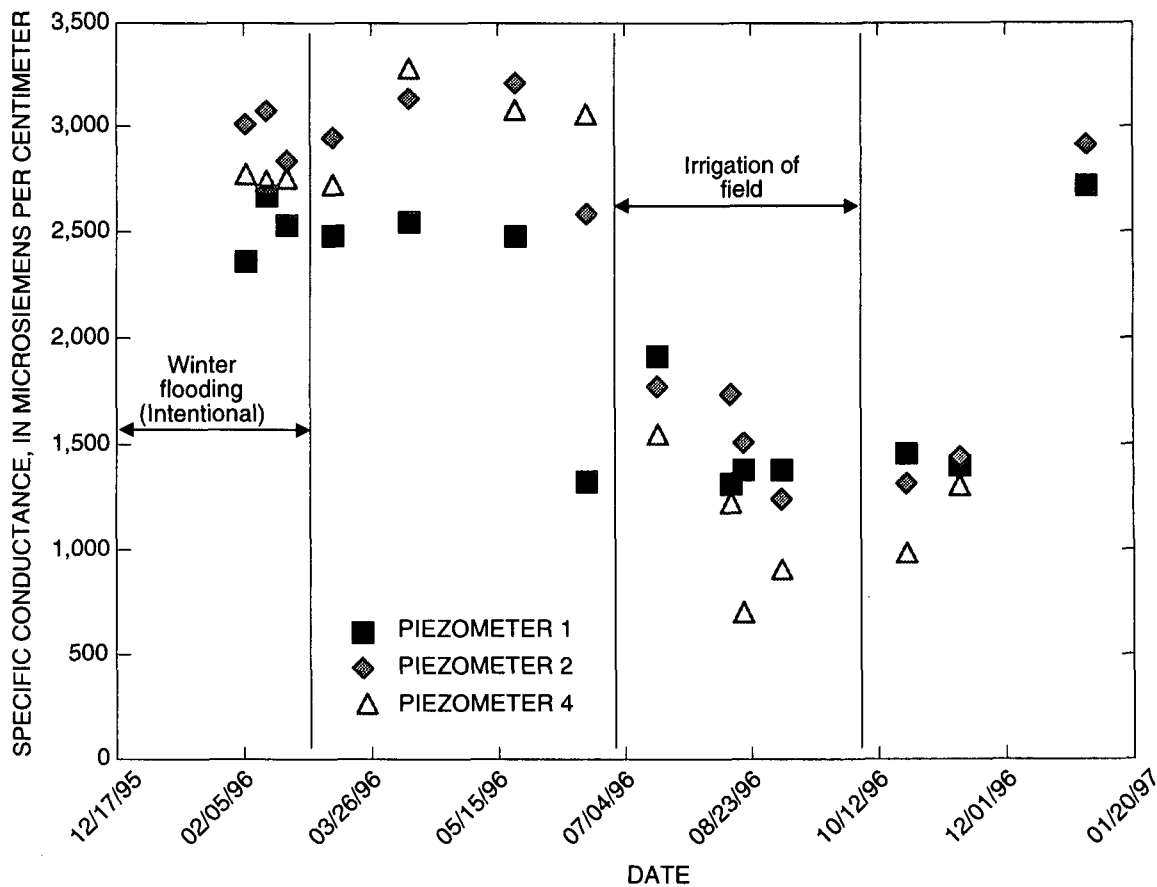


Figure 11. Specific conductance of piezometer samples, December 1995–January 1997, Twitchell Island, California.

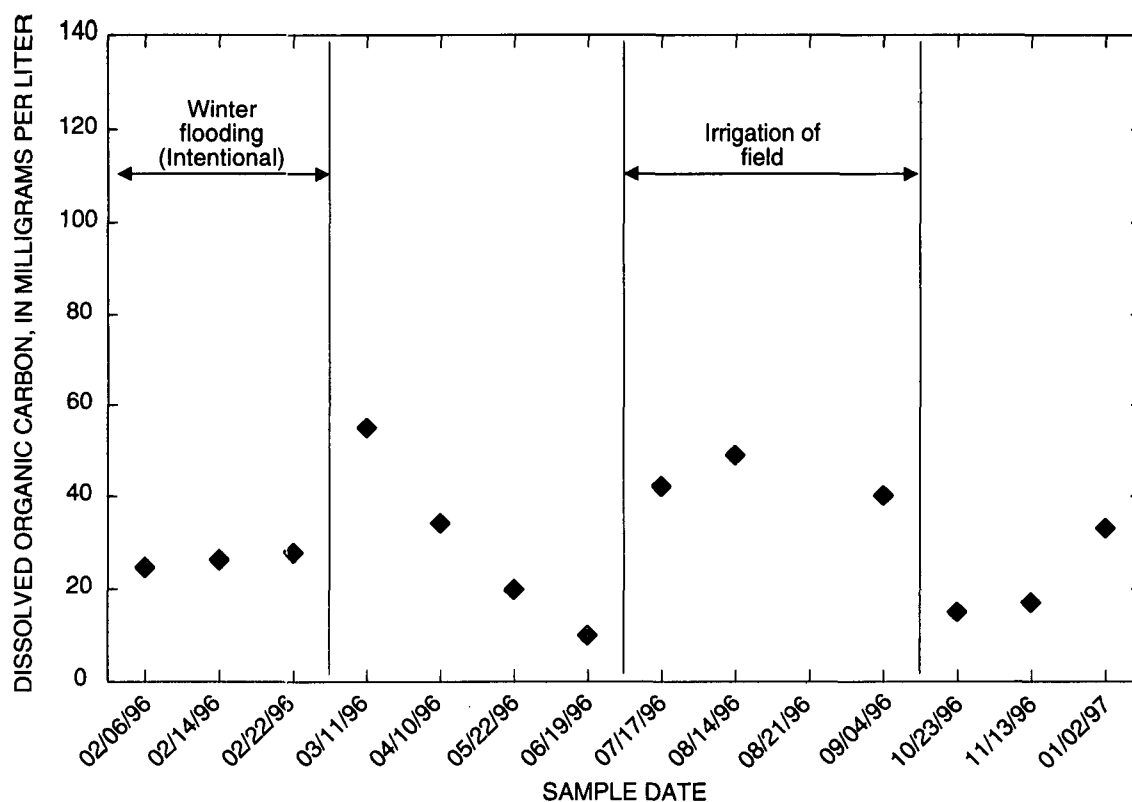


Figure 12. Dissolved organic carbon concentrations in samples from the drainage ditch, February 1996–January 1997, Twitchell Island, California.

COMPOSITION AND REACTIVITY OF DISSOLVED ORGANIC CARBON

The previous section discussed the release of DOC from the two soil zones in the context of the land- and water-management practices for one agricultural field. In addition to the concentrations of DOC produced, one of the major goals of this study was to assess the quality of the DOC, especially in relation to potential formation of THMs. The quality of DOC is examined in a tiered, analytical approach that provides increasing amounts of compositional information at each level. SUVA (UVA/DOC) provides information about the molecular aromatic structure of the bulk DOC in a water sample and is the first parameter used to assess DOC quality. The fractionation of bulk DOC into HPOA and HPIA using XAD-8 and XAD-4 resins, respectively, fractionates the bulk DOC into two categories of organic compounds based on their solubility (Aiken and others, 1992). In general, the HPOA fraction contains the humic substances (humic and fulvic acids) and is more aromatic than the HPIA fraction, which is more aliphatic. Selected samples of each of

the isolated fractions were analyzed for SUVA as an indicator of the aromaticity of the fraction. Selected isolates of each fraction also were analyzed by ^{13}C -NMR spectroscopy, providing valuable structural and functional group information that, when taken as a whole, can help establish the nature and source of the organic isolates.

The propensity for DOC to form THMs, as measured by the THMFP of the samples, is examined for whole-water samples in relation to the UVA (aromaticity) of the bulk DOC. The THMFPs of selected DOC isolates are compared to isolate properties, as determined by SUVA and ^{13}C -NMR, to assess reactivity of HPOA and HPIA fractions in relation to their composition and source and to factors affecting DOC production under the conditions studied.

Specific Ultraviolet Absorbance

Median SUVA values were significantly lower ($\alpha=0.05$) for the lysimeter samples (fig. 13a) compared to the piezometer samples (fig. 13b), indicating that

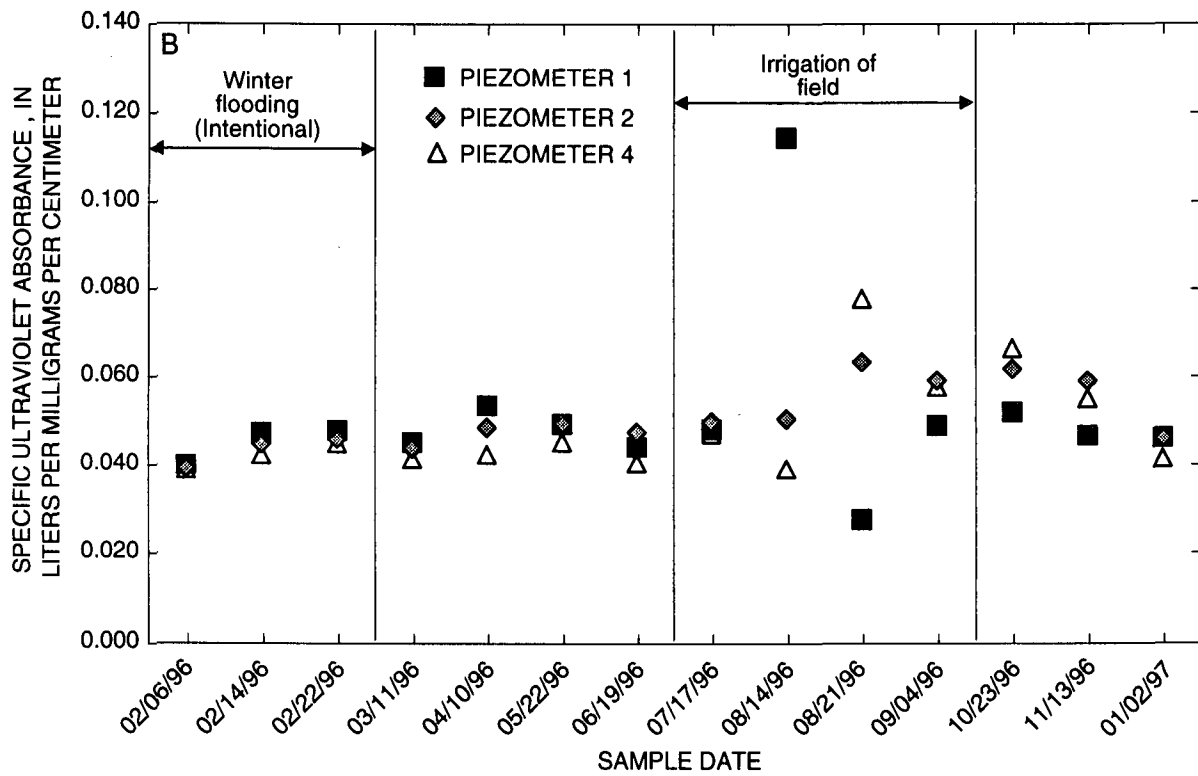
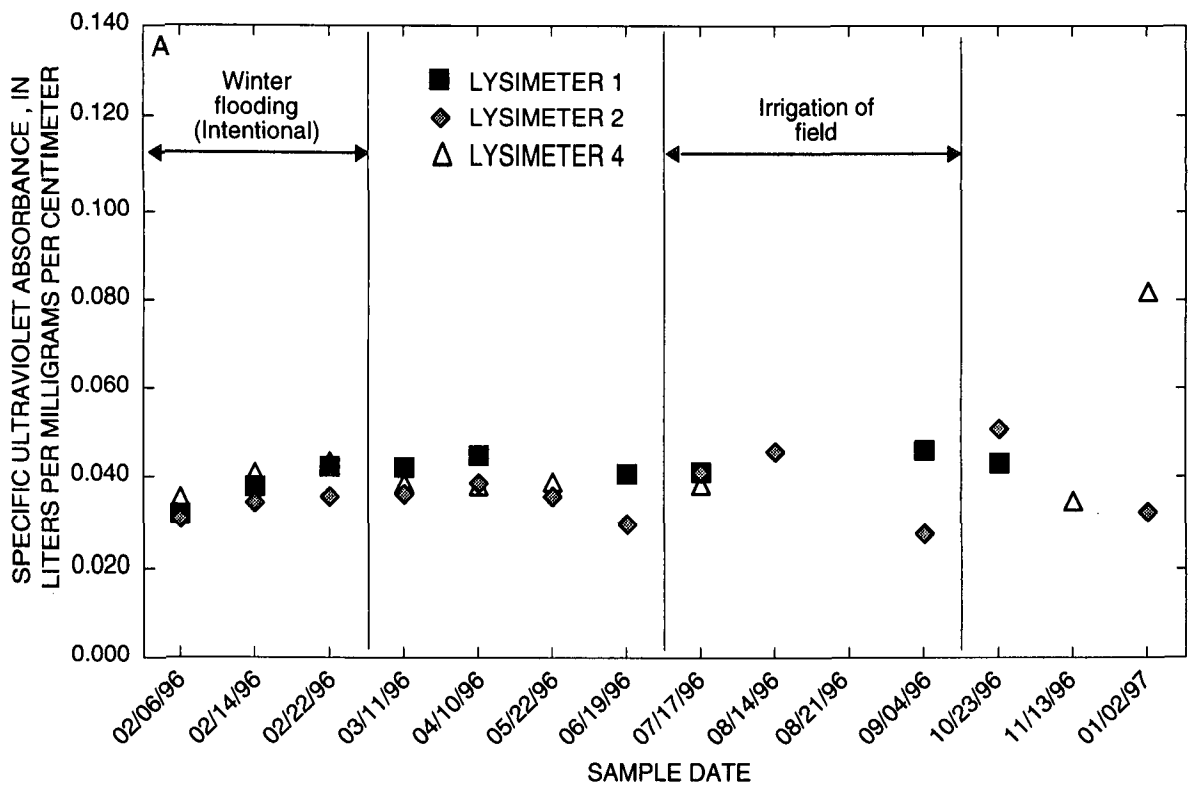


Figure 13. Specific ultraviolet absorbance for (A) lysimeter samples, (B) piezometer samples, (C) drainage ditch samples, February 1996–January 1997, Twitchell Island, California.

DOC produced from reduced, less-decomposed peat is more aromatic than DOC generated from oxidized peat. This result is not surprising because of the greater abundance of aromatic carbon (phenolic compounds) generally formed in reduced environments such as sphagnum bogs and water-logged soils compared to well-oxygenated environments (Thurman, 1985). The SUVA values of the drainage ditch samples generally reflect a mixture of lysimeter and piezometer samples (fig. 13c), indicating mixed contributions of DOC from the USZ and LSZ. One exception is the sample collected on October 23 that had the highest SUVA value (0.107 L/mg-cm) of all ditch samples (fig. 13c) and had a DOC concentration of only 14.9 mg/L. The source of this water with anomalously high SUVA value is unknown.

Fractionation of Dissolved Organic Carbon into Hydrophobic and Hydrophilic Acids

Complete DOC fractionation data for lysimeter, piezometer, and drainage ditch samples are presented

in appendix C, table C1. For purposes of this discussion, averaged data are used when replicate analyses were available. The discussion focuses only on data for the HPOA and HPIA fractions, the DOC extracted by and eluted from the XAD-8 and XAD-4 resins, respectively. These two fractions combined account for the majority of DOC in all samples (58 to 76 percent), probably contain most of the THM precursors, and are the fractions for which other compositional and structural data are available.

In general, the fractionation data (fig. 14) indicate that (1) the sum of the HPOA and HPIA DOC fractions are significantly greater for the piezometer samples compared to the lysimeter samples, indicating that the lysimeter samples contained more DOC that was not sorbed by the resins (probably ultra hydrophilic acids); (2) the quality of the ditch samples was very similar to that of the piezometer samples, reflecting a potentially greater DOC contribution to the ditch from the LSZ; and (3) the HPOA fraction for the piezometers was significantly greater than that for the lysimeters ($\alpha=0.05$), indicating that greater amounts of

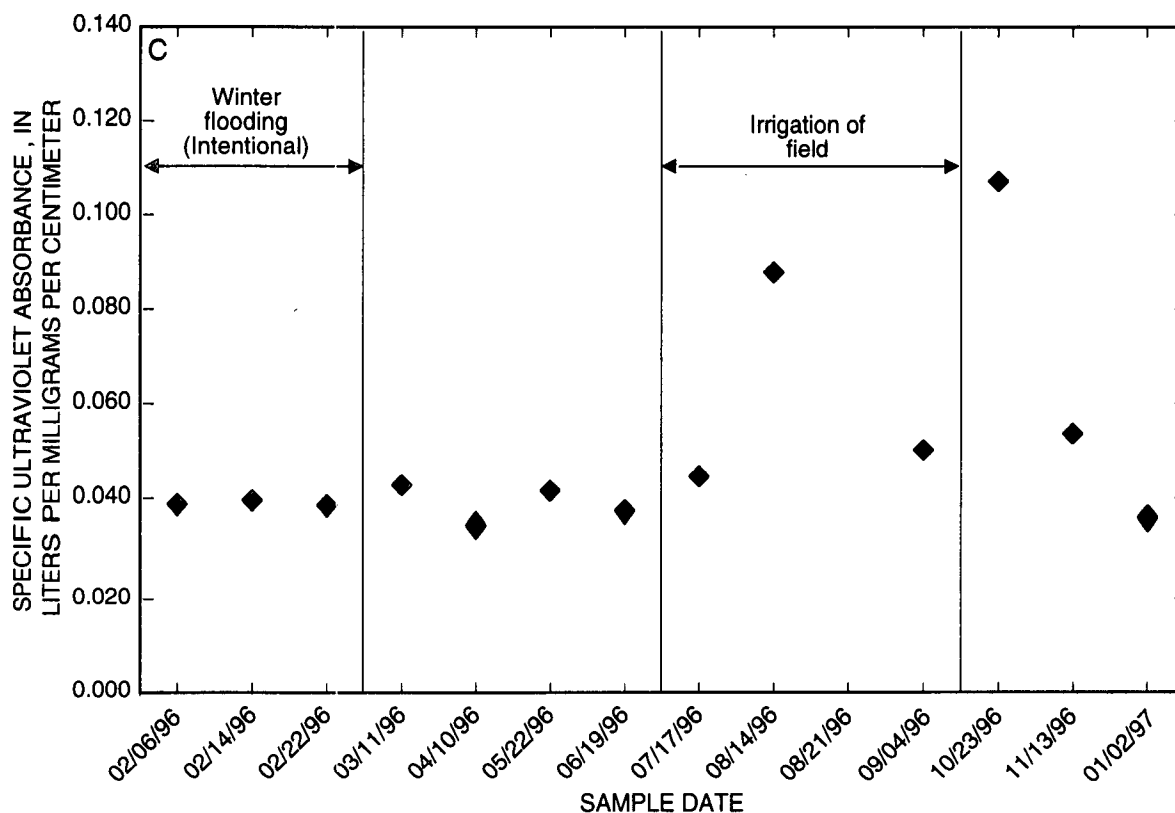


Figure 13.—Continued.

humic substances were produced from the LSZ. This result is in agreement with the SUVA data for the whole-water samples that had significantly higher values of SUVA for the piezometer samples compared to the lysimeter samples. Together, these results support the conclusion that more aromatic forms of DOC are produced under anaerobic conditions (piezometer samples) than under aerobic conditions (lysimeter samples) and imply that more THM precursors should be produced by the LSZ under anaerobic conditions.

Trihalomethane Formation Potential

THMFP measurements were made on water samples using either the DWR Bryte Laboratory dose-based method or a reactivity-based method similar to that described by Krasner and Scimanti, (1993). The DWR Bryte Laboratory dose-based method (referred to as the TFPC Assay, California Department of Water Resources, 1994a) involves adding a constant chlorine dose (120 mg/L, buffered to pH 8.2) to samples with a

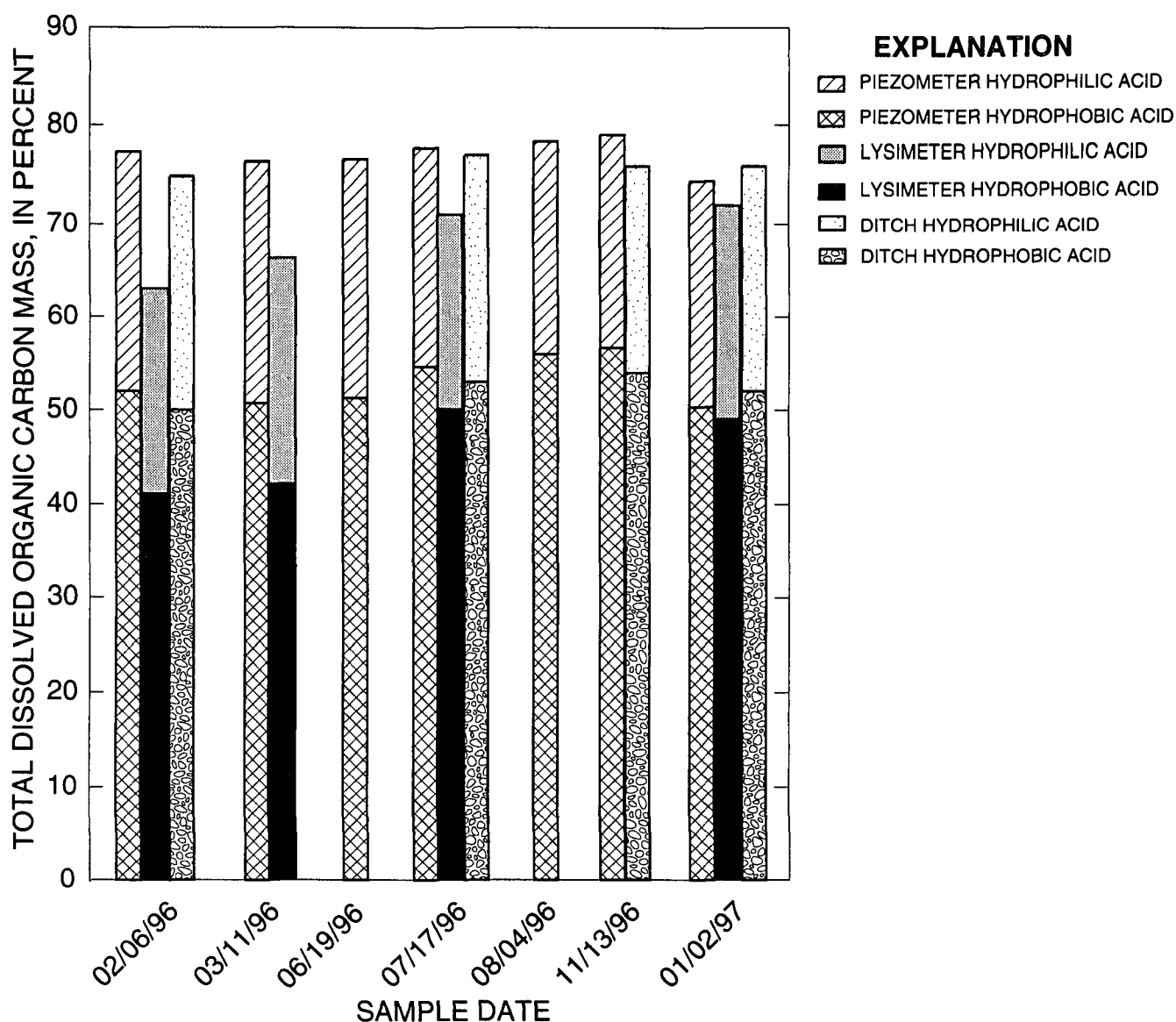


Figure 14. Fractionation of dissolved organic carbon into hydrophobic and hydrophilic acids, for lysimeter, piezometer, and drainage ditch samples, February 1996–January 1997, Twitchell Island, California.

UVA of less than 0.6 per centimeter (cm^{-1}). If the UVA of a sample is greater than 0.6 cm^{-1} , the sample is diluted so that the UVA is less than 0.5 cm^{-1} . In contrast, the reactivity-based method (Krasner and Scilimenti, 1993) applies a chlorine dose based on the DOC and NH_4 concentration of each sample (California Department of Water Resources, 1994b). The reactivity-based THMFP method was adopted part way through the study because Krasner and Scilimenti (1993) showed that results from the dose-based method were highly dependent on sample dilution, whereas dilution did not affect THMFP results for the reactivity-based method.

Samples collected from the beginning of the study through September 1996 were analyzed by the dose-based THMFP method only, samples collected in October 1996 were analyzed by the reactivity-based THMFP method only, and 22 samples collected from November 1996 through January 1997 were analyzed using both methods. Dose-based and reactivity-based THMFP results for samples analyzed by both methods were significantly correlated, $R^2=0.983$ (fig. 15), and indicate that the dose-based THMFP results consistently are about 11 percent higher than the

reactivity-based THMFP results. Because results of both methods are highly correlated (indicating no dilution effect problem for the dose-based method for these samples) and the data record for the dose-based THMFP determinations is much longer, the results and discussion below for whole-water sample THMFP utilize the dose-based THMFP data. The exceptions to this are the THMFPs for samples collected on October 23, 1996, which were analyzed by using only the reactivity-based method.

For samples collected from the USZ (lysimeter), from the LSZ (piezometer), and from the drainage ditch, the linear relation between DOC and THMFP ($R^2=0.864$) (fig. 16) is excellent. The variance about the regression line in figure 16 indicates the variability in DOC quality and composition in relation to THM precursors. This high correlation most likely is due to the predominance of peat as the major source of DOC. In other systems that are not as homogeneous (for example, systems that contain more diverse sources of DOC or higher amounts of mineral soil), such a high correlation would not be expected. For example, Owen and others (1993) examined seven different source

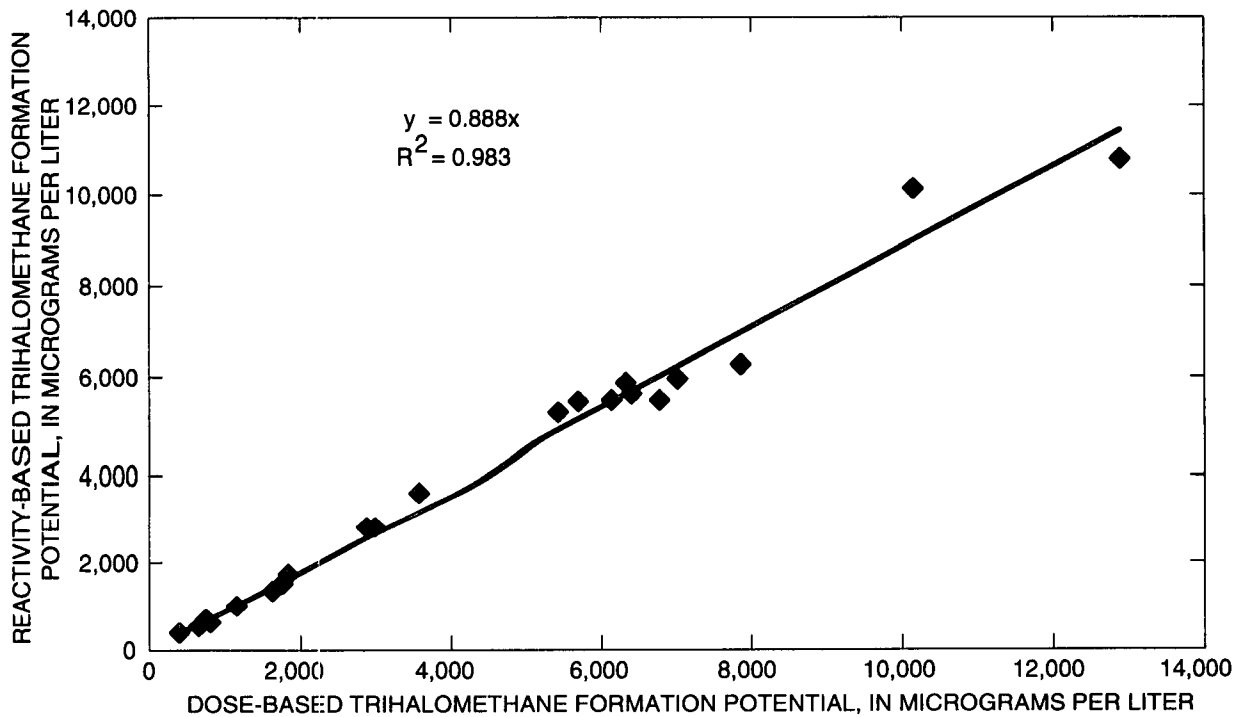


Figure 15. Comparison of reactivity-based and dose-based trihalomethane formation potential measurements, Twitchell Island, California.

waters from throughout the United States and found poor correlation between DOC and THMF_P ($R^2 < 0.50$).

Although the correlation is high for samples from this study, use of DOC to predict THMF_P could lead to considerable error in estimating THMF_P, especially at higher DOC concentrations. For example, the regression equation predicts a THMF_P of 67 micromolar (μM) (8,200 $\mu g/L$) for a sample containing about 85 mg/L DOC. For this DOC concentration, actual THMF_P concentrations range from about 57 μM (7,000 $\mu g/L$) to 78 μM (9,500 $\mu g/L$) (fig. 16). Thus, use of this relation to predict THM precursor loading, for example, could lead to significant errors in the load prediction. In addition, high correlation between DOC and THMF_P is not expected for samples from less homogeneous areas that contain diverse sources of DOC.

The linear relation between UVA and THMF_P (fig. 17, $R^2 = 0.702$) for the lysimeter, the piezometer, and the drainage ditch samples also is good. Because UVA is an indicator of DOC aromaticity and aromatic forms of DOC are considered primary THM precursors (Rook, 1976, 1977; Reckow and others, 1990), the higher correlation between THMF_P and DOC ($R^2 = 0.864$), compared to that for THMF_P and UVA,

was not expected. The THMF_P and UVA data normalized to carbon were not linearly correlated ($R^2 = 0.156$) (fig. 18). Specific THMF_P (THMF_P/DOC or STHMF_P) provides an indication of the average potential for the carbon in a sample to form THMs, a measure of the potential THM precursor content on a molar basis normalized to carbon. The generally accepted model for THM formation is that the primary THM precursors are aromatic forms of carbon (such as resorcinol), in which case a strong linear relation is expected between STHMF_P and SUVA. The lack of correlation between STHMF_P and SUVA suggests that a more detailed assessment of aromatic compound species may help to better identify THM precursor compounds, and that forms of DOC other than aromatic compounds also may be significant THM precursors in these samples.

Upper and Lower Soil Zones

Comparisons of THMF_P for whole-water samples collected from the lysimeters (USZ) and the piezometers (LSZ) are limited because of the paucity of lysimeter THMF_P data. As mentioned earlier in this

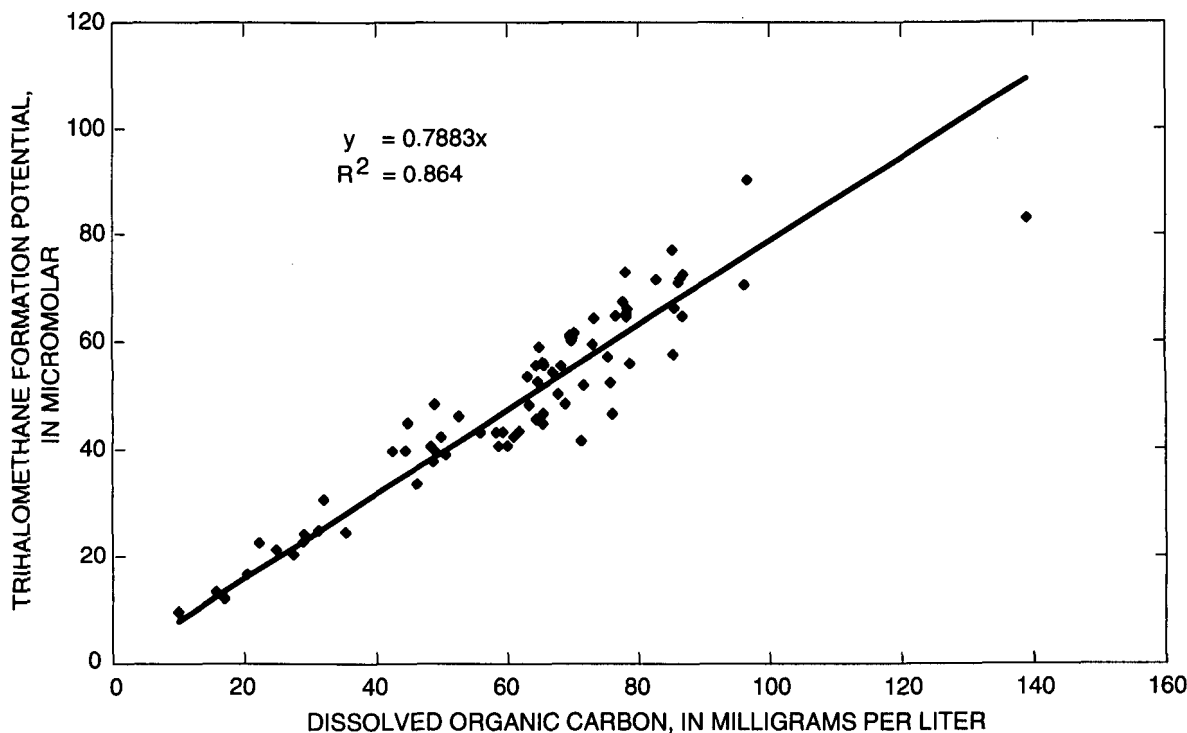


Figure 16. Relation between trihalomethane formation potential and dissolved organic carbon for lysimeter, piezometer, and drainage ditch samples, Twitchell Island, California.

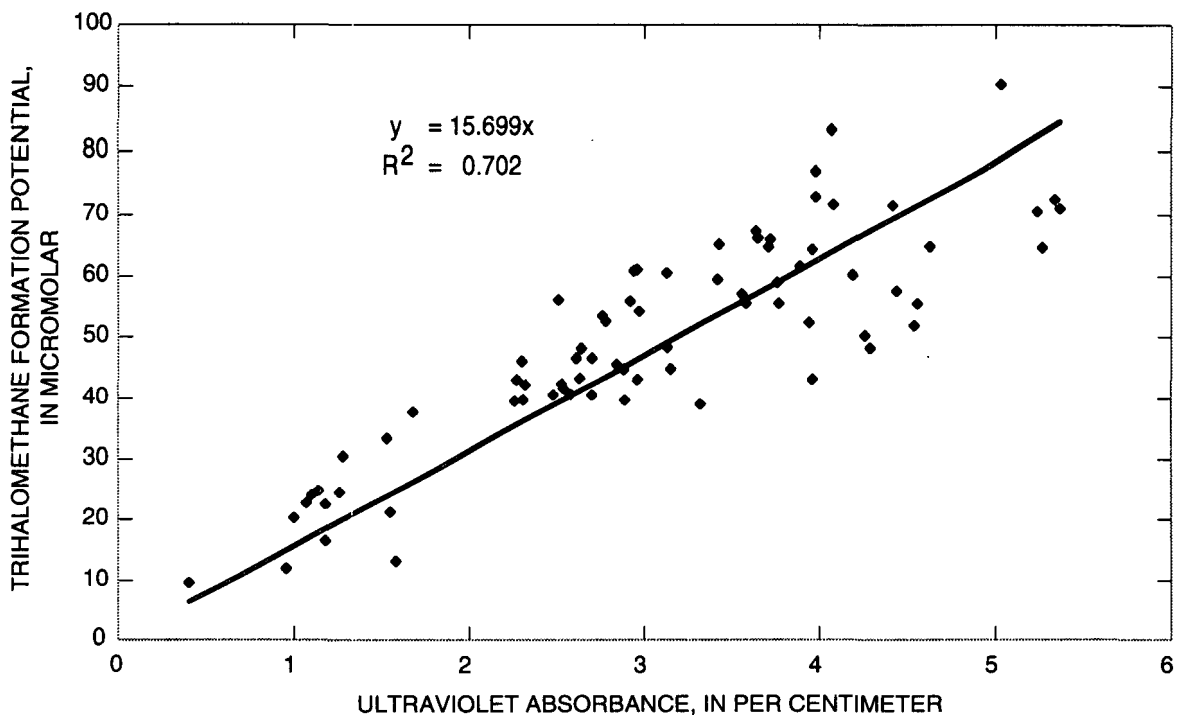


Figure 17. Relation between ultraviolet absorbance and trihalomethane formation potential for lysimeter, piezometer, and drainage ditch samples, Twitchell Island, California.

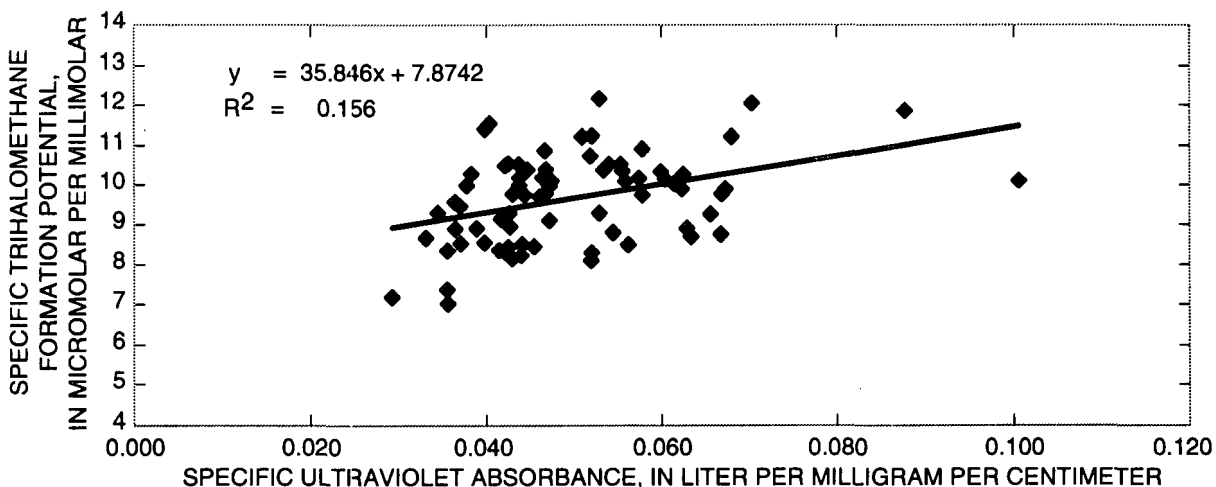


Figure 18. Relation between specific trihalomethane formation potential and specific ultraviolet absorbance for lysimeter, piezometer, and drainage ditch samples, Twitchell Island, California.

report, the lysimeters produced insufficient volumes of water for THMFP analysis; even during irrigation, obtaining sufficient sample volume for THMFP analysis was difficult. Samples were obtained from all lysimeters for THM analyses during the September 4, 1996, sampling by plugging the irrigation spud ditch so that

irrigation water backed up in the ditch system and partially flooded the field.

The THMFP results for the lysimeter (fig. 19) and the piezometer (fig. 20) samples generally followed trends similar to the lysimeter and the piezometer DOC results (figs. 7 and 10) over the course of this

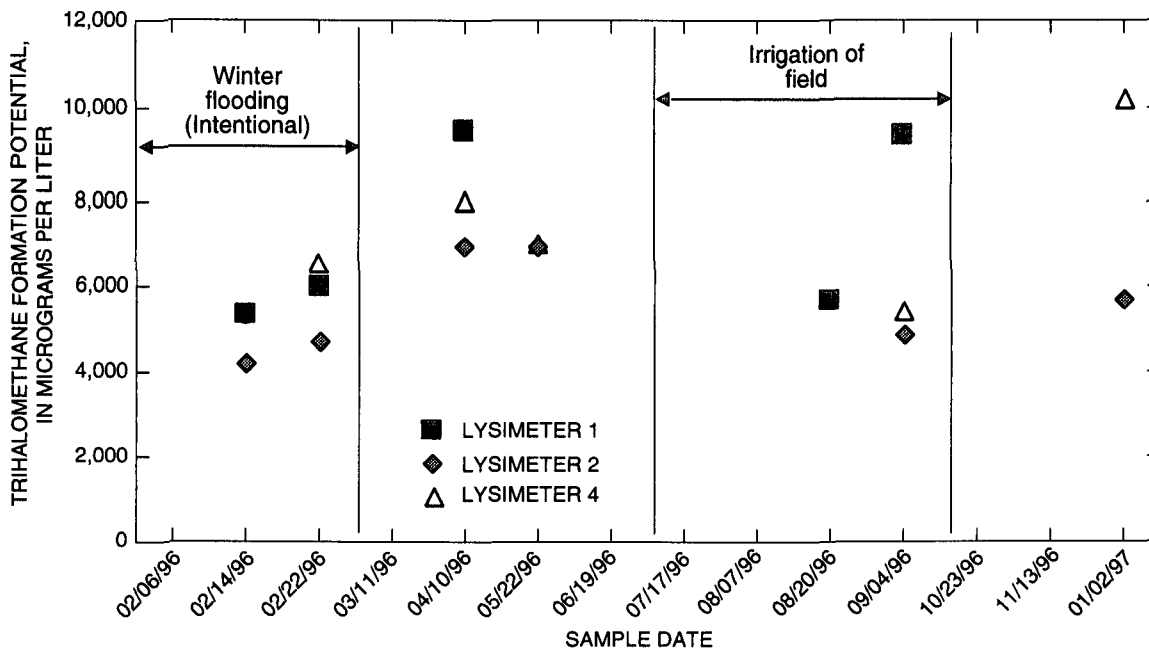


Figure 19. Concentrations of trihalomethane formation potential measurements for lysimeter samples, February 1996–January 1997, Twitchell Island, California.

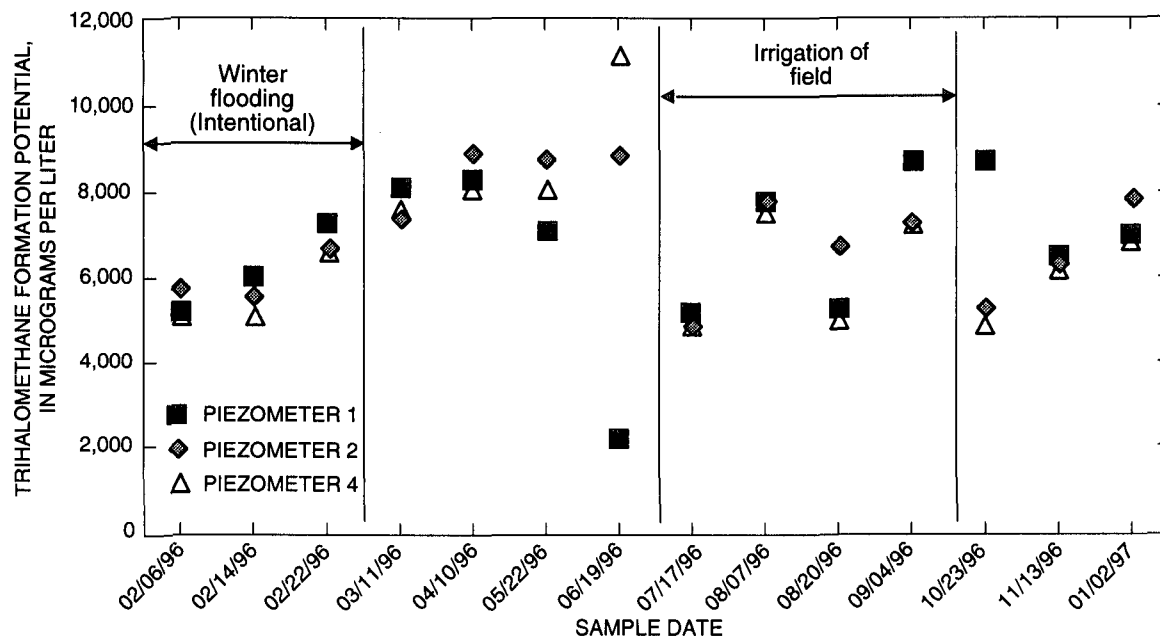


Figure 20. Concentrations of trihalomethane formation potential for piezometer samples, February 1996–January 1997, Twitchell Island, California.

study. This similarity also is reflected by the correlation between DOC and THMFP ($R^2=0.864$) (fig. 16). The same processes affecting the release of DOC from the USZ and the LSZ, as discussed in the Dissolved Organic Carbon Concentrations section of this report, also affect the release of THM precursors.

No significant difference ($\alpha=0.05$) was observed between the median concentrations of THMFP for the lysimeter (5,950 $\mu\text{g/L}$) and the piezometer (6,750 $\mu\text{g/L}$) samples. The STHMFP medians for lysimeters [9.02 micromolars per millimolar ($\mu\text{M}/\text{mM}$)] and piezometers (9.84 $\mu\text{M}/\text{mM}$) also were not significantly different ($\alpha=0.05$). This result is in contrast to DOC, for which concentrations of piezometer DOC were significantly greater than lysimeter DOC. The smaller number of lysimeter samples (17) analyzed for THMFP, relative to the piezometer samples (42), may not accurately represent the seasonal variability of USZ water. The lysimeter samples analyzed for THMFP were mainly from wetter periods during the year (winter flooding and irrigation) when the USZ is relatively

saturated, and results may have been influenced by near-saturated soil moisture conditions that are similar to those in the LSZ.

Trihalomethane Formation Potential of Isolated Fractions

The THMFP of isolated XAD-8 (HPOA) and XAD-4 (HPIA) DOC fractions were measured using a modified reactivity-based method similar to the method used by the DWR Bryte Laboratory (Krasner and Sclimenti, 1993) that produced the reactivity-based THMFP data discussed at the beginning of this section. The method is described in detail in appendix D and differs from the DWR Bryte Laboratory method in two ways: (1) the pH of the incubation was buffered to pH 7.0 instead of pH 8.2, and (2) the temperature was maintained at 20°C instead of 25°C. These differences in the reactivity-based THMFP methods caused an apparent systematic difference in THMFP results. Figure 21 shows the relation between THMFP results for

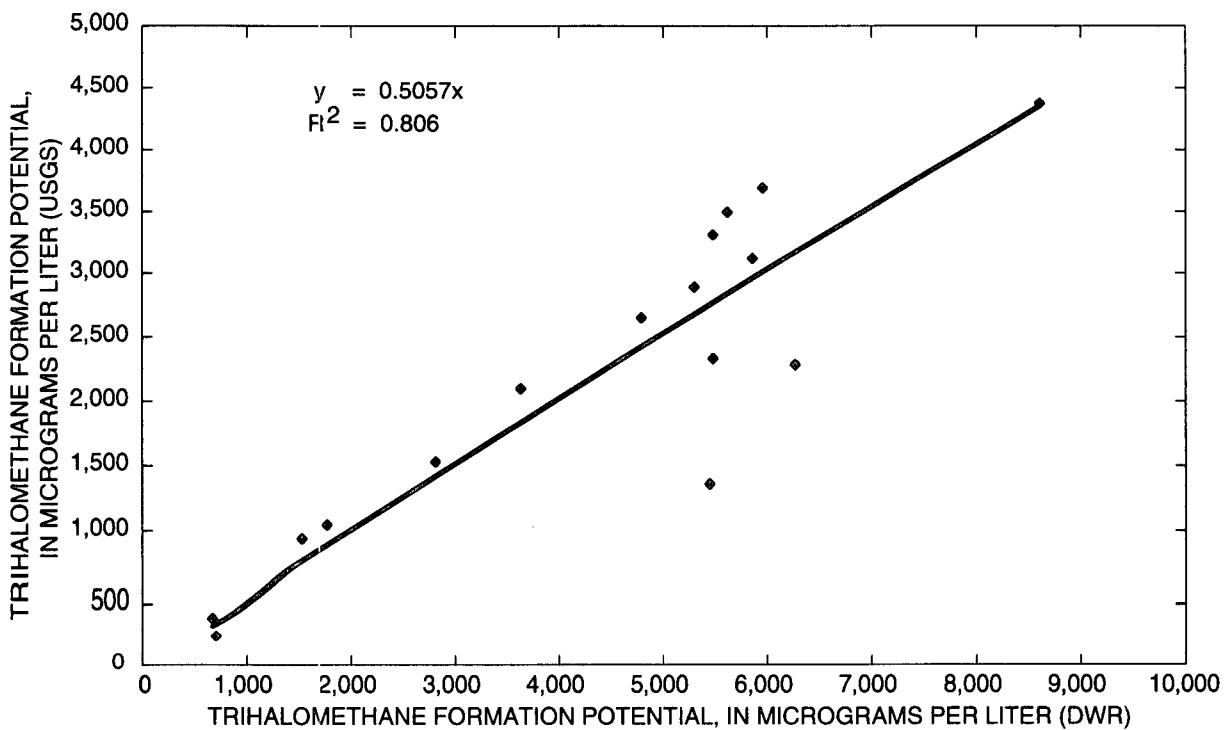


Figure 21. Comparison of reactivity-based trihalomethane formation potential measurements made by the California Department of Water Resources (DWR) and the U.S. Geological Survey (USGS), Twitchell Island, California.

the whole-water samples analyzed by both methods. In general, the results from the two methods are linearly correlated ($R^2=0.806$), and the THMFP concentrations from the method buffered to pH 8.2 (25°C) were about twice those of the method buffered to pH 7.0 (20°C).

Many investigators have shown that THMFP measurements are highly pH dependent (Rook, 1974; Symons and others, 1975; Rathbun, 1996), THMFP concentration increasing with increasing pH. Differences in temperature also will affect THMFP, with more volatile THM species being produced at the higher temperature. Thus, the effects of differences in these two variables help to explain the differences in THMFP results in figure 21 for the two methods.

In this section of the report, results from the modified reactivity-based THMFP method (pH 7.0, 20°C) for whole-water samples are used for comparison purposes because the DOC-isolate samples were analyzed using only this method. Although results

using this modified method differ from results for the other reactivity-based method (pH 8.2, 25°C) and the dose-based THMFP method, THMFP comparisons between whole-water samples and DOC-isolate samples require using data obtained by the same method.

As described in appendix D, DOC isolates (XAD-8 and XAD-4) were redissolved and the resulting solutions analyzed for THMFP and SUVA. Therefore, STHMFP was used to compare the whole-water and the isolate data. Figure 22 shows that the STHMFP of the HPOA fraction was greater than that for the HPIA fraction for five of the seven samples analyzed. But the median STHMFP value for the HPOA fractions [43.8 micrograms per milligram ($\mu\text{g}/\text{mg}$)] was not significantly greater ($\alpha=0.05$) than that for the HPIA fractions (41.7 $\mu\text{g}/\text{mg}$). This result was not expected because it is generally thought that the humic fraction (HPOA) contains most of the THM and DBP precursors (Owen and others, 1993). For these samples,

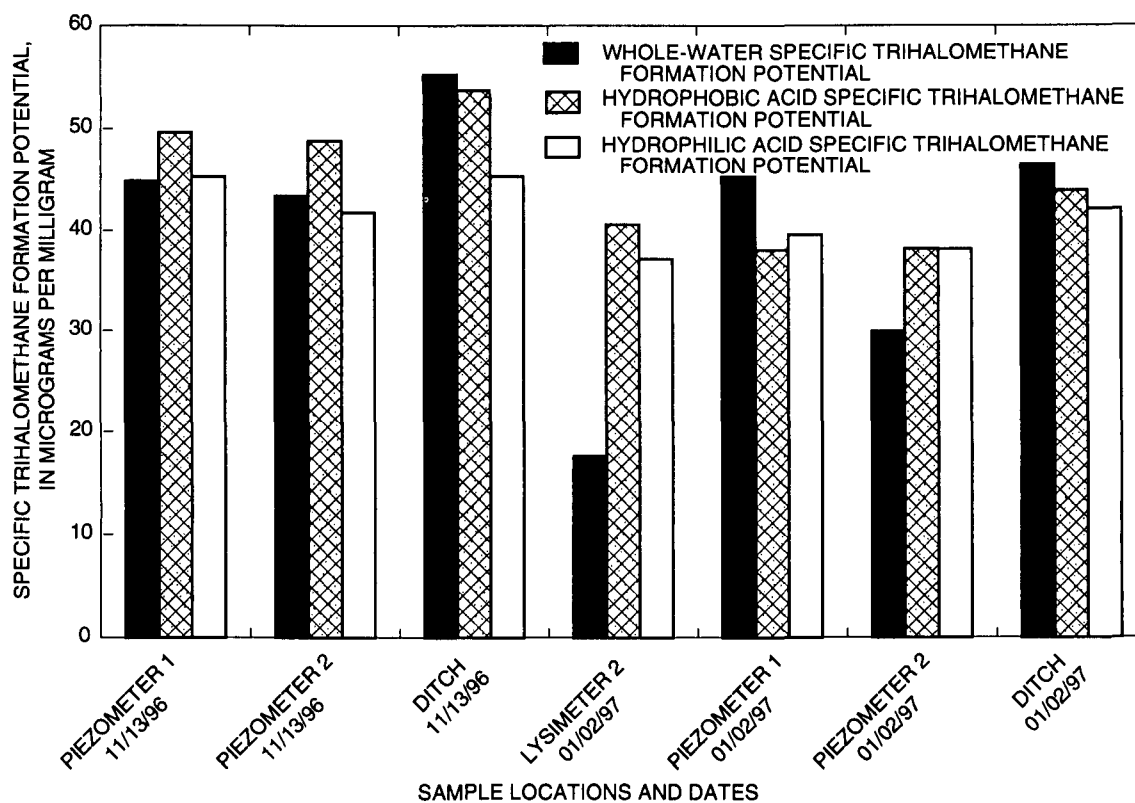


Figure 22. Specific trihalomethane formation potential of whole water and hydrophobic and hydrophilic acid fractions, November 1996–January 1997, Twitchell Island, California.

almost equivalent amounts of STHMFP were observed for both humic (XAD-8) and nonhumic (XAD-4) fractions. Owen and others (1993) observed similar results for seven source waters from throughout the United States. They found that the reactivity of the nonhumic and humic fractions were similar and state that this result “is somewhat contrary to conventional wisdom ... namely that it is the humic fraction that serves as DBP precursor material.”

The SUVA of the HPOA fractions is significantly higher ($\alpha=0.05$) than that for the HPIA fractions (fig. 23), indicating greater aromaticity of this DOC fraction. The greater aromaticity of the HPOA fraction compared to the HPIA fraction is apparent in figure 24, where the ^{13}C -NMR data clearly indicate the greater aromatic composition of the HPOA isolates compared to the HPIA isolates. The ^{13}C -NMR data provide solid

evidence that supports the use of SUVA as an indicator of DOC aromaticity for samples in this study.

The relatively small differences in STHMFP between the HPOA and HPIA fractions (fig. 22) did not reflect the significantly greater aromaticity of the HPOA fraction over that of the HPIA fraction (fig. 24). It is generally thought that the HPOA fraction contains most of the aromatic forms of carbon, which is supported by data in figure 22, and that aromatic forms of carbon are the primary THM precursors (Rook, 1976, 1977; Reckhow and others, 1990). Even though the HPOA fraction was higher in aromatic composition (fig. 24) and carbon (fig. 14) compared to the HPIA fraction, the THMFP concentration contributed by the HPOA fraction was not significantly greater than that contributed by the HPIA fraction (fig. 22). This result indicates that DOC aromaticity alone cannot fully explain or predict THM precursor content.

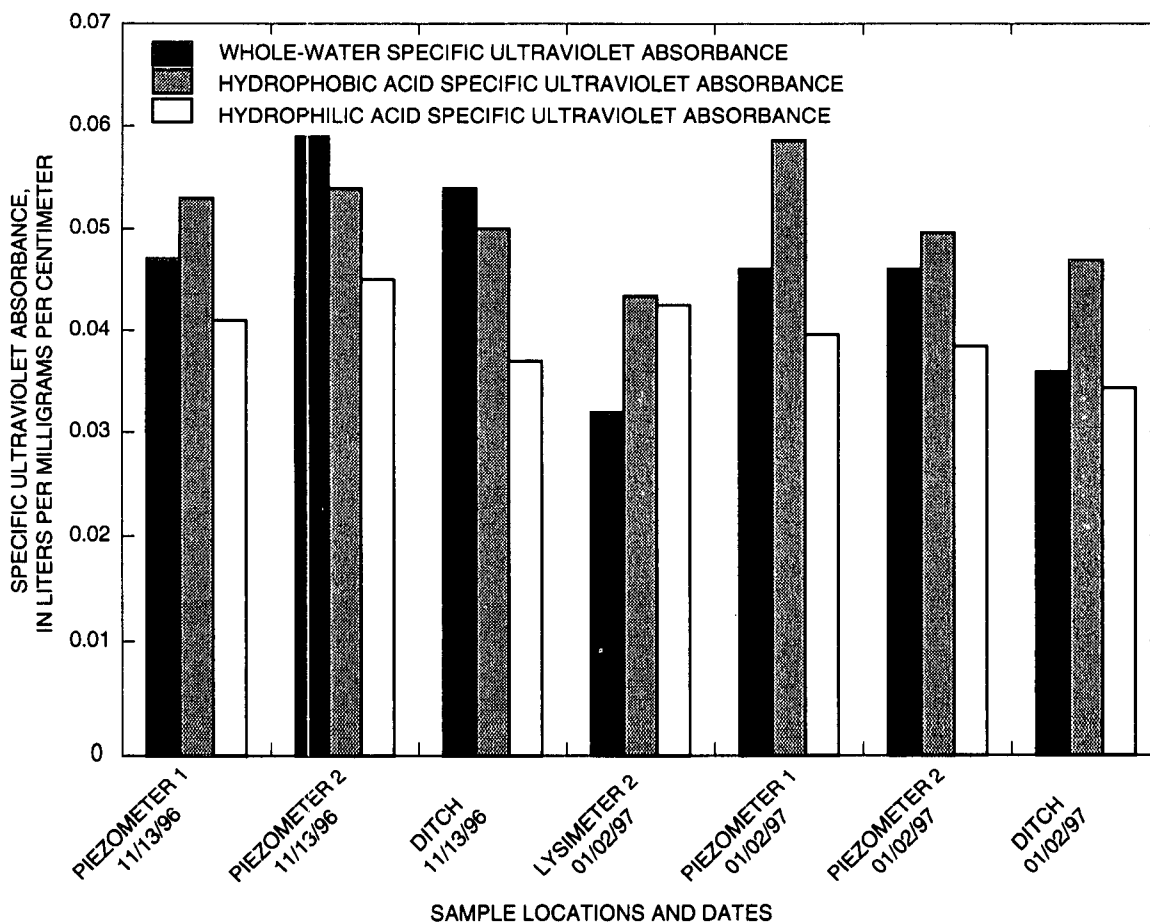


Figure 23. Specific ultraviolet absorbance of whole water and hydrophobic and hydrophilic acid fractions, November 1996–January 1997, Twitchell Island, California.

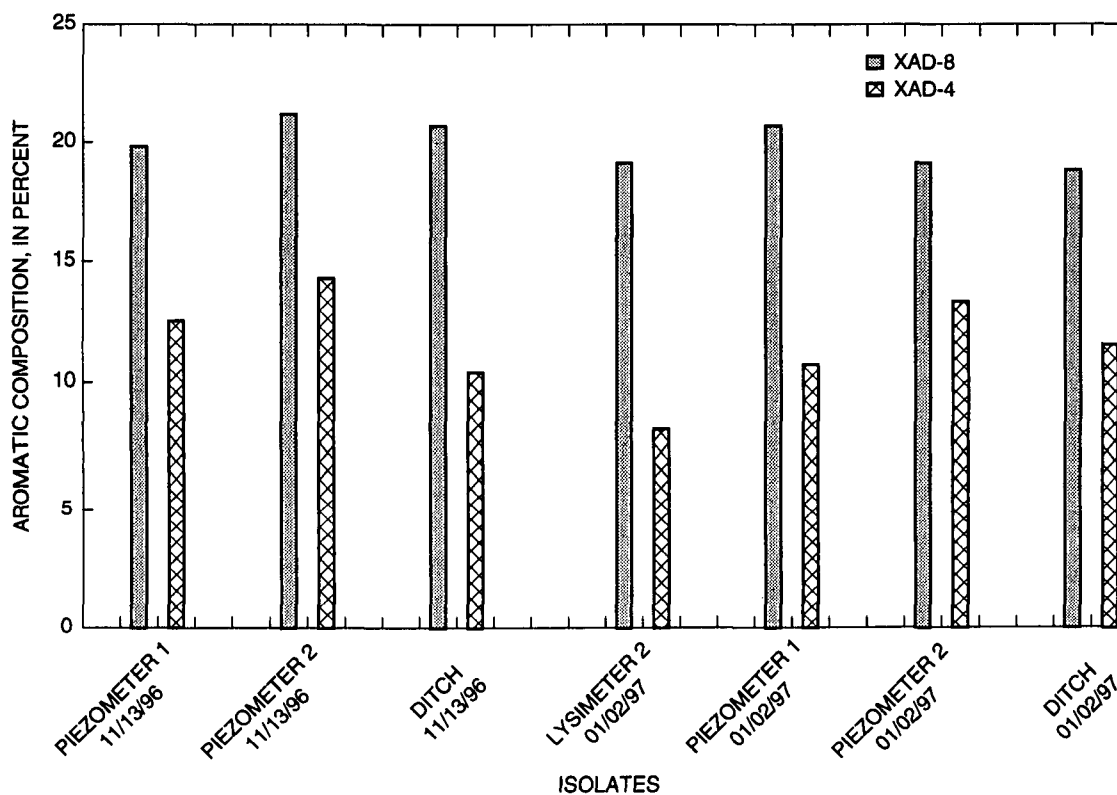


Figure 24. Aromatic composition of XAD isolates from lysimeter and piezometer samples, November 1996–January 1997, Twitchell Island, California.

SUMMARY AND CONCLUSIONS

Water exported from the Delta is an important drinking-water source for more than 20 million people in California. This water has been shown to contain elevated concentrations of dissolved organic carbon (DOC) and bromide (Br). If this water is chlorinated for drinking, it can, at times, exceed the U.S. Environmental Protection Agency's maximum contaminant level (MCL) of 0.100 mg/L for trihalomethanes (THMs). An estimated 20 to 50 percent of the THM precursors in Delta water exported at the H.O. Banks pumping plant for drinking water originates from elevated concentrations of DOC in drainage water from peat soils on Delta islands. This cooperative study between the U.S. Geological Survey's Drinking Water Initiative and California Department of Water Resources was undertaken to elucidate some of the factors affecting and processes controlling the concentration and quality of DOC released from peat soils and to relate the chemical composition of DOC to its propensity to form THMs. Knowledge and understanding of the factors that affect

and processes that control the release of DOC and THM precursors from Delta soils is a necessary first step in the development of management alternatives to reduce THM precursor loads from Delta islands.

The generally accepted conceptual model for THM formation assumes that aromatic forms of carbon (such as resorcinol) are primary precursors to THMs. Natural environments with reducing conditions, such as peat bogs and water-logged soils, tend to produce greater amounts of aromatic DOC compared to well-oxygenated environments. Thus, one of the principal hypotheses of this study was that the reduced peat soils beneath the shallow ground water on Delta islands would have a tendency to release greater amounts of aromatic carbon (THM precursors) relative to near-surface oxidized peat soils. To test this hypothesis, soil water was sampled from near-surface, oxidized, well-decomposed peat soil in the upper soil zone (USZ) and deeper, reduced, fibrous peat soil in the lower soil zone (LSZ) from one agricultural field in the west-central Delta. Soil redox conditions also are influenced by water-management practices—irrigation and

intentional flooding of fields and drainage ditch depths that help control ground-water levels. Therefore, results from this study have implications for potential management alternatives to reduce production of THM precursors in Delta drainage water.

The general approach of the study was to examine the chemical variability of DOC samples from the USZ and the LSZ during a 1-year period. The chemical character of the DOC was related to its propensity to form THMs while taking into consideration the effects of redox conditions and land- and water-management practices on the biogeochemical processes affecting the release of DOC from the soils.

The analytical approach to the study involved analysis of whole-water samples for DOC, ultraviolet absorbance (UVA) at 254 nm, trihalomethane formation potential (THMFP), and various inorganic constituents. Considerable focus was given to the aromaticity of carbon in whole-water samples and isolated carbon fractions as indicators of THM precursor content. The quality of the DOC was evaluated by first examining the whole-water specific UVA (SUVA, UVA/DOC) as an indication of DOC aromaticity. Whole-water DOC was isolated and fractionated into hydrophobic acid (HPOA) using XAD-8 resin and hydrophilic acid (HPIA) using XAD-4 resin, where the HPOA fraction contains the more aromatic humic and fulvic acids and the HPIA fraction contains the less aromatic and more aliphatic forms of carbon. The amount of DOC isolated on these columns, the proportion of HPOA and HPIA, as well as analysis of the intrinsic chemical structure of the isolates by carbon-13 nuclear magnetic resonance (^{13}C -NMR), all provided insight into the processes controlling the aromaticity of a sample. Selected isolates from XAD fractionations were further analyzed for THMFP and related to SUVA values of the isolates and to the more quantitative ^{13}C -NMR measure of aromatic carbon, which also provided further DOC structural and functional group information. Isolate THMFPs were interpreted in terms of isolate properties (SUVA and ^{13}C -NMR results) to assess the reactivity of HPOA and HPIA fractions in relation to their composition, source, and factors affecting DOC production under the conditions studied.

Conclusions

- Waters from the anaerobic LSZ contained slightly higher concentrations of DOC and greater amounts of humic material than waters from the aerobic USZ, indicating that carbon released from peat soils under anaerobic conditions is a substantial contributor to DOC and that the quality of the DOC released from the two zones differs.
- DOC in waters from the LSZ contained a higher proportion of aromatic compounds, the putative THM precursors, than that from the USZ.
- DOC in waters from the drainage ditch were compositionally more similar to the DOC in waters from the LSZ than that from the USZ, suggesting the major source of DOC in ditch water was the LSZ.
- DOC aromaticity alone cannot explain fully or predict THM precursor content. This finding indicates that:
 1. UVA is not a suitable tool for predicting THMFP in these waters because this measurement is most sensitive for aromatic carbon.
 2. Processes other than those that control bulk aromatic carbon content control THM precursor concentrations in these waters, which explains the historical observation that on a regional basis, there is a poor correlation between UVA and THMFP on a carbon-normalized basis.
- The highest DOC levels, the highest variability in DOC, and the highest THMFP levels followed summer irrigation and winter flooding periods, which suggests that repetitive cycles of wetting and drying promotes the release of DOC and THM precursors in these soils.

Summary of Supporting Observations

Dissolved Organic Carbon Concentrations

- DOC concentrations in the oxidized USZ were highly variable. For the oxidized USZ, median DOC for lysimeter samples ranged from 46.4 to 83.2 mg/L. Variations in DOC are attributable to effects of water-management practices (flooding

and irrigation) and precipitation on microbial soil processes and subsequent release and transport of DOC.

- DOC concentrations in the reduced LSZ were generally slightly higher than that from the USZ. Median DOC for the reduced LSZ (piezometer samples) ranged from 49.3 to 82.3 mg/L and were significantly higher ($\alpha=0.05$) than DOC from the USZ. In general (1) variations in piezometer DOC, at times, apparently were caused by drainage from soils above; and (2) the lowest and most variable concentrations of DOC are associated with the irrigation period, during which the drop in specific conductance of samples clearly indicated dilution of ground water by irrigation water.
- DOC concentrations in the ditch draining the field were always lower than the median DOC for either USZ or LSZ waters for all sampling dates, ranging from 9.8 to 54.9 mg/L. Lower values are consistent with mixing of waters from several different sources, including lower DOC irrigation waters. Interpretation of ditch DOC is complicated by the multiple sources of water and DOC that contribute to the drainage ditch throughout the year.

Quality and Composition of Dissolved Organic Carbon

- The DOC from the LSZ had significantly higher ($\alpha=0.05$) aromaticity than the USZ as measured by SUVA. This indicates that the deeper, more reduced fibrous peat releases more aromatic forms of carbon compared to the near-surface, oxidized decomposed peat.
- Isolation of DOC as HPOA (XAD-8) and HPIA (XAD-4) fractions accounted for 58 to 76 percent of the total DOC, demonstrating that our analytical scheme accounted for the majority of DOC in all samples.
- The sum of the HPOA and HPIA DOC fractions were significantly greater ($\alpha=0.05$) for piezometer samples compared to lysimeter samples, indicating that the lysimeter samples contained more forms of DOC not retained and eluted by the resins (probably ultra-hydrophilic acids).
- Water from the LSZ contained more humic materials than that from the USZ. Piezometer samples had

greater HPOA fractions (humic substances) compared to those in lysimeter samples, were richer in the more aromatic HPOA, and were in agreement with SUVA results for whole-water samples.

These results support the conclusion that more aromatic forms of DOC are produced under anaerobic conditions compared to aerobic conditions.

- The composition of the drainage ditch samples, as indicated by the HPOA and HPIA distributions, closely resembled that of the piezometer samples, potentially reflecting a greater DOC contribution to the ditch from the LSZ.
- DOC isolated in the HPOA fraction was more aromatic than that isolated in the HPIA fraction. For the seven DOC samples isolated and fractionated, the SUVA of the HPOA isolates was significantly higher ($\alpha=0.05$) than the SUVA for the HPIA isolates, denoting greater aromaticity of the HPOA fractions relative to the HPIA fractions. This difference is explicitly demonstrated by the ^{13}C -NMR data, which clearly show greater aromatic carbon composition of the HPOA isolates in comparison to that of the HPIA isolates.

Trihalomethane Formation

- DOC concentration, THMFP, and UVA were all highly related. Linear correlations were found between THMFP and DOC ($R^2=0.864$) and THMFP and UVA ($R^2=0.702$) for samples from lysimeters, piezometers, and the ditch, indicating that THM precursors increased with increasing DOC and UVA for whole-water samples.
- In contrast, no significant correlation was found between STHMFP (THMFP/DOC) and SUVA, indicating that no significant relation exists between carbon aromaticity and THMFP on a carbon basis. This result suggests that a more detailed assessment of aromatic compound species may help to better identify THM precursor compounds and that forms of DOC other than aromatic compounds also may be significant THM precursors in these samples.
- There is no consistent difference in the capacity of USZ and LSZ waters to form THMs. Even though median values of THMFP and STHMFP were

greater for piezometer samples (6,750 $\mu\text{g/L}$ and 9.84 $\mu\text{M/mM}$, respectively) compared to those for lysimeter samples (5,950 $\mu\text{g/L}$ and 9.02 $\mu\text{M/mM}$, respectively), the differences were not significant ($\alpha=0.05$). A smaller number of lysimeter samples (17) were analyzed relative to piezometer samples (42) because of lack of available water in the USZ during dry parts of the year when the field was not irrigated. Thus, results from the lysimeter samples may not be representative of THM precursor release from the USZ throughout the year.

- The aromaticity of DOC appears to be unrelated to THMFP on a carbon-normalized basis. Although the HPOA fractions were obviously more aromatic than the HPIA fractions, the median STHMFP for the HPOA isolates (43.8 $\mu\text{g/mg}$) was not significantly greater ($\alpha=0.05$) than the median for the HPIA isolates (41.7 $\mu\text{g/mg}$). This result again emphasizes that DOC aromaticity alone cannot explain fully or predict THM precursor content and that further investigation of aromatic and non-aromatic forms of carbon will be needed to better identify THM precursors.

Other Significant Observations

- The anaerobic redox condition of the LSZ was characterized by extremely low dissolved oxygen (<0.38 mg/L) and platinum-electrode redox potentials (<310 mV) indicative of anoxic conditions.
- Twenty-one water samples analyzed for THMFP using the dose-based method and the reactivity-based method were linearly correlated ($R^2=0.983$), with the dose-based results consistently 11 percent greater than the reactivity-based results, indicating no dilution effect problem for the dose-based method for these samples.

Implications of Study Results

Throughout the year of study (February 1996–January 1997), slightly higher concentrations of DOC with greater aromaticity were released from the LSZ soils, suggesting that using shallower ditches to drain fields may decrease concentrations of DOC in the ditch. Additionally, although variable, the highest DOC concentrations from the USZ soils occurred during and

soon after the period when the field was flooded (winter) or irrigated (summer). These higher DOC concentrations are mainly attributable to enhanced microbial activity resulting from soil wetting and drying cycles. This irrigation period is coincident with relatively low Delta channel flows, so the effect of potentially high DOC concentrations in the USZ during irrigation may have a magnified effect on DOC loads released to the channels from irrigation drainage. An important distinction is that these observations are concentration related and do not reflect the load of precursor released by the soil over time. Determination of loads was not within the scope of this study.

The DOC and aromaticity of LSZ samples generally were greater than those of the USZ samples, but no significant differences were found for THMFP results for samples from the two zones over the annual cycle. Data from this study suggest that aromaticity alone is not an accurate indicator of THM precursors. This result implies that THM precursors do not arise from the same source as most of the aromaticity; thus, a more accurate indicator of THMFP than UVA is needed for screening water quality in the Delta.

Another implication is that the processes that concentrate THM precursors are not significantly affected by redox conditions and appear to be unrelated to the processes that concentrate aromatic DOC in the LSZ. This finding explains why there is no observed general regional relation between SUVA and THMFP in Delta waters. This lack of relation is likely related to the type of organic material released by peat soils, and care should be exercised in extrapolating this finding to other locations. Also, this finding is based on concentration measurements and may not be true for the total amount (loads) of precursors released from the soils. However, if studies confirm the finding on a regional basis, it may be possible to directly identify the source of the THM precursors and to seek a remedy for high THM precursor concentrations in Delta waters.

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APPENDICES

APPENDIX A: FIELD AND SAMPLE COLLECTION METHODS

Installation of Samplers

Four sampling sites were established along an east-west transect at the northern end of the agricultural field (fig. 2). These sites were spaced about 40 ft apart and about 50 ft south of the ditch that drains the field. The sites were located to sample subsurface drainage from the field. At each site, lysimeters (1.5-in. diameter, 6-in. long, with 0.2- μ m pores) were installed to sample soil water from 0.5 to 1.5 ft below land surface, and piezometers (1.25-in. diameter, 2 ft long, with 0.02-in. slots) were installed to sample ground water from 4.5 to 6.5 ft below land surface (fig. 3). The lysimeters, piezometers, and extension tubes were constructed of 316L stainless steel to prevent carbon contamination from sampling materials.

The holes for the installation of the lysimeters and the piezometers were drilled using a gas-powered, tower-mounted drill with a 4-in. bit. The holes were evacuated using a 1-in. water pump. The piezometers were lowered onto a bed of sand (#2/12), and the annular space was packed with sand to about 1 ft above the sampling interval. The remaining annular space was filled with bentonite grout to land surface. The lysimeters were placed on a bed of silica flour, a silica flour slurry was packed around the sampler, and bentonite grout was used to seal the hole from the top of the sampler to land surface. After installation, the piezometers initially were developed using a peristaltic pump until the effluent was clear. Lysimeters initially were developed after the field was flooded.

Sample Collection and Field Measurements

Lysimeters are designed to sample soil water from unsaturated soils, which, in contrast to piezometer sampling of ground water, usually do not yield large sample volumes. Thus, development of lysimeters prior to sampling involved evacuating or purging the lysimeter using a peristaltic pump and either Teflon or c-flex tubing and stainless-steel tubing. These sampling materials were used to prevent carbon contamination of samples. After initial purging, the lysimeters were evacuated every 15 to 20 minutes, and the soil water samples were collected in 1-gal, baked, amber glass bottles placed in a bucket of ice to keep the samples

chilled and to slow microbial decomposition of DOC. Because of the small volume of soil water available under unsaturated soil conditions, lysimeter sampling continued throughout the day to yield the maximum amount of sample possible.

Temperature of the lysimeter samples was measured immediately on the purged soil water. A 15- to 20-mL subsample from the lysimeter sample was measured for pH and specific conductance in the field. The pH and specific conductance meters and probes were calibrated, checked, and recalibrated, if necessary, before each measurement. The pH values for the lysimeter samples are questionable because of degassing of CO₂ and exposure to atmospheric gases during sampling.

Samples were pressure filtered (0.45 μ m) in the field using a peristaltic pump. The pump, tubing, and filter were flushed with at least 1 L of deionized water and 75 to 100 mL of sample water prior to collecting the samples. Analysis of organic-free water filtered through the set up after the deionized water rinse yielded a DOC concentration of < 0.2 mg/L, indicating no contamination of samples from the filtering procedure.

Piezometers also were sampled using a peristaltic pump and Teflon or c-flex tubing and stainless-steel tubing. Prior to sample collection, at least three casing volumes (about 2.5 gal) of water were purged, and then 20-mL test samples were collected every 5 to 10 minutes to test piezometer development. Specific conductance of the 20-mL test samples was measured, and samples for laboratory analysis were collected only after successive specific-conductance measurements were within 5 percent of each other, indicating that aquifer water was being pumped. Sample water was collected in 1-gal, baked, amber glass bottles, and temperature and pH were immediately measured for a 20-mL subsample. Piezometer samples were pressure filtered, as described above, for the lysimeter samples, except that 1,000 mL of sample water was filtered through the filtering apparatus following the deionized water rinse and before filling the sample bottles.

Lysimeter and piezometer samples were filtered into sample bottles, preserved, and stored on ice until they reached the laboratory for analysis. The DWR Bryte Laboratory analyzed samples for DOC, UVA, THMFP (dose-based), Br, Ca, Mg, K, Cl, SO₄, and alkalinity. Methods of sample preservation and analysis are reported in California Department of Water Resources (1994b). Split samples also were collected

for analysis of DOC, UVA, and THMFP by the USGS Laboratory in Boulder, Colo., as described in appendixes B and D. All samples sent to the USGS Laboratory were packed in ice and shipped to be received at the laboratory within 24 hours.

In August 1996, it was determined that other redox parameters should be analyzed, and, in September 1996, the reactivity-based method to determine THMFP was added to the analyses. The redox parameters added to the laboratory analysis included total Fe and Mn and N species (nitrite, nitrate, and ammonium). In addition, a flow-through chamber was used to collect piezometer samples and to monitor other parameters. The reactivity-based method for determination of THMFP is described above in the Trihalomethane Formation Potential section of this report.

Use of the flow-through chamber for monitoring DO, Pt-electrode Eh, and pH allows accurate measurement of these parameters for ground water without contamination by minimizing exposure to atmospheric gases (U.S. Geological Survey, 1980). Water was pumped through the air-tight, flow-through chamber

(fitted with DO, Pt-electrode, and pH probes) from the bottom to exclude any air. Meters and probes were calibrated and water was pumped through the flow-through chamber during piezometer development. After at least three casing volumes of water had been pumped through the chamber, DO, Eh, pH, and specific conductance were monitored, and piezometer samples were not collected until these parameters had stabilized (indicated by successive readings not changing by more than about 5 percent). This technique is not applicable to lysimeter sampling because lysimeters usually sample unsaturated soil, and sample degassing and exposure to atmospheric gases affect DO, pH, and Eh measurements. Included in this appendix are tables reporting the DWR Bryte Laboratory analyses for lysimeter, piezometer, and ditch samples and field parameters. Table A1 lists the field parameters measured (excluding Eh), table A2 presents the mineral data collected, table A3 gives the DOC related analyses and THMFP and haloacetic acid (HAA) results, and table A4 lists the redox-related parameters measured.

Table A1. Field parameters measured for lysimeter, piezometer, and drainage ditch samples, Twitchell Island, California

[$\mu\text{S}/\text{cm}$, microsiemens per centimeter; $^{\circ}\text{C}$, degrees Celsius; mg/L , milligrams per liter; na, not analyzed; TwitLys, lysimeter; TwitPiz, piezometer; TwitDitch, ditch]

Site	Date	Time	Specific conductance ($\mu\text{S}/\text{cm}$)	pH, water, field (standard units)	Temperature, water ($^{\circ}\text{C}$)	Dissolved oxygen (mg/L)
TwitLys1	02/06/96	na	2,670	6.0	18.1	na
TwitLys2	02/06/96	na	2,460	6.5	19.2	na
TwitLys4	02/07/96	na	2,870	6.2	14.4	na
TwitLys1	02/14/96	05:10 pm	2,590	5.6	14.2	na
TwitLys2	02/14/96	04:25 pm	2,655	5.7	14.3	na
TwitLys4	02/14/96	04:50 pm	2,700	6.1	14.2	na
TwitLys1	02/22/96	02:00 pm	2,450	5.6	11.8	na
TwitLys2	02/22/96	01:35 pm	2,610	5.8	11.7	na
TwitLys4	02/22/96	na	2,740	6.2	12.5	na
TwitLys1	03/11/96	09:05 am	2,570	6.2	15.5	na
TwitLys2	03/11/96	09:30 am	2,750	5.9	15.1	na
TwitLys4	03/11/96	10:10 am	2,850	6.1	15.0	na
TwitLys1	04/10/96	09:51 am	2,720	6.3	15.1	na
TwitLys2	04/10/96	10:10 am	2,960	6.0	16.9	na
TwitLys4	04/10/96	11:05 am	3,250	6.5	16.6	na
TwitLys1	05/22/96	12:05 pm	2,570	7.5	na	na
TwitLys2	05/22/96	10:40 am	4,120	5.8	17.6	na
TwitLys4	05/22/96	11:10 am	3,320	6.1	18.7	na
TwitLys1	06/19/96	10:10 am	2,580	6.4	26.0	na
TwitLys1	07/17/96	10:21 am	2,050	6.4	24.7	na
TwitLys2	07/17/96	10:19 am	1,450	6.6	25.1	na
TwitLys4	07/17/96	10:14 am	1,560	6.9	24.3	na
TwitLys2	08/07/96	09:35 am	1,687	6.0	27.3	na
TwitLys4	08/07/96	09:45 am	1,360	6.7	27.0	na
TwitLys1	08/20/96	10:23 am	1,541	6.0	25.8	na
TwitLys2	08/20/96	10:25 am	1,483	6.6	29.5	na
TwitLys4	08/20/96	11:04 am	1,255	6.7	32.7	na
TwitLys1	09/04/96	10:42 am	1,880	6.4	23	na
TwitLys2	09/04/96	10:45 am	1,000	6.8	27	na
TwitLys4	09/04/96	10:48 am	6,960	7.0	25.1	na
TwitLys1	01/02/97	na	na	na	na	na
TwitLys2	01/02/97	10:35 am	6,110	5.8	13.3	na
TwitLys4	01/02/97	10:40 am	6,780	6.0	14.7	na
TwitPiz1	02/06/96	11:00 am	2,360	5.8	14.7	na
TwitPiz1	02/06/96	12:30 pm	2,500	5.8	15.5	na
TwitPiz2	02/06/96	01:35 pm	3,010	5.9	14.2	na
TwitPiz4	02/07/96	01:00 pm	2,770	5.9	14.1	na
TwitPiz1	02/14/96	12:40 pm	2,670	5.7	15.1	na
TwitPiz2	02/14/96	01:35 pm	3,070	5.9	14.7	na
TwitPiz2	02/14/96	01:55 pm	3,070	5.9	14.7	na
TwitPiz4	02/14/96	02:13 pm	2,740	5.9	15.7	na
TwitPiz1	02/22/96	08:55 am	2,520	5.7	14.1	na
TwitPiz2	02/22/96	09:20 am	2,830	5.8	14.0	na
TwitPiz4	02/22/96	10:25 am	2,750	6.0	13.1	na
TwitPiz1	03/11/96	09:15 am	2,490	5.9	15.2	na
TwitPiz2	03/11/96	10:06 am	2,940	6.0	14.9	na
TwitPiz4	03/11/96	12:10 pm	2,720	5.8	15.5	na

Table A1. Field parameters measured for lysimeter, piezometer, and drainage ditch samples, Twitchell Island, California—Continued

Site	Date	Time	Specific conductance ($\mu\text{S}/\text{cm}$)	pH, water, field (standard units)	Temperature, water ($^{\circ}\text{C}$)	Dissolved oxygen (mg/L)
TwitPiz4	03/11/96	12:10 pm	2,640	5.8	15.5	na
TwitPiz1	04/10/96	09:35 am	2,540	6.0	15.6	na
TwitPiz1	04/10/96	09:35 am	2,540	6.0	15.6	na
TwitPiz2	04/10/96	10:00 am	3,130	6.0	16.1	na
TwitPiz4	04/10/96	11:05 am	3,280	6.1	15.7	na
TwitPiz1	05/22/96	10:20 am	2,480	6.0	17.5	na
TwitPiz2	05/22/96	10:40 am	3,210	5.9	16.7	na
TwitPiz4	05/22/96	11:30 am	3,080	5.8	17.2	na
TwitPiz4	05/22/96	11:30 am	3,080	5.8	17.2	na
TwitPiz1	06/19/96	10:05 am	1,320	6.2	20.3	na
TwitPiz2	06/19/96	10:35 am	2,590	6.1	18.6	na
TwitPiz2	06/19/96	10:35 am	2,590	6.1	18.6	na
TwitPiz4	06/19/96	12:20 pm	3,060	5.9	18.6	na
TwitPiz1	07/17/96	12:45 pm	1,920	5.9	21.3	na
TwitPiz2	07/17/96	02:00 pm	1,790	6.0	20.3	na
TwitPiz4	07/17/96	03:20 pm	1,550	5.8	21.3	na
TwitPiz1	08/07/96	10:20 am	1,317	6.0	27.3	na
TwitPiz2	08/07/96	10:45 am	1,740	6.0	23.7	na
TwitPiz4	08/15/96	01:09 pm	1,226	6.0	21.0	na
TwitPiz1	08/20/96	12:10 pm	1,388	6.1	21.2	na
TwitPiz2	08/20/96	10:26 am	1,510	6.0	21.6	na
TwitPiz2	08/20/96	10:26 am	1,510	6.0	21.6	na
TwitPiz4	08/20/96	02:10 pm	701	6.0	22.2	na
TwitPiz1	09/04/96	12:00 pm	1,382	6.0	21	2.94
TwitPiz2	09/04/96	12:45 pm	1,244	6.1	21	1.93
TwitPiz4	09/04/96	02:54 pm	906	6.2	21.4	1.4
TwitPiz1	10/23/96	10:45 am	1,454	5.3	18.7	.1
TwitPiz1	10/23/96	10:45 am	1,454	5.3	18.7	.1
TwitPiz2	10/23/96	11:45 am	1,317	6.2	19.3	.09
TwitPiz4	10/23/96	01:10 pm	984	6.2	19	.11
TwitPiz1	11/13/96	11:25 am	1,393	6.1	19.03	1.86
TwitPiz2	11/13/96	12:10 pm	1,427	6.1	18.05	.38
TwitPiz4	11/13/96	01:35 pm	1,305	6.0	17.6	na
TwitPiz1	01/02/97	11:35 am	2,717	6.0	14.1	.15
TwitPiz2	01/02/97	12:30 pm	2,912	6.0	14.6	.10
TwitDitch1	02/07/96	03:00 pm	1,067	6.0	na	na
TwitDitch1	02/14/96	02:35 pm	942	6.6	16.3	na
TwitDitch1	02/22/96	11:55 am	731	7.1	12.1	na
TwitDitch1	03/11/96	11:42 am	2,110	6.0	16.3	na
TwitDitch1	04/10/96	11:30 am	1,610	6.5	19.6	na
TwitDitch1	05/22/96	12:35 pm	1,460	6.5	27.1	na
TwitDitch1	06/19/96	02:50 pm	1,456	6.7	29.1	na
TwitDitch1	07/17/96	12:34 pm	810	6.3	23.7	na
TwitDitch1	08/15/96	02:27 pm	811	6.4	26.1	na
TwitDitch1	08/20/96	01:40 pm	321	6.4	29.0	na
TwitDitch1	09/04/96	01:40 pm	715	6.4	19.8	na
TwitDitch1	10/23/96	12:00 pm	713	6.5	13.3	na
TwitDitch1	11/13/96	01:30 pm	1,242	6.1	17.1	na

Table A2. Mineral data for lysimeter, piezometer, and drainage ditch samples, Twitchell Island, California

[Values are in milligrams per liter; °C , degrees Celsius; TwitLys, lysimeter; TwitPiz, piezometer; TwitDitch, ditch; na, not analyzed. Samples are from the California Department of Water Resources]

Site	Date	Hardness as CaCO ₃	Calcium, dis- solved	Magne- sium, dis- solved	Sodium, dis- solved	Potas- sium, dis- solved	Alka- linity, lab, as CaCO ₃	Sulfate, dis- solved	Chloride, dis- solved	Bromide	Solids, residue at 180°C	Boron, dis- solved
TwitLys1	02/06/96	908	179	112	230	9.1	na	584	467	0.44	na	na
TwitLys2	02/06/96	802	158	99	207	6.9	na	490	407	.52	na	na
TwitLys4	02/07/96	988	198	120	247	9.7	na	629	480	.4	na	na
TwitLys1	02/14/96	970	189	121	242	9.7	na	636	501	.7	na	0.4
TwitLys2	02/14/96	932	182	116	228	7.8	109	619	467	.72	1,820	.3
TwitLys4	02/14/96	1,060	210	130	256	10	na	741	509	.7	na	.3
TwitLys1	02/22/96	914	183	119	231	10	114	540	477	.59	1,930	.4
TwitLys2	02/22/96	886	181	111	222	7.7	114	562	431	.79	1,870	.3
TwitLys4	02/22/96	1,010	202	123	243	10	167	627	467	.7	2,280	.4
TwitLys1	03/11/96	915	180	113	229	9.3	na	543	461	.52	na	na
TwitLys2	03/11/96	876	171	109	253	8.0	na	536	445	.96	na	na
TwitLys4	03/11/96	1,070	214	130	252	10.4	na	688	515	.62	na	na
TwitLys1	04/10/96	1,130	226	137	258	9.3	187	778	526	.9	2,150	.5
TwitLys2	04/10/96	1,210	241	148	266	8.7	177	738	540	.82	2,320	.4
TwitLys4	04/10/96	1,330	268	160	300	9.9	na	891	609	.58	na	na
TwitLys2	05/22/96	1,400	280	170	308	9.3	190	876	640	1.04	2,940	.4
TwitLys1	08/20/96	447	102	54	158	5.9	na	313	253	na	na	.4
TwitLys2	01/02/97	2,140	447	250	537	14	92	1,540	1,160	.68	4,180	.4
TwitLys4	01/02/97	2,980	619	349	1,130	29	98	2,080	2,120	1.16	6,860	.9
TwitPiz1	02/06/96	834	166	102	214	8.0	130	510	422	.68	1,670	.5
TwitPiz1	02/06/96	825	164	101	207	8.2	128	509	419	.68	1,730	.5
TwitPiz2	02/06/96	1,110	218	138	276	7.4	114	781	556	.59	2,260	.6
TwitPiz4	02/07/96	1,010	197	126	242	8.8	111	715	483	.6	2,120	.4
TwitPiz1	02/14/96	903	177	112	243	6.5	119	620	479	.7	1,850	.7
TwitPiz2	02/14/96	1,110	220	137	281	7.4	128	730	550	.64	2,260	.4
TwitPiz2	02/14/96	1,120	221	138	282	7.4	126	743	552	.64	2,230	.4
TwitPiz4	02/14/96	1,030	202	127	260	8.5	132	684	505	.66	2,030	.4
TwitPiz1	02/22/96	892	176	110	249	6.9	123	578	452	.72	2,000	.7
TwitPiz2	02/22/96	1,120	223	138	273	7.8	136	729	534	.66	2,190	.4
TwitPiz4	02/22/96	1,040	206	127	264	8.9	141	682	475	.7	2,140	.4
TwitPiz1	03/11/96	854	169	105	246	7.4	139	556	431	.76	1,920	.7
TwitPiz2	03/11/96	1,150	229	141	280	8.0	145	762	537	.68	2,350	.5
TwitPiz4	03/11/96	1,140	226	139	267	9.5	165	713	516	.78	2,280	.5
TwitPiz4	03/11/96	1,140	226	139	269	9.6	165	704	516	.8	2,220	.5
TwitPiz1	04/10/96	908	179	112	232	8.4	172	584	436	.85	1,810	.6
TwitPiz1	04/10/96	917	181	113	170	8.4	170	588	440	.94	1,870	.5
TwitPiz2	04/10/96	1,300	260	158	313	8.8	162	852	603	.76	2,470	.5
TwitPiz4	04/10/96	1,400	280	171	319	9.3	183	944	657	.92	2,660	.4
TwitPiz1	05/22/96	844	170	102	213	9.0	214	511	415	.96	2,030	.3
TwitPiz2	05/22/96	1,240	246	152	296	9.1	207	795	586	.88	2,600	.4
TwitPiz4	05/22/96	1,340	268	163	312	9.0	219	866	604	1.01	2,110	.4
TwitPiz4	05/22/96	1,280	255	157	299	9.0	218	848	613	1.00	2,870	.4

Table A2. Mineral data for lysimeter, piezometer, and drainage ditch samples, Twitchell Island, California—Continued

Site	Date	Hardness as CaCO ₃	Calcium, dis- solved	Magne- sium, dis- solved	Sodium, dis- solved	Potas- sium, dis- solved	Alka- linity, lab, as CaCO ₃	Sulfate, dis- solved	Chloride, dis- solved	Bromide	Solids, residue at 180°C	Boron, dis- solved
TwitPiz1	06/19/96	353	74	41	86	8.0	210	58	221	0.72	725	0.2
TwitPiz2	06/19/96	1,040	212	125	260	9.3	242	624	496	.85	2,140	.3
TwitPiz2	06/19/96	1,040	209	126	251	9.2	225	657	501	.83	2,270	.3
TwitPiz4	06/19/96	1,260	251	153	296	8.8	239	795	563	1.02	2,620	.4
TwitPiz1	07/17/96	550	113	65	212	5.4	59	410	338	.37	1,420	.5
TwitPiz2	07/17/96	526	107	63	167	5.8	92	371	297	.4	1,290	.6
TwitPiz4	07/17/96	481	97	58	164	4.8	78	354	261	.37	1,200	.4
TwitPiz1	08/07/96	342	76	37	97	7.8	190	90	231	.71	787	.2
TwitPiz1	08/07/96	324	69	37	112	4.3	149	176	170	.47	832	.5
TwitPiz2	08/07/96	496	108	55	157	5.7	183	284	263	.68	1,200	.7
TwitPiz4	08/15/96	334	73	37	112	4.4	150	178	163	.45	832	.5
TwitPiz1	08/20/96	278	62	30	126	5.5	139	183	191	.52	834	.5
TwitPiz2	08/20/96	329	71	37	116	4.4	73	105	173	.44	840	.6
TwitPiz2	08/20/96	305	66	34	107	4.4	130	186	170	.42	798	.5
TwitPiz4	08/20/96	171	37	19	70	2.8	na	na	91	.24	495	.4
TwitPiz1	09/04/96	320	69	36	134	4.5	152	184	168	.59	912	.6
TwitPiz2	09/04/96	316	69	35	112	4.1	152	134	176	.54	791	.6
TwitPiz4	09/04/96	239	53	26	79	3.3	135	81	131	.47	607	.5
TwitPiz1	10/23/96	370	79	42	165	5.0	210	168	262	.91	1,140	.6
TwitPiz1	10/23/96	370	79	42	171	5.2	210	157	276	.92	1,060	.6
TwitPiz2	10/23/96	311	67	35	99	4.6	189	84	198	.7	794	.5
TwitPiz4	10/23/96	268	58	30	85	3.7	179	40	175	.72	676	.4
TwitPiz1	11/13/96	363	78	41	129	5.3	269	104	215	1.01	977	.5
TwitPiz2	11/13/96	382	82	43	115	4.6	252	116	210	.84	987	.6
TwitPiz4	11/13/96	357	77	40	102	4.0	258	89	186	.83	832	.5
TwitPiz1	01/02/97	785	166	90	236	10	167	630	431	.77	1,930	.5
TwitPiz2	01/02/97	942	199	108	220	6.8	173	677	498	.76	2,100	.7
TwitPiz4	01/02/97	942	201	107	215	6.5	185	606	479	na	1,970	.6
TwitPiz8	01/02/97	na	na	na	na	na	na	na	na	na	na	na
TwitPiz9	01/02/97	836	164	84	180	6.8	279	423	449	.91	1,760	.6
TwitDitch1	02/07/96	348	75	39	81	5.9	24	319	100	.12	748	.2
TwitDitch1	02/14/96	315	67	36	76	7.7	36	270	102	.13	688	.2
TwitDitch1	02/22/96	245	52	28	57	7.6	48	193	80	.11	520	.2
TwitDitch1	03/11/96	807	165	96	183	5.1	76	584	324	.41	1,650	.4
TwitDitch1	04/10/96	829	111	134	59	3.3	53	389	263	.57	1,120	na
TwitDitch1	05/22/96	518	102	64	115	3.4	74	295	270	.85	1,080	.3
TwitDitch1	06/19/96	512	96	66	103	3.9	142	16	391	1.63	1,020	.4
TwitDitch1	07/17/96	493	102	58	134	3.1	101	292	247	.42	1,110	.6
TwitDitch1	08/15/96	223	48	25	61	2.3	89	73	135	.53	604	.7
TwitDitch1	08/20/96	66	13	8	30	2.2	30	34	48	.17	220	.2
TwitDitch1	09/04/96	182	38	21	61	3.4	123	14	131	.55	512	.5
TwitDitch1	10/23/96	186	38	22	66	4.9	119	8	156	.61	519	.3
TwitDitch1	11/13/96	357	72	43	92	4.9	174	22	266	1.11	793	.3
TwitDitch1	01/02/97	513	113	56	112	8.8	26	440	206	.21	1,120	.2

Table A3. Lysimeter, piezometer, and drainage ditch sample results for speciation of trihalomethane formation potential and associated parameters, Twitchell Island, California

[CHCl₃, chloroform; CHCl₂Br, bromodichloromethane; CHBr₂Cl, chlorodibromomethane; CHBr₃, bromoform; TwitLys, lysimeter; TwitPiz, piezometer; TwitDitch, ditch; na, not analyzed; <, less than. Values in micrograms per liter, except ultraviolet absorbance, which is in per centimeter units. Trihalomethane formation potential determined using dose-based method, unless otherwise noted in Method column. Samples from the California Department of Water Resources]

Site	Date	CHCl ₃	CHCl ₂ Br	CHBr ₂ Cl	CHBr ₃	Dissolved organic carbon	Trihalomethane formation potential	Ultra-violet absorbance	Halo-acetic acid 1	Halo-acetic acid 2	Halo-acetic acid 3	Halo-acetic acid 4	Halo-acetic acid 5	Halo-acetic acid 6	Method
TwitLys1	02/14/96	4,800	420	50	50	58.3	5,320	2.27	na	na	na	na	na	na	
TwitLys2	02/14/96	3,600	450	58	40	46.2	4,148	1.53	na	na	na	na	na	na	
TwitLys4	02/14/96	4,800	440	60	60	61.8	5,360	2.63	na	na	na	na	na	na	
TwitLys1	02/22/96	5,300	530	60	60	63.3	5,950	2.64	na	na	na	na	na	na	
TwitLys2	02/22/96	4,100	480	52	40	48.7	4,672	1.68	na	na	na	na	na	na	
TwitLys4	02/22/96	5,900	420	60	60	64.6	6,440	2.78	na	na	na	na	na	na	
TwitLys1	04/10/96	8,600	720	80	80	85.2	9,480	3.98	na	na	na	na	na	na	
TwitLys2	04/10/96	6,200	600	60	60	65.5	6,920	2.51	na	na	na	na	na	na	
TwitLys4	04/10/96	7,200	630	60	60	73.6	7,950	na	na	na	na	na	na	na	
TwitLys2	05/22/96	6,100	700	60	60	78.7	6,920	2.92	na	na	na	na	na	na	
TwitLys4	05/22/96	6,200	610	80	80	71.6	6,970	na	na	na	na	na	na	na	
TwitLys1	07/17/96	na	na	na	na	na	na	.159	na	na	na	na	na	na	
TwitLys1	08/20/96	5,300	360	26	0	63.6	5,686	na	na	na	na	na	na	na	
TwitLys1	09/04/96	8,800	550	<80	<80	92.6	9,350	na	na	na	na	na	na	na	
TwitLys2	09/04/96	4,600	240	<60	<60	42.8	4,840	na	na	na	na	na	na	na	
TwitLys4	09/04/96	5,100	250	<60	<60	47.5	5,350	na	na	na	na	na	na	na	
TwitLys1	01/02/97	na	na	na	na	na	na	na	na	na	na	na	na	na	
TwitLys2	01/02/97	5,200	500	<60	<60	76	5,700	2.7	na	na	na	na	na	na	
TwitLys2	01/02/97	4,900	550	<60	<60	76	5,450	2.7	<60	<60	<60	<60	2,300	2,300	Reactivity-based
TwitLys4	01/02/97	9,300	850	<80	<80	139	10,150	4.07	na	na	na	na	na	na	
TwitLys4	01/02/97	9,200	930	<80	<80	139	10,130	4.07	<80	<80	<80	<80	4,500	5,300	Reactivity-based
TwitPiz1	02/06/96	4,600	430	60	60	71.3	5,150	2.540	na	na	na	na	na	na	
TwitPiz1	02/06/96	4,700	420	60	60	61.0	5,240	2.530	na	na	na	na	na	na	
TwitPiz2	02/06/96	5,200	420	60	60	65.5	5,740	2.610	na	na	na	na	na	na	
TwitPiz4	02/07/96	4,500	410	50	50	58.7	5,010	2.480	na	na	na	na	na	na	
TwitPiz1	02/14/96	5,400	420	70	70	68.8	5,960	3.130	na	na	na	na	na	na	
TwitPiz2	02/14/96	5,100	390	60	60	64.4	5,610	2.840	na	na	na	na	na	na	
TwitPiz2	02/14/96	5,000	400	60	60	65.4	5,520	2.880	na	na	na	na	na	na	
TwitPiz4	02/14/96	4,500	410	60	60	60.0	5,030	2.580	na	na	na	na	na	na	
TwitPiz1	02/22/96	6,700	450	70	70	73.1	7,290	3.420	na	na	na	na	na	na	
TwitPiz2	02/22/96	6,100	430	60	60	66.9	6,650	2.970	na	na	na	na	na	na	

Table A3. Lysimeter, piezometer, and drainage ditch sample results for speciation of trihalomethane formation potential and associated parameters, Twitchell Island, California—Continued

Site	Date	CHCl ₃	CHCl ₂ Br	CHBr ₂ Cl	CHBr ₃	Dissolved organic carbon	Trihalo-methane formation potential	Ultra-violet absorbance	Halo-acetic acid 1	Halo-acetic acid 2	Halo-acetic acid 3	Halo-acetic acid 4	Halo-acetic acid 5	Halo-acetic acid 6	Method
TwitPiz4	02/22/96	6,000	440	60	60	63.0	6,560	2.760	na	na	na	na	na	na	
TwitPiz1	03/11/96	7,400	540	80	80	78.4	8,100	3.720	na	na	na	na	na	na	
TwitPiz2	03/11/96	6,800	490	70	70	70.0	7,430	3.130	na	na	na	na	na	na	
TwitPiz4	03/11/96	6,800	550	70	70	69.7	7,490	2.940	na	na	na	na	na	na	
TwitPiz4	03/11/96	6,800	580	70	70	69.6	7,520	2.960	na	na	na	na	na	na	
TwitPiz6	03/21/96	1,500	190	20	20	10.4	1,730	.759	na	na	na	na	na	na	
TwitPiz7	03/21/96	4,900	300	60	60	39.3	5,320	2.540	na	na	na	na	na	na	
TwitPiz1	04/10/96	7,500	620	80	80	77.7	8,280	3.640	na	na	na	na	na	na	
TwitPiz1	04/10/96	8,000	570	<80	<80	77.4	8,570	3.660	na	na	na	na	na	na	
TwitPiz2	04/10/96	8,300	450	80	80	78.1	8,910	3.980	na	na	na	na	na	na	
TwitPiz4	04/10/96	7,300	540	80	80	78.3	8,000	3.430	na	na	na	na	na	na	
TwitPiz5	04/11/96	1,400	200	20	20	10.1	1,640	.769	na	na	na	na	na	na	
TwitPiz6	04/11/96	3,600	420	50	50	27.9	4,120	1.960	na	na	na	na	na	na	
TwitPiz7	04/11/96	9,800	680	90	90	85.4	10,660	4.240	na	na	na	na	na	na	
TwitPiz1	05/22/96	6,300	600	80	80	75.4	7,060	3.560	na	na	na	na	na	na	
TwitPiz2	05/22/96	8,100	580	0	90	86.4	8,770	4.080	na	na	na	na	na	na	
TwitPiz4	05/22/96	7,200	600	80	80	86.8	7,960	3.710	na	na	na	na	na	na	
TwitPiz4	05/22/96	7,400	570	80	80	85.6	8,130	3.650	na	na	na	na	na	na	
TwitPiz5	05/28/96	1,200	180	20	20	10.6	1,420	.814	na	na	na	na	na	na	
TwitPiz6	05/28/96	7,100	610	120	120	77.3	7,950	5.730	na	na	na	na	na	na	
TwitPiz7	05/28/96	15,100	2,800	410	250	171.4	18,560	12.300	na	na	na	na	na	na	
TwitPiz1	06/19/96	1,600	400	120	30	20.4	2,150	1.180	na	na	na	na	na	na	
TwitPiz2	06/19/96	7,900	650	100	100	86.2	8,750	5.370	na	na	na	na	na	na	
TwitPiz2	06/19/96	8,100	630	100	100	86.9	8,930	5.340	na	na	na	na	na	na	
TwitPiz4	06/19/96	10,100	800	100	100	96.6	11,100	5.030	na	na	na	na	na	na	
TwitPiz5	06/20/96	1,400	220	29	20	11.7	1,669	.857	na	na	na	na	na	na	
TwitPiz6	06/20/96	6,500	620	100	100	67.0	7,320	5.040	na	na	na	na	na	na	
TwitPiz7	06/20/96	21,100	2,700	330	300	207.9	24,430	13.340	na	na	na	na	na	na	
TwitPiz1	07/17/96	4,800	350	0	0	49.9	5,150	2.320	na	na	na	na	na	na	
TwitPiz2	07/17/96	4,500	340	0	0	44.5	4,840	2.310	na	na	na	na	na	na	
TwitPiz4	07/17/96	4,500	310	0	0	49.0	4,810	2.260	na	na	na	na	na	na	
TwitPiz5	07/17/96	1,100	240	44	0	8.3	1,384	.686	na	na	na	na	na	na	
TwitPiz6	07/17/96	6,800	630	0	0	59.1	7,430	4.860	na	na	na	na	na	na	
TwitPiz7	07/17/96	18,200	2,000	0	0	155.6	20,200	15.700	na	na	na	na	na	na	
TwitPiz1	08/07/96	2,200	390	85	0	24.8	2,675	1.550	na	na	na	na	na	na	

Table A3. Lysimeter, piezometer, and drainage ditch sample results for speciation of trihalomethane formation potential and associated parameters, Twitchell Island, California—Continued

Site	Date	CHCl ₃	CHCl ₂ Br	CHBr ₂ Cl	CHBr ₃	Dissolved organic carbon	Trihalo-methane formation potential	Ultra-violet absorbance	Halo-acetic acid 1	Halo-acetic acid 2	Halo-acetic acid 3	Halo-acetic acid 4	Halo-acetic acid 5	Halo-acetic acid 6	Method
TwitPiz1	08/07/96	7,400	370	0	0	73.3	7,770	3.960	na	na	na	na	na	na	
TwitPiz2	08/07/96	7,400	450	0	0	76.6	7,850	4.630	na	na	na	na	na	na	
TwitPiz4	08/15/96	7,100	350	0	0	70.3	7,450	3.890	na	na	na	na	na	na	
TwitPiz5	08/16/96	1,100	250	48	0	9.0	1,398	.718	na	na	na	na	na	na	
TwitPiz6	08/16/96	11,900	800	0	0	99.8	12,700	7.890	na	na	na	na	na	na	
TwitPiz7	08/16/96	19,900	2,400	290	0	172.0	22,590	11.720	na	na	na	na	na	na	
TwitPiz1	08/20/96	4,900	350	0	0	55.9	5,250	2.960	na	na	na	na	na	na	
TwitPiz2	08/20/96	6,400	320	0	0	65.6	6,720	3.770	na	na	na	na	na	na	
TwitPiz2	08/20/96	6,400	320	0	0	64.4	6,720	3.580	na	na	na	na	na	na	
TwitPiz4	08/20/96	4,700	200	0	0	48.3	4,900	2.700	na	na	na	na	na	na	
TwitPiz1	09/04/96	8,200	470	<90	<90	82.8	8,670	4.420	na	na	na	na	na	na	
TwitPiz2	09/04/96	6,900	390	<90	<90	69.9	7,290	4.190	na	na	na	na	na	na	
TwitPiz4	09/04/96	6,800	340	<80	<80	65.0	7,140	3.760	na	na	na	na	na	na	
TwitPiz5	09/04/96	970	270	66	<20	8.4	1,306	.629	na	na	na	na	na	na	
TwitPiz6	09/04/96	9,300	510	<80	<80	94.5	9,810	na	na	na	na	na	na	na	
TwitPiz1	10/23/96	7,900	710	<100	<100	96.2	8,610	5.240	na	na	na	na	na	na	Reactivity-based
TwitPiz1	10/23/96	8,000	710	<100	<100	96.2	8,710	5.260	na	na	na	na	na	na	Reactivity-based
TwitPiz2	10/23/96	4,800	500	<80	<80	59.3	5,300	3.960	na	na	na	na	na	na	Reactivity-based
TwitPiz4	10/23/96	4,300	490	<70	<70	50.6	4,790	3.320	na	na	na	na	na	na	Reactivity-based
TwitPiz5	10/23/96	560	270	96	<10	6.8	926	.556	na	na	na	na	na	na	Reactivity-based
TwitPiz1	11/13/96	5,800	610	<80	<80	75.7	6,410	3.940	na	na	na	na	na	na	
TwitPiz1	11/13/96	5,000	620	<80	<80	75.7	5,620	3.940	na	na	na	na	na	na	Reactivity-based
TwitPiz2	11/13/96	5,800	530	<100	<100	71.6	6,330	4.540	na	na	na	na	na	na	
TwitPiz2	11/13/96	5,300	560	<100	<100	71.6	5,860	4.540	na	na	na	na	na	na	Reactivity-based
TwitPiz4	11/13/96	5,600	540	<90	<90	67.7	6,140	4.260	na	na	na	na	na	na	
TwitPiz4	11/13/96	4,900	580	<90	<90	67.7	5,480	4.260	na	na	na	na	na	na	Reactivity-based
TwitPiz5	11/13/96	490	230	94	<10	5.8	814	.433	na	na	na	na	na	na	
TwitPiz5	11/13/96	320	200	99	<10	5.8	619	.433	na	na	na	na	na	na	Reactivity-based
TwitPiz6	11/13/96	12,000	890	<150	<150	132.0	12,890	8.78	na	na	na	na	na	na	
TwitPiz6	11/13/96	10,000	800	<180	<180	132.0	10,800	8.78	na	na	na	na	na	na	Reactivity-based
TwitPiz1	01/02/97	6,500	520	<90	<90	85.4	7,020	4.44	na	na	na	na	na	na	
TwitPiz1	01/02/97	5,400	560	<90	<90	85.4	5,960	4.44	<90	<90	<90	<90	3,400	5,400	Reactivity-based
TwitPiz2	01/02/97	7,300	560	<100	<100	78.3	7,860	5.27	na	na	na	na	na	na	
TwitPiz2	01/02/97	5,700	570	<100	<100	78.3	6,270	5.27	<100	<100	<100	<100	3,300	5,000	Reactivity-based
TwitPiz4	01/02/97	6,200	580	<100	<100	68.2	6,780	4.56	na	na	na	na	na	na	

Table A3. Lysimeter, piezometer, and drainage ditch sample results for speciation of trihalomethane formation potential and associated parameters, Twitchell Island, California—Continued

Site	Date	CHCl ₃	CHCl ₂ Br	CHBr ₂ Cl	CHBr ₃	Dissolved organic carbon	Trihalo-methane formation potential	Ultra-violet absor-bance	Halo-acetic acid 1	Halo-acetic acid 2	Halo-acetic acid 3	Halo-acetic acid 4	Halo-acetic acid 5	Halo-acetic acid 6	Method
TwitPiz4	01/02/97	4,900	580	<100	<100	68.2	5,480	4.56	<100	<100	<100	<100	2,400	3,000	Reactivity-based
TwitPiz5	01/02/97	na	na	na	na	na	na	na	na	na	na	na	na	na	
TwitPiz6	01/02/97	2,700	180	<30	<30	35.2	2,880	1.26	na	na	na	na	na	na	Reactivity-based
TwitPiz6	01/02/97	2,600	210	<30	<30	35.2	2,810	1.26	<30	<30	<30	<30	1,600	2,300	
TwitPiz6	01/02/97	na	na	na	na	na	na	na	na	na	na	na	na	na	
TwitPiz7	01/02/97	na	na	na	na	na	na	na	na	na	na	na	na	na	
TwitPiz8	01/02/97	na	na	na	na	na	na	na	na	na	na	na	na	na	
TwitPiz9	01/02/97	4,900	530	<100	<100	74.6	5,430	5.35	na	na	na	na	na	na	Reactivity-based
TwitPiz9	01/02/97	4,600	600	<100	<100	74.6	5,200	5.35	<100	<100	<100	<100	2,200	2,700	
TwitDitch1	02/07/96	2,300	110	40	40	27.4	2,490	1.000	na	na	na	na	na	na	
TwitDitch1	02/14/96	2,600	120	30	30	28.9	2,780	1.070	na	na	na	na	na	na	
TwitDitch1	02/22/96	2,800	78	30	30	29.1	2,938	1.100	na	na	na	na	na	na	
TwitDitch1	03/11/96	5,200	330	60	60	52.6	5,650	2.300	na	na	na	na	na	na	
TwitDitch1	04/10/96	3,300	400	59	30	32.1	3,789	1.280	na	na	na	na	na	na	
TwitDitch1	05/22/96	2,600	440	72	30	31.3	3,142	1.140	na	na	na	na	na	na	
TwitDitch1	06/19/96	540	470	400	75	10.0	1,485	.404	na	na	na	na	na	na	
TwitDitch1	07/17/96	4,500	330	0	0	42.5	4,830	2.890	na	na	na	na	na	na	
TwitDitch1	08/15/96	5,500	360	0	0	48.9	5,860	4.290	na	na	na	na	na	na	
TwitDitch1	08/20/96	2,600	130	0	0	22.3	2,730	1.180	na	na	na	na	na	na	
TwitDitch1	09/04/96	5,100	360	<70	<70	44.8	5,460	3.150	na	na	na	na	na	na	
TwitDitch1	10/23/96	1,300	380	91	<40	15.7	1,771	1.580	na	na	na	na	na	na	Reactivity-based
TwitDitch1	11/13/96	1,100	460	200	<20	17.0	1,760	.956	na	na	na	na	na	na	
TwitDitch1	11/13/96	830	440	260	<20	17.0	1,530	.956	na	na	na	na	na	na	Reactivity-based
TwitDitch1	01/02/97	2,800	190	<30	<30	35.4	2,990	1.26	na	na	na	na	na	na	
TwitDitch1	01/02/97	2,600	210	<30	<30	35.4	2,810	1.26	<30	<30	<30	<30	1,600	2,600	Reactivity-based

Table A4. Iron, manganese, and nitrogen species (as N) data for lysimeter, piezometer, and drainage ditch samples, Twitchell Island, California

[Values are in milligrams per liter; TwitLys, lysimeter; TwitPiz, piezometer; TwitDitch, ditch; na, not analyzed <, less than. Samples are from the California Department of Water Resources]

Site	Date	Nitrate, dissolved (as N)	Nitrite plus Nitrate, dissolved (as N)	Nitrogen, ammonia, dissolved (as N)	Iron	Manganese, dissolved
TwitLys2	05/22/96	3.5	na	na	na	na
TwitLys1	01/02/97	na	na	na	na	na
TwitLys2	01/02/97	10	2.3	0.86	na	na
TwitLys4	01/02/97	49	11	.62	na	na
TwitPiz1	05/22/96	40	na	na	na	na
TwitPiz2	05/22/96	1.5	na	na	na	na
TwitPiz2	05/22/96	1.4	na	na	na	na
TwitPiz4	05/22/96	2.5	na	na	na	na
TwitPiz1	07/17/96	.8	.03	1.90	5.66	0.115
TwitPiz2	07/17/96	.8	0	2.90	9.46	.129
TwitPiz4	07/17/96	1.2	.01	1.10	4.31	.712
TwitPiz1	08/07/96	<.1	0	13.00	8.8	1.81
TwitPiz1	08/07/96	<.1	0	2.20	8.2	1.3
TwitPiz2	08/07/96	<.1	0	4.40	20.7	1.74
TwitPiz4	08/15/96	.2	0	2.00	6.2	1.26
TwitPiz1	08/20/96	8.8	0	8.40	9.2	1.55
TwitPiz2	08/20/96	.1	0	3.40	14.6	1.23
TwitPiz2	08/20/96	3.3	0	3.40	12.2	1.14
TwitPiz4	08/20/96	1.3	0	1.20	5.7	.619
TwitPiz1	09/04/96	8.9	.29	2.10	9.4	1.18
TwitPiz2	09/04/96	13	na	3.20	16.8	1.05
TwitPiz4	09/04/96	5.9	.03	1.30	8	.881
TwitPiz1	10/23/96	2.2	.52	3.00	na	na
TwitPiz2	10/23/96	na	.02	2.10	13.9	.92
TwitPiz4	10/23/96	<.1	.02	2.20	10.8	1.02
TwitPiz1	11/13/96	40	na	6.30	8.9	1.42
TwitPiz2	11/13/96	27	na	4.20	18.3	1.21
TwitPiz4	11/13/96	15	na	2.80	14.4	1.33
TwitPiz1	01/02/97	.4	.16	3.0	na	na
TwitPiz2	01/02/97	<.1	<.01	5.0	na	na
TwitPiz4	01/02/97	.2	.07	3.7	na	na
TwitPiz8	01/02/97	na	na	na	na	na
TwitPiz9	01/02/97	<.1	<.01	10	na	na
TwitDitch1	05/22/96	9.6	na	na	na	na
TwitDitch1	07/17/96	1.7	0	.90	11.3	.767
TwitDitch1	08/15/96	1	0	.88	27.8	1.28
TwitDitch1	08/20/96	.6	.05	.28	1.4	.352
TwitDitch1	09/04/96	.4	.02	.62	9.1	.578
TwitDitch1	10/23/96	<.1	.02	2.70	11	.832
TwitDitch1	11/13/96	13	na	2.60	3.66	1.15
TwitDitch1	01/02/97	55	13	1.0	na	na

APPENDIX B: DISSOLVED ORGANIC CARBON AND ULTRAVIOLET ABSORPTION MEASUREMENTS

Filtered (0.45 µm) samples collected for the measurement of DOC and UVA at 254 nm were packed in ice and shipped to the USGS Laboratory in Boulder, Colo. DOC measurements were made with an OI model 700 total organic carbon analyzer. UVA measurements were made with a Hewlett Packard 8453 spectrophotometer. All measurements were made within 1 week of sample collection. The DOC, UVA, and SUVA data collected during the study are presented in tables B1, B2, and B3 respectively. SUVA is calculated by dividing the UVA values by the DOC concentration. This normalizes the UVA data to carbon and represents the amount of aromaticity per milligram of DOC in a sample.

Quality assurance/quality control (QA/QC) for the DOC and UVA measurements consisted of selecting two or three samples at random and analyzing another sample aliquot (split) at the end of a set of analyses. The QA/QC data and summary statistics for the DOC and UVA measurements are presented in tables B4 and B5 respectively. The difference between a sample and its split can be used to distinguish differences between sample analyses that are significant from those differences caused by random error, which occur in every measurement. For example, if the difference in DOC concentration or UVA between any two samples is less than or equal to the mean differences in tables B4 and B5, then that difference is a result of random error and the samples have essentially the same value. Only if the difference between two samples is greater than the mean difference listed in tables B4 and B5 can we be confident that a significant difference in DOC or UVA values exists.

Table B1. Dissolved organic carbon concentrations for lysimeter, piezometer, and drainage ditch samples, Twitchell Island, California
 [Values are in milligrams per liter; na, not analyzed]

Date	Lysimeter 1	Lysimeter 2	Lysimeter 4	Piezometer 1	Piezometer 2	Piezometer 4	Ditch
02/06/96	54.1	42.1	51.9	61.4	63.2	60.1	24.5
02/14/96	58.8	44.2	62.3	69.0	66.0	60.8	26.1
02/22/96	61.0	46.4	63.8	71.4	65.1	59.6	27.7
03/11/96	68.1	69.2	65.6	79.3	68.6	70.6	54.9
04/10/96	80.1	64.5	68.6	75.6	77.9	78.9	34.1
05/22/96	na	77.0	70.8	73.3	83.1	82.0	19.9
06/19/96	45.5	46.3	na	20.8	82.4	93.0	9.8
07/17/96	52.7	42.1	54.5	50.0	44.2	49.3	42.2
08/14/96	na	63.3	na	25.8	72.7	69.0	
09/04/96	91.7	42.9	na	82.3	66.4	63.9	40.2
10/23/96	121.3	41.7	na	87.0	51.8	45.4	14.9
11/13/96	128.3	80.6	38.1	78.1	71.9	69.2	17.0
12/11/96	66.8	22.1	50.4	82.8	69.5	78.2	na
01/02/97	65.9	21.4	48.1	81.6	76.3	77.6	33

Table B2. Ultraviolet absorbance data for lysimeter, piezometer, and drainage ditch samples, Twitchell Island, California

[Values are in per centimeter; na, not analyzed. Ultraviolet absorbance at 254 nanometers]

Date	Lysimeter 1	Lysimeter 2	Lysimeter 4	Piezometer 1	Piezometer 2	Piezometer 4	Ditch
02/06/96	1.714	1.290	1.831	2.464	2.478	2.338	0.951
02/14/96	2.220	1.510	2.546	3.280	2.970	2.580	1.034
02/22/96	2.578	1.647	2.770	3.424	3.002	2.689	1.072
03/11/96	2.867	2.495	2.521	3.592	3.005	2.927	2.350
04/10/96	3.588	2.490	2.606	4.046	3.788	3.352	1.204
05/22/96	na	2.740	2.753	3.620	4.116	3.718	.830
06/19/96	1.892	1.362	na	.920	3.920	3.764	.368
07/17/96	2.164	1.720	2.080	2.414	2.204	2.330	1.887
08/14/96	na	2.894	na	1.540	4.128	3.762	na
09/04/96	4.212	1.170	na	4.036	3.934	3.690	2.021
10/23/96	5.227	2.116	na	4.523	3.201	3.026	1.595
11/13/96	6.010	3.401	1.317	3.654	4.253	3.814	.913
12/11/96	2.730	.983	2.139	4.676	4.634	4.563	na
01/02/97	na	2.475	3.934	3.781	3.532	3.220	1.201

Table B3. Specific ultraviolet absorbance data for lysimeter, piezometer, and drainage ditch samples, Twitchell Island, California

[Values are in liter per centimeter per milligram; na, not applicable. Ultraviolet absorbance at 254 nanometers]

Date	Lysimeter 1	Lysimeter 2	Lysimeter 4	Piezometer 1	Piezometer 2	Piezometer 4	Ditch
02/06/96	0.032	0.031	0.035	0.040	0.039	0.039	0.039
02/14/96	.038	.034	.041	.048	.045	.042	.040
02/22/96	.042	.035	.043	.048	.046	.045	.039
03/11/96	.042	.036	.038	.045	.044	.041	.043
04/10/96	.045	.039	.038	.054	.049	.042	.035
05/22/96	na	.036	.039	.049	.050	.045	.042
06/19/96	.042	.029	na	.044	.048	.040	.038
07/17/96	.041	.041	.038	.048	.050	.047	.045
08/14/96	na	.046	na	.060	.057	.055	na
09/04/96	.046	.027	na	.049	.059	.058	.050
10/23/96	.043	.051	na	.052	.062	.067	.107
11/13/96	.047	.042	.035	.047	.059	.055	.054
12/11/96	.041	.044	.042	.056	.067	.058	na
01/02/97	na	.116	.082	.046	.046	.041	.036

Table B4. Quality assurance and quality control for dissolved organic carbon data, Twitchell Island, California

[Values are in milligrams per liter]

Site	Date	Sample dissolved organic carbon	Split dissolved organic carbon	Difference
Piezometer 1	02/07/96	61.4	61.0	0.4
Piezometer 2	02/14/96	66.0	66.8	.8
Piezometer 4	03/11/96	70.6	71.5	.9
Piezometer 1	04/10/96	75.6	74.8	.8
Lysimeter 2	05/22/96	77.0	77.4	.4
Piezometer 4	05/22/96	82.0	84.1	2.1
Ditch	05/22/96	19.9	21.7	1.8
Lysimeter 2	06/19/96	46.3	46.4	.1
Piezometer 2	06/19/96	82.4	82.6	.2
Piezometer 2	06/19/96	82.4	85.6	3.2
Ditch	06/19/96	9.8	9.8	.0
Lysimeter 1	07/17/96	52.7	51.8	.9
Lysimeter 4	07/17/96	54.5	53.5	1.0
Pump	07/17/96	14.1	14.1	.0
Lysimeter 2	08/14/96	63.3	67.1	3.8
Piezometer 2	08/14/96	72.7	72.5	.2
Piezometer 2	08/14/96	72.7	72.8	.1
Piezometer 1	09/04/96	82.3	80.4	1.9
Ditch	09/04/96	40.2	41.0	.8
Lysimeter 1	10/23/96	121.3	119.0	2.3
Piezometer 1	10/23/96	87.0	87.7	.7
Ditch	10/23/96	14.9	15.4	.5
Lysimeter 4	11/13/96	38.1	38.7	.6
Piezometer 4	11/13/96	69.2	67.5	1.7
Pump	11/13/96	5.8	5.8	.0
Lysimeter 4	01/02/97	48.1	49.8	1.7
Piezometer 4	01/02/97	77.6	79.3	1.7
Mean difference				1.1
Standard deviation				1.01
95 percent confidence interval about the mean				1.1 (\pm) 0.4

Table B5. Quality assurance and quality control for ultraviolet absorbance data, Twitchell Island, California

[Values are in per centimeter]

Site	Date	Sample ultraviolet absorbance	Split ultraviolet absorbance	Difference
Piezometer 1	02/07/96	2.464	2.462	0.002
Lysimeter 3	02/14/96	1.786	1.806	.020
Piezometer 2	02/14/96	2.970	3.013	.043
Lysimeter 3	02/22/96	1.958	2.061	.103
Piezometer 3	02/22/96	2.568	2.468	.100
Piezometer 4	03/11/96	2.927	2.930	.003
Piezometer 1	04/10/96	4.046	3.906	.140
Lysimeter 2	05/22/96	2.740	2.738	.002
Piezometer 4	05/22/96	3.718	3.680	.038
Ditch	05/22/96	.830	.830	.000
Lysimeter 2	06/19/96	1.362	1.390	.028
Piezometer 2	06/19/96	3.920	4.232	.312
Piezometer 2	06/19/96	3.920	4.050	.130
Ditch	06/19/96	.368	.377	.009
Lysimeter 1	07/17/96	2.164	2.152	.012
Pump	07/17/96	.691	.636	.055
Lysimeter 1	10/23/96	5.227	5.287	.060
Piezometer 1	10/23/96	4.523	4.517	.006
Ditch	10/23/96	1.595	1.600	.005
Lysimeter 4	11/13/96	1.317	1.316	.001
Piezometer 4	11/13/96	3.814	3.737	.077
Pump	11/13/96	.313	.313	.000
			Mean difference	0.052
			Standard deviation	0.073
			95 percent confidence interval about the mean	0.052 (±) 0.032

APPENDIX C: DISSOLVED ORGANIC CARBON FRACTIONATION AND ISOLATION

A major component of this study involved the fractionation (separation) of the DOC into five operationally defined categories and the isolation of the organic matter of two of these categories for analysis by ^{13}C -NMR spectroscopy. These techniques are necessary in the investigation of the role of organic compounds in geochemical processes because the reactivity of an organic compound is determined by its structure, and the DOC content of surface and ground water is composed of thousands of individual compounds, each with its own unique structure. Structure refers to molecular weight and the relative amount of functional groups (carboxylic acid, ether, amine, and so forth). Because each compound has a unique structure and many of these compounds are present in low concentrations, the fractionation and subsequent identification of all compounds individually is impractical. However, it is possible to fractionate compounds with similar structures together into the following operationally defined categories: HPOA, hydrophobic neutrals (HPON), HPIA, hydrophilic neutrals (HPIN), and low molecular weight hydrophilic acids. This fractionation was accomplished with the use of XAD-8 and XAD-4 resin. A description of the physical and chemical properties of these resins is given in Aiken and others (1992).

The HPOA and HPIA 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 k' is 50 for the column, 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," and they define HPIA "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." The capacity factor, k' , is the grams of solute on resin per gram of solute in column void volume.

The ability to isolate compounds that possess similar structures greatly facilitates the study of THM formation. Because the compounds in each operationally defined category have similar structures, each category of organic carbon will react differently with chlorine. For example, Rook (1977) and Reckhow and

others (1990) have suggested that the formation of THMs is a result of the reaction of chlorine with aromatic rings in humic substances. Humic substances are classified among the HPOA and are defined as an extremely complex and diverse group of poorly biodegradable decomposition products and byproducts of natural organic matter, which are produced by both plants and animals and whose structure is not well defined (Snoeyink and Jenkins, 1980). Thus, by being able to fractionate the portion of the DOC that is reactive with chlorine, its overall structure can be determined, and the amount of the total DOC that it constitutes can be calculated. This fractionation will lead to a better understanding of the processes controlling the formation and seasonal variability of THM precursors in a given environment and the development of possible land and water use strategies that can be employed to keep the formation of THMs to a minimum.

Samples collected for fractionation and isolation were filtered (0.45 μm) in the field into stainless steel containers, shipped in ice to the USGS Laboratory in Boulder, Colo. and refrigerated until they were fractionated on the columns. The piezometer samples were fractionated on 295-mL capacity columns. These columns process sample volumes of 15 L with a DOC concentration of no greater than 20 mg/L for maximum adsorption efficiency. The piezometer samples always had concentrations greater than 20 mg/L so they were diluted with 0.01 normality (N) HCl to a concentration of about 15 to 20 mg/L before being run on the column. The samples were acidified to pH 2 by the addition of 12.1 N HCl before they were run on the columns. Acidifying the sample enhances adsorption on the nonionic resin by neutralizing negatively charged species. After acidification, the samples were run on the two XAD resin columns connected in series with Teflon tubing at a constant rate of 60 mL/min. Samples were run through the XAD-8 column first and then through the XAD-4 column. To ensure collection of a sufficient amount of material for analysis by ^{13}C -NMR spectroscopy, enough sample was collected to fractionate each sample through two sets of columns concurrently. After all of the sample was run through the columns, each column was separately back eluted with 0.1 N NaOH to desorb the material adsorbed on the column. One liter of 0.1 N NaOH was run through the columns at 20 mL/min. and collected in volumetric flasks. The eluates were immediately acidified to pH 2 by the addition of 12.1 N HCl.

The next step in the procedure was to remove salts from the samples. After back elution, the eluates were pumped back onto the respective XAD columns and Cl was removed by flushing with deionized water until the water coming out of the bottom of the column had a specific conductance of less than 750 $\mu\text{S}/\text{cm}$.

Both columns were again back eluted with 0.1 *N* NaOH and the eluate passed through columns containing hydrogen-saturated cation exchange resin. The cation exchange columns were flushed with deionized water until the specific conductance of the water coming out of the bottom of the column had a specific conductance of less than 50 $\mu\text{S}/\text{cm}$, signifying removal of Na. After the desalting procedure, the sample was freeze dried and analyzed by ^{13}C -NMR spectroscopy.

The lysimeter samples were fractionated on 20-mL columns because a sufficient volume of sample to run them on the 295-mL columns could not be collected, except for a sample collected from lysimeter 2 on January 2, 1997, which was fractionated on the 295-mL column. The 20-mL columns process a sample volume of 1 L with a DOC concentration of no greater than 20 mg/L for maximum adsorption efficiency. The lysimeter samples always had concentrations greater than 20 mg/L, so they were diluted with 0.01 *N* HCl to a concentration of about 15 to 20 mg/L before being run on the column. One liter of sample was run through the XAD-8 column, and the effluent was collected in an Erlenmeyer flask. The XAD-8 effluent was then run through the XAD-4 column and the XAD-4 effluent was collected in an Erlenmeyer flask. The samples were run through both columns at a rate of 4 mL/min. After all the sample was run through the columns, each column was separately back eluted with 100 mL of 0.1 *N* NaOH at a rate of 2 mL/min. The eluates were collected in volumetric flasks and acidified to pH 2 with 12.1 *N* HCl. Because the 20-mL columns process only 1 L of sample, not enough organic material is adsorbed on the resins to isolate for analysis by ^{13}C -NMR spectroscopy.

The fractionation of the samples onto the XAD-8 and XAD-4 resins allows for a calculation of the mass of each operationally defined category (fraction), expressed as the percent of the original total DOC mass for a particular sample. Data for each fractionation sample collected during the study are listed in table C1. The percent of the total mass that each fraction represents was calculated by summing the masses of each fraction for a sample and dividing the mass of each fraction by the total mass and then multiplying by 100.

These fractionation calculations were performed on both runs of the 295-mL columns (table C2).

The mass of each operationally defined category for the 295-mL columns was calculated in the following manner: An initial DOC sample was collected from each sample after it was acidified, but before it was run on the column. Once the sample was running through the columns, a DOC sample was collected from the effluent of each column at 2-L intervals and at the end of the run. Each eluate was analyzed for its DOC concentration before it was desalted. A plot of DOC concentration versus volume of sample passed through the column was made for each sample (fig. C1). The area under the XAD-8 curve represents the mass of C in the XAD-8 effluent. The area under the XAD-4 curve represents the mass of C in the XAD-4 effluent. The total mass of C put on the columns was calculated by multiplying the initial DOC concentration by the sample volume (15 L). The mass of the HPOA fraction was calculated by multiplying the DOC concentration of the XAD-8 eluate by its volume (1 L), and the mass of the HPIA fraction is calculated by multiplying the DOC concentration of the XAD-4 eluate by its volume (1 L). The mass of the HPON fraction is calculated by subtracting the sum of the mass of C in the XAD-8 effluent and the mass of C in the XAD-4 eluate from the initial mass of C put on the column. The HPIN fraction is calculated by subtracting the sum of the mass of C in the XAD-4 effluent and the mass of C in the XAD-4 eluate from the mass of C run through the XAD-4 column (the XAD-8 effluent). The HPON and HPIN are those compounds that adsorb onto the XAD-8 and XAD-4 resins, respectively, but are not dissolved during the back elution with NaOH. The mass of the low molecular weight HPIA fraction is the mass of C in the XAD-4 effluent.

The mass of the operationally defined categories for the 20-mL columns was calculated differently than for the 295-mL columns because the columns were not connected in series. An aliquot of sample, usually 20 mL, was removed from the 1-L sample before being run on the XAD-8 column to measure the DOC concentration of the sample. The sample volume was brought back up to 1 L with deionized water before being run on the XAD-8 column. This procedure was done so that a constant volume was being run through the columns. After the sample was run through the XAD-8 column, an aliquot of the XAD-8 effluent, usually 20 mL, was removed so that the DOC concentration of the XAD-8 effluent could be measured. The

Table C1. Lysimeter, piezometer, and drainage ditch sample results for fractionation of dissolved organic carbon, Twitchell Island, California

[HPOA, hydrophobic acids; HPIA hydrophilic acids; HPON, hydrophobic neutrals; HPIN, hydrophilic neutrals; LMW HPIA, low molecular weight hydrophilic acids. Values are in percent of the total dissolved organic carbon mass]

Site	Date	HPOA	HPIA	HPON	HPIN	LMW HPIA
Lysimeter 1	02/06/96	43	7	6	11	32
Lysimeter 2	02/06/96	39	21	16	0	24
Lysimeter 4	02/07/96	41	23	8	0	28
Piezometer 1	02/06/96	51	26	2	0	21
Piezometer 2	02/06/96	51	26	4	0	20
Piezometer 4	02/07/96	54	24	2	0	20
Lysimeter 1	03/11/96	42	23	9	0	27
Lysimeter 2	03/11/96	43	25	5	0	27
Lysimeter 4	03/11/96	41	25	0	14	21
Piezometer 1	03/11/96	53	24	4	0	19
Piezometer 2	03/11/96	50	27	4	0	20
Piezometer 4	03/11/96	49	26	7	0	19
Ditch	03/11/96	50	25	4	0	21
Piezometer 1	06/19/96	53	25	2	0	20
Piezometer 2	06/19/96	50	26	5	0	19
Piezometer 4	06/19/96	51	25	5	0	19
Lysimeter 1	07/18/96	50	24	3	3	21
Lysimeter 2	07/18/96	50	21	8	0	22
Lysimeter 4	07/18/96	50	18	5	2	24
Piezometer 1	07/17/96	53	22	7	0	18
Piezometer 2	07/17/96	56	25	1	0	19
Piezometer 4	07/17/96	55	22	7	0	16
Ditch	07/17/96	53	24	4	0	19
Piezometer 1	09/04/96	55	22	7	0	17
Piezometer 2	09/04/96	55	22	3	1	19
Piezometer 4	09/04/96	58	23	2	0	17
Piezometer 1	11/13/96	58	22	3	0	17
Piezometer 2	11/13/96	55	22	4	0	19
Piezometer 4	11/13/96	57	23	3	0	18
Ditch	11/13/96	54	22	5	0	19
Lysimeter 2	01/02/97	49	23	8	1	20
Piezometer 1	01/02/97	52	24	6	0	19
Piezometer 2	01/02/97	49	25	6	0	20
Piezometer 4	01/02/97	50	24	6	0	20
Ditch	01/02/97	52	24	4	0	20

Table C2. Quality-assurance and quality-control data for the 295-mL column fractionation of dissolved organic carbon, Twitchell Island, California

[HPOA, hydrophobic acids; HPIA hydrophilic acids; HPON, hydrophobic neutrals; HPIN, hydrophilic neutrals; LMW HPIA, low molecular weight hydrophilic acids; Diff, differences between replicate analyses (Runs 1 and 2) for each dissolved organic carbon fraction shown. Values are in percent of the total dissolved organic carbon mass]

Site	Date	HPOA			HPIA			HPON			HPIN			LMW HPIA		
		Run 1	Run 2	Diff	Run 1	Run 2	Diff	Run 1	Run 2	Diff	Run 1	Run 2	Diff	Run 1	Run 2	Diff
Piezometer 1	02/06/96	51	52	1	26	27	1	2	1	1	0	0	0	21	20	1
Piezometer 2	02/06/96	51	51	0	26	26	0	4	2	2	0	0	0	20	20	0
Piezometer 4	02/07/96	54	55	1	24	26	2	2	0	2	0	0	0	20	18	2
Piezometer 1	03/11/96	49	53	4	25	24	1	8	4	4	0	0	0	18	19	1
Piezometer 2	03/11/96	50	49	1	27	27	0	4	4	0	0	0	0	20	20	0
Piezometer 4	03/11/96	49	48	1	26	26	0	7	7	0	0	0	0	19	19	0
Ditch	03/11/96	50	47	3	25	25	0	4	15	11	0	0	0	21	14	7
Pump	03/11/96	52	54	2	26	25	1	2	0	2	0	0	0	20	22	2
Piezometer 2	06/19/96	50	48	2	26	25	1	5	7	2	0	0	0	19	20	1
Piezometer 4	06/19/96	51	51	0	25	24	1	5	5	0	0	0	0	19	20	1
Pump	06/19/96	56	53	3	24	23	1	6	8	2	0	0	0	15	16	1
Piezometer 1	07/17/96	55	53	2	22	22	0	1	7	6	0	0	0	22	18	4
Piezometer 2	07/17/96	56	55	1	25	23	2	1	3	2	0	0	0	25	23	2
Piezometer 4	07/17/96	55	59	4	22	22	0	7	2	5	0	0	0	16	18	2
Ditch	07/17/96	53	52	1	24	24	0	4	5	1	0	0	0	19	19	0
Pump	07/17/96	63	62	1	21	19	2	0	0	0	0	1	1	16	19	3
Piezometer 1	09/04/96	55	57	2	22	22	0	7	3	4	0	0	0	17	18	1
Piezometer 2	09/04/96	58	55	3	23	22	1	0	3	3	0	1	1	19	19	0
Piezometer 4	09/04/96	56	58	2	22	23	1	0	2	2	0	0	0	22	17	5
Piezometer 1	11/13/96	60	58	2	24	22	2	0	3	3	0	0	0	17	17	0
Piezometer 2	11/13/96	55	54	1	22	23	1	4	6	2	0	0	0	19	18	1
Ditch	11/13/96	54	62	8	22	22	0	5	0	0	0	0	0	19	16	0

volume of the effluent was brought back up to 1 L with deionized water before being run on the XAD-4 column. The DOC concentration of both eluates and the XAD-4 effluent also was measured. The total mass of C put on the columns was calculated by multiplying the DOC concentration of the sample by the sample volume (1 L) minus the volume taken for DOC analysis. The mass of the HPOA fraction was calculated by multiplying the DOC concentration of the XAD-8 eluate by its volume (0.100 L) and the mass of the HPIA fraction was calculated by multiplying the DOC concentration of the XAD-4 eluate by its volume (0.100 L). The mass of the HPON fraction is calculated by subtracting the sum of the mass of C in the XAD-8 effluent

(calculated by multiplying the volume of the XAD-8 effluent collected by its concentration) and XAD-8 eluate from the mass of C put on the XAD-8 column. The mass of the HPIN fraction was calculated by subtracting the sum of the mass of C in the XAD-4 effluent (calculated by multiplying the volume of the XAD-4 effluent collected by its concentration) and XAD-4 eluate from the mass of C put on the XAD-4 column. The mass of C put on the XAD-4 column was the product of the concentration of the XAD-8 effluent and the volume of the XAD-8 effluent collected minus the amount taken for DOC analysis. The mass of the low molecular weight HPIA fraction was the mass of C in the XAD-4 effluent.

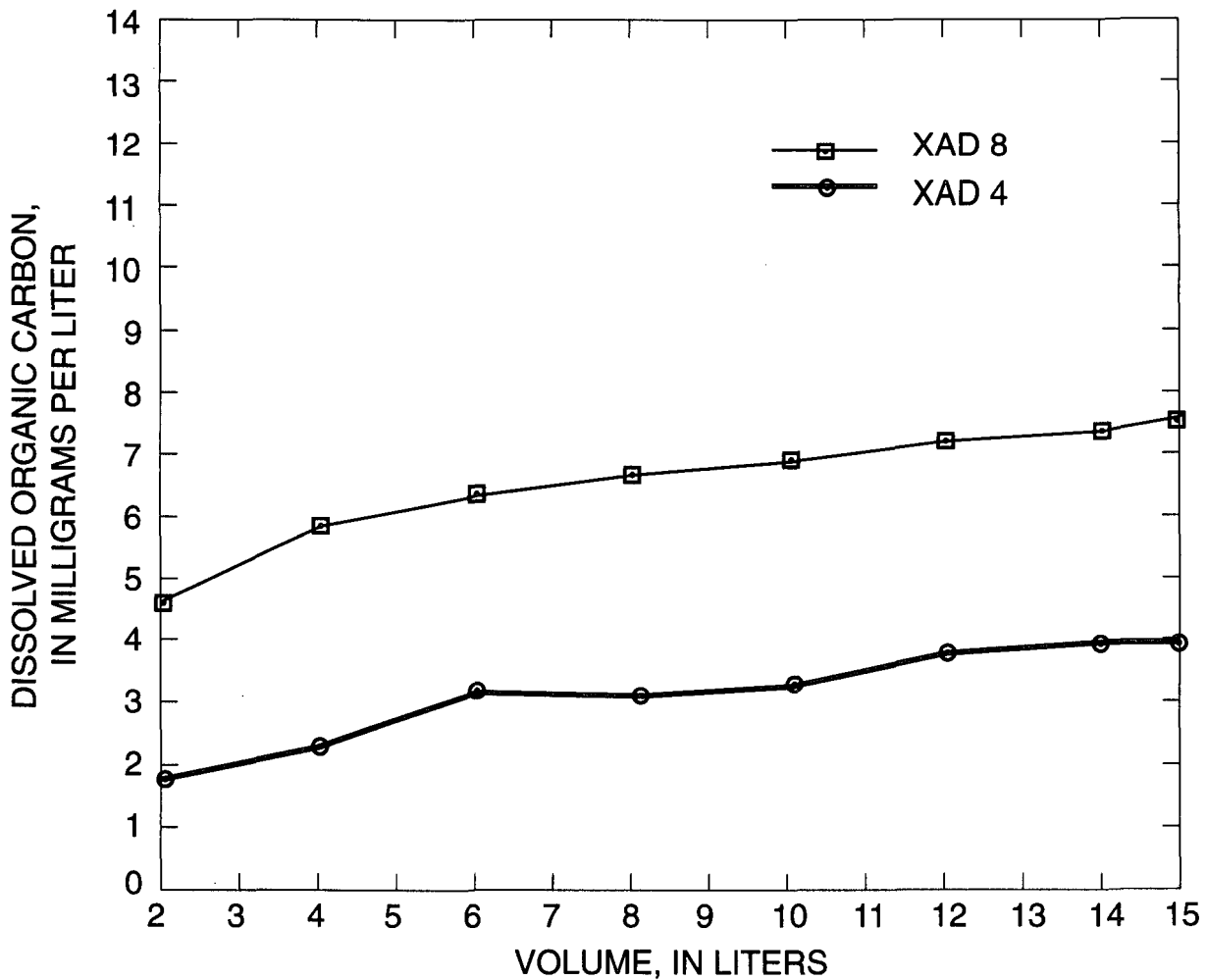


Figure C1. Dissolved organic carbon concentration as a function of volume of sample passed through 295-milliliter XAD columns for the piezometer 2 (Run 2) sample collected July 17, 1996, Twitchell Island, California.

APPENDIX D: U.S. GEOLOGICAL SURVEY TRICHALOMETHANE METHODS

Background

It has been known for more than 20 years that dissolved natural organic materials (NOM) form THM and other DBPs on chlorination of drinking waters (Rook, 1974; 1977). The formation of DBP during treatment is problematic because of the carcinogenic properties of these compounds (Rook, 1974). However, little is known about the natural processes that form and(or) concentrate the chemical precursors to DBP.

The chemical structure of NOM and associated DBP precursors vary with many environmental and chemical parameters, including the source of the organic material, age of the organic material, diagenetic history, soil type, season, molecular size, pH of the source waters, and so forth. Examination of the formation of DBP in waters collected over an annual cycle from different flowpaths in the Twitchell Island study site should provide insights into the sources and processes that lead to elevated NOM concentrations and elevated DBP formation in these waters.

The primary sources of NOM in Twitchell Island pore waters are organic material in the peat soils or degrading above- and below-ground crop biomass. Secondary heterotrophic productivity may alter the chemical composition of the organic material and thus either concentrate or degrade DBP precursors. Some NOM (only 2 mg/L as DOC) is present in water siphoned onto the island, but represents only a small fraction of NOM present in the samples analyzed as part of this study.

Given the sources, NOM can arise from three distinct soil zones: the upper oxidized zone, the lower reducing zone, and the zone periodically exposed to oxidizing and reducing conditions during water-table fluctuations. The extent of each of these zones can vary seasonally, depending on irrigation practice, intentional winter flooding, and seasonal rainfall.

As discussed in the body of this report, samples were collected from two soil zones for determination of THMFP and pertinent physical and chemical parameters. Ancillary physical and chemical parameters are reported in appendix A.

The Chemistry of Disinfection Byproduct Formation

Dissolved chlorine, used for disinfection of drinking water, disproportionates to hypochlorous acid (HOCl) and chlorine. HOCl, in turn, rapidly reacts with ammonia to form chloramines and with Br to form hypobromous acid (HOBr). Together, HOCl, HOBr, and chloramines react with inorganic and organic compounds present in the treated waters. In particular, they react with NOM to form THM and other DBP.

The reactions that form THM are additions and substitutions to chemical structures commonly found in NOM, generally additions to olefins and substitutions in aliphatic and aromatic compounds. The abundance of these chemical structures determines the speed and extent to which THM forms on treatment, as well as they carry information about the source and diagenetic history of the NOM (Reckhow and Edzwald, 1989).

Thus, intrinsic, source-related properties of the reactive chemical structures in NOM determine the amount of THM formed during chlorination. Several studies have been undertaken with model compounds to provide insights into the reactivity of structures within NOM (Rook, 1976; 1977). Aromatic structures, such as substituted benzenes, and other electron-rich structures, such as ketones, generally are reactive, but reactivity estimates for a variety of olefinic structures were unavailable. Reactions generally can be grouped into the aromatic type and ketone type for the purpose of understanding the activity of NOM structures.

In addition to the intrinsic chemical structure of the NOM, the speed and extent of formation of THM during chlorination depend on a number of physical and chemical parameters. The chlorine dose, the duration of the reaction, the presence of bromide and ammonium, the NOM concentration, and the temperature and pH at which the reaction is conducted contribute to the amount of THM formed. Therefore, controlling these parameters when comparing differences in THMFP among samples and making sure all samples were analyzed using comparable tests are important.

Methods Employed by the U.S. Geological Survey Laboratory for Trihalomethane Formation Potential Analysis

Several tests for the capacity of natural waters to form DBP are currently in use (Reckhow and Edzwald, 1989). The results obtained using these tests are highly dependent on the method used, so care should be taken in comparing data using different analytical methodologies. Two different tests were conducted as part of this study to determine the THMFP of the tested waters. The majority of the data was generated using the dose-based test (THMFP_{db}), in which a fixed amount of chlorine is added to the sample (California Department of Water Resources, 1994b). Data of this type were collected throughout the study and were used to generate the seasonal comparisons. The second type of test was the reactivity-based test (THMFP_{rb}), in which the chlorine demand is calculated to determine chlorine dose. For an accounting of which THMFP method was applied to which samples and how the results of different methods compare, see the Trihalomethane Formation Potential section. The THMFP tests used here are significantly different from the commonly used simulated distribution system (SDS) test.

Whole-water samples were kept refrigerated until analyzed and were analyzed within 1 week of collection. The freeze-dried eluates were prepared for the THMFP test by dissolving 5 mg of material in 0.5 L of a 0.001N NaHCO₃ solution. Aliquots of the sample were taken for DOC and UVA measurements. The rest of the sample was then treated in exactly the same manner as the whole-water samples.

To determine the chlorine demand of each sample, prior to chlorination, the DOC and ammonia concentrations were determined for all samples. All samples were chlorinated with a dose based on the inorganic and organic demand according to the following formula, based on the method of Krasner and Scrimanti (1993):

$$[\text{Cl}_2] = (3 \times [\text{DOC}]) + (7.6 \times [\text{NH}_3])$$

Ammonia concentrations were determined using a HACH kit according to the method 8038 of the HACH Water Analysis Book (HACH, 1992). The procedure employs direct nesslerization of whole-water samples, reacting 25 mL of each sample with Nessler reagent for 1 minute, then measurement of solution color against a blank on a spectrophotometer at 425 nm. DOC measurements were made in duplicate by

persulfate oxidation on a Oceanics International model 700 TOC analyzer.

The THMFP_{rb} for each sample was determined using a modified version of method 5710 B described in Eaton (1995). Briefly, samples were buffered to pH 8.4 with a freshly prepared NaH₂PO₄•2H₂O/Na₂HPO₄ buffer solution, and the pH corrected to 7 using 0.5 M HCl or 0.5 M NaOH. Samples were then transferred into a 72-mL serum vial and sealed using a Teflon-faced septa without leaving a headspace (to prevent volatilization of THM). The chlorination solution was injected by syringe through the septum, allowing the displaced volume to exit through a second syringe. The bottles were then incubated for 7 days at 20°C in a controlled-temperature recirculating bath.

The chlorination reaction was terminated by pouring 30 mL of the sample into a 40-mL screw-top vial fitted with a Teflon-faced septa, followed by 2 mL of sodium sulfite solution (1.5 M). Chlorine residual was determined on the remaining sample using HACH procedure 8167 (HACH, 1992).

Samples were extracted from the aqueous phase by first adding sodium chloride (8 g) to reduce solubility of ether and to increase partitioning of THM into the organic phase, vigorously shaking the vial for 20 seconds, then adding 3 mL of methyl tert butyl ether and shaking for 2 minutes. After allowing 10 minutes for separation of the organic and aqueous layers, 1.5 mL of the organic layer was removed to an autosampler vial using a Pasteur pipet and then immediately sealing the vial.

Quantification of THM was accomplished using a Hewlett Packard 5890 II gas chromatograph fitted with an auto injector, a capillary split-splitless inlet, and a Nickel⁶³ electron capture detector. Baseline chromatographic separation was obtained using a DB-1 fused silica capillary chromatography column (30 M x 0.25 mm i.d.). The column oven was programmed to hold an initial temperature of 40°C for 4 minutes, increased to a final temperature of 100°C at a rate of 15°C/min, and held for 3 minutes.

THMs were identified by comparing the peak retention time to that of authentic standards. THMs were quantified by comparing the peak area of sample analyses to the areas resulting from the injection of calibration standards of known concentration. THMFP data obtained using this method for samples from this study are presented in table D1.

Table D1. Results of speciation of trihalomethane formation potential and associated parameters for lysimeter, piezometer, drainage ditch, and pump samples, Twitchell Island, California

[CHCl₃, chloroform; CHCl₂Br, bromodichloromethane; CHBr₂Cl, chlorodibromomethane; CHBr₃, bromoform; DOC, dissolved organic carbon; THMFP, trihalomethane formation potential; SUVA, specific ultraviolet absorbance; nd, not detected. Values in micrograms per liter, except DOC, which is in milligrams per liter, THMFP/DOC, which is in micrograms per milligram, and SUVA, which is in per centimeter units]

Site	Date	CHCl ₃	CHCl ₂ Br	CHBr ₂ Cl	CHBr ₃	DOC	THMFP	THMFP/DOC	SUVA
Lysimeter 1	10/23/96	5108.6	690.5	68.8	nd	121.3	5,867.9	48.4	0.043
Lysimeter 2	10/23/96	2176	401.8	47.7	7.4	41.7	2,632.9	63.1	.051
Piezometer 1	10/23/96	3836.1	486.4	51.1	nd	87.0	4,373.6	50.3	.052
Piezometer 2	10/23/96	2464.5	377.9	48.3	nd	51.8	2,890.7	55.8	.062
Piezometer 4	10/23/96	2219.4	381.4	49.8	nd	45.4	2,650.6	58.4	.067
Ditch	10/23/96	698	254.5	86	7.2	14.9	1,045.7	70.2	.107
Pump	10/23/96	201.6	121.4	67.1	10.8	5.7	400.9	70.3	.059
Lysimeter 1	11/13/96	4427.3	749.4	96.7	nd	128.3	5,273.4	41.1	.047
Lysimeter 2	11/13/96	3113.9	628.3	112.9	13.3	80.6	3,868.4	48.0	.042
Piezometer 1	11/13/96	2924.9	491.5	78	nd	78.1	3,494.4	44.7	.047
Piezometer 2	11/13/96	2683.8	389.5	43.8	nd	71.9	3,117.1	43.4	.059
Piezometer 4	11/13/96	2820.9	421.9	56.9	9.5	69.2	3,309.2	47.8	.055
Ditch	11/13/96	438.4	281.2	181	37.8	17.0	938.4	55.2	.054
Pump	11/13/96	98.5	84.7	56.6	10.1	5.8	249.9	43.1	.054
Lysimeter 1	12/11/96	2686.4	542.6	117.9	10.6	66.8	3,357.5	50.3	.041
Lysimeter 2	12/11/96					22.1	0	0	.044
Lysimeter 4	12/11/96	1910.7	330.9	52.9	3.1	50.4	2,297.6	45.6	.042
Piezometer 1	12/11/96	3264.1	481.5	71.1	nd	82.8	3,816.7	46.1	.056
Piezometer 2	12/11/96	2509.4	411.1	71.1	nd	69.5	2,991.6	43.0	.067
Piezometer 4	12/11/96	3323.8	554.8	84.2	nd	78.2	3,962.8	50.7	.058
Lysimeter 2	01/02/97	1058.6	241.8	54.1	4.7	21.4	1,359.2	63.5	.116
Piezometer 1	01/02/97	3187.3	443.3	55.1	nd	81.6	3,685.7	45.2	.046
Piezometer 2	01/02/97	2014.1	237.4	27.3	nd	76.3	2,278.8	29.9	.046
Piezometer 4	01/02/97	1991.1	295.9	42.6	nd	77.6	2,329.6	30.0	.041
Ditch	01/02/97	1367.2	151.3	12.2	nd	33.0	1,530.7	46.4	0.036

Table D1. Results of speciation of trihalomethane formation potential and associated parameters for lysimeter, piezometer, drainage ditch, and pump samples, Twitchell Island, California—Continued

Site	Date	CHCl ₃	CHCl ₂ Br	CHBr ₂ Cl	CHBr ₃	DOC	THMFP	THMFP/DOC	SUVA
Pump	01/02/97	1816.2	257.8	22.5	nd	41.6	2,096.5	50.4	0.043
P1 XAD8 Eluate	Jul-96	193.0	3.5	nd	0.5	4.4	197.0	44.8	.058
P1 XAD4 Eluate	Jul-96	128.0	4.1	0.1	nd	3.1	132.2	42.6	.038
P4 XAD8 Eluate	Jul-96	166.5	2.8	nd	nd	3.9	169.3	43.4	.053
P4 XAD4 Eluate	Jul-96	140.8	3.2	nd	nd	4.0	144.0	36.0	.040
Ditch XAD8 Eluate	Jul-96	181.9	3.3	nd	nd	4.1	185.2	45.2	.060
Ditch XAD4 Eluate	Jul-96	154.3	4.4	.1	nd	3.6	158.8	44.1	.049
P1 XAD8 Eluate	11/13/96	239.0	3.8	.2	nd	4.9	243.0	49.6	.053
P1 XAD4 Eluate	11/13/96	203.7	3.9	.2	nd	4.6	207.8	45.2	.041
P2 XAD8 Eluate	11/13/96	215	2.8	.1	nd	4.6	217.9	47.4	.054
P2 XAD8 Eluate	11/13/96	227	3.4	.2	nd	4.6	230.6	50.1	.054
P2 XAD4 Eluate	11/13/96	208.6	4.0	.2	nd	5.1	212.8	41.7	.045
Ditch XAD8 Eluate	11/13/96	200.4	3.1	.2	nd	3.8	203.7	53.6	.050
Ditch XAD4 Eluate	11/13/96	226.3	4.0	.2	nd	5.1	230.5	45.2	.037
L2 XAD8 Eluate	Jan-97	171.3	5.7	.3	1.1	4.4	178.4	40.5	.043
L2 XAD4 Eluate	Jan-97	154.3	7.5	.3	.9	4.4	163.0	37.0	.043
P1 XAD8 Eluate	Jan-97	160.8	2.3	nd	nd	4.3	163.1	37.9	.059
P1 XAD4 Eluate	Jan-97	172.2	4.4	.2	1.0	4.5	177.8	39.5	.040
P2 XAD8 Eluate	Jan-97	168.5	2.7	nd	nd	4.5	171.2	38.0	.050
P2 XAD4 Eluate	Jan-97	167.3	3.8	nd	nd	4.5	171.1	38.0	.038
Ditch XAD8 Eluate	Jan-97	203.8	6.3	.1	nd	4.8	210.2	43.8	.047
Ditch XAD4 Eluate	Jan-97	172.5	8.1	.2	nd	4.3	180.8	42.0	.034

APPENDIX E: CARBON-13 NUCLEAR MAGNETIC RESONANCE ANALYSES

Introduction

The study of the nature, reactivity, and environmental significance of organic matter in aquatic systems is hampered by the inherent chemical complexity of the organic matter. Fractionation of DOC on XAD resins results in fractions of the DOC that are themselves complicated, heterogeneous mixtures. Typically, the complicated mixtures obtained from the fractionation of DOC into compound classes are characterized by elemental, molecular weight, acid-base titration and amino acid analyses, and by ^{13}C -NMR, ^1H -NMR, and IR spectroscopy. The fact that the fractions are complex, heterogeneous mixtures limits the amount of information that can be obtained about the composition of the mixture using each of the above methods, but these techniques do provide valuable structural and functional group information that, taken as a whole, can be used to establish the nature and source of organic isolates.

Selected samples collected during this study were analyzed by ^{13}C -NMR to learn more about the differences in chemical composition between different sampling locations and to relate the reactivity of these isolates to their chemical composition. ^{13}C -NMR is an important technique for obtaining structural information on complicated mixtures of organic compounds, such as humic substances and coal. In recent years, use of this technique to study humic substances has increased dramatically, and a number of review articles describing the technique and its application to environmental studies have been published (Wershaw, 1985; Wershaw and Mikita, 1987; Preston, 1987; Steelink and others, 1990; Cook and others, 1996).

Two different ^{13}C -NMR techniques were applied in this study. Quantitative spectra were obtained on two samples using liquid state ^{13}C -NMR. This technique is time consuming and requires a rela-

tively large amount of sample. Two samples were analyzed by liquid state NMR. A larger set of samples was also analyzed by cross-polarization (CP) magic angle spinning (MAS) ^{13}C -NMR analysis, which provides qualitative data that allow comparison between samples. This method has the advantages of short analysis times and small amounts of sample. Unfortunately, there are problems inherent to this technique that interfere with the acquisition of quantitative spectra (Cook and others, 1996).

In all cases, the ^{13}C -NMR spectra are comprised of six major bands. The general assignments for these major bands are as follows:

1. Aliphatic I (0-60 ppm)—primarily sp^3 hybridized carbons bonded to other carbons; carbons bonded to nitrogen and sulfur also can occur in this region. Methoxyl carbons occur in the approximate range from 54 to 60 ppm;
2. Aliphatic II (60-90 ppm)—hetero-aliphatic carbons, primarily sp^3 hybridized carbons bonded to oxygens, including ether, alcohol, and carbohydrate carbons;
3. Acetal (90-110 ppm)—acetal and ketal carbons and anomeric carbons of carbohydrates;
4. Aromatic (110-160 ppm)—primarily aromatic and olefinic carbons;
5. Carboxyl (160-190 ppm)—carboxylic acid carbons. Ester, amide, and lactone carbons also can overlap with the carboxyl carbons; and
6. Ketone (190-230 ppm)—primarily ketones and aldehydes.

In general, the broad-banded nature of the spectra presented in this report indicates that the samples are complex organic mixtures.

Results

Quantitative ^{13}C -NMR spectra for the HPOA fractions collected from the drainage ditch (March 1996) and Piezometer 3 (March 1996) are presented in figures E1 and E2. In general, these spectra are very

similar. As discussed in the Description of Study Site and Study Design section of the report, there appeared to be a connection between the drainage ditch and site 3, and this similarity further confirms this hypothesis. The most prominent peak in each spectrum is the carboxyl peak, which indicates that these fractions of the DOC are organic acids. Each sample also has a large response in the aromatic carbon, which indicates that the samples are highly aromatic in nature. Integrating the spectra provides the percent distribution of carbon types in the samples. These data are presented in table

E1. Compared to similar samples from other environments (fig. E3), the samples from Twitchell Island are more aromatic and contain fewer aliphatic-II and anomeric carbon atoms associated with carbohydrates. The differences associated with these samples are due, in large part, to differences in sources of dissolved organic matter in each environment. Based on a large data set, the Lake Fryxell and Suwannee HPOA samples represent extremes with regard to aromatic carbon content. The Lake Fryxell sample represents organic matter derived from algae and bacteria, whereas the

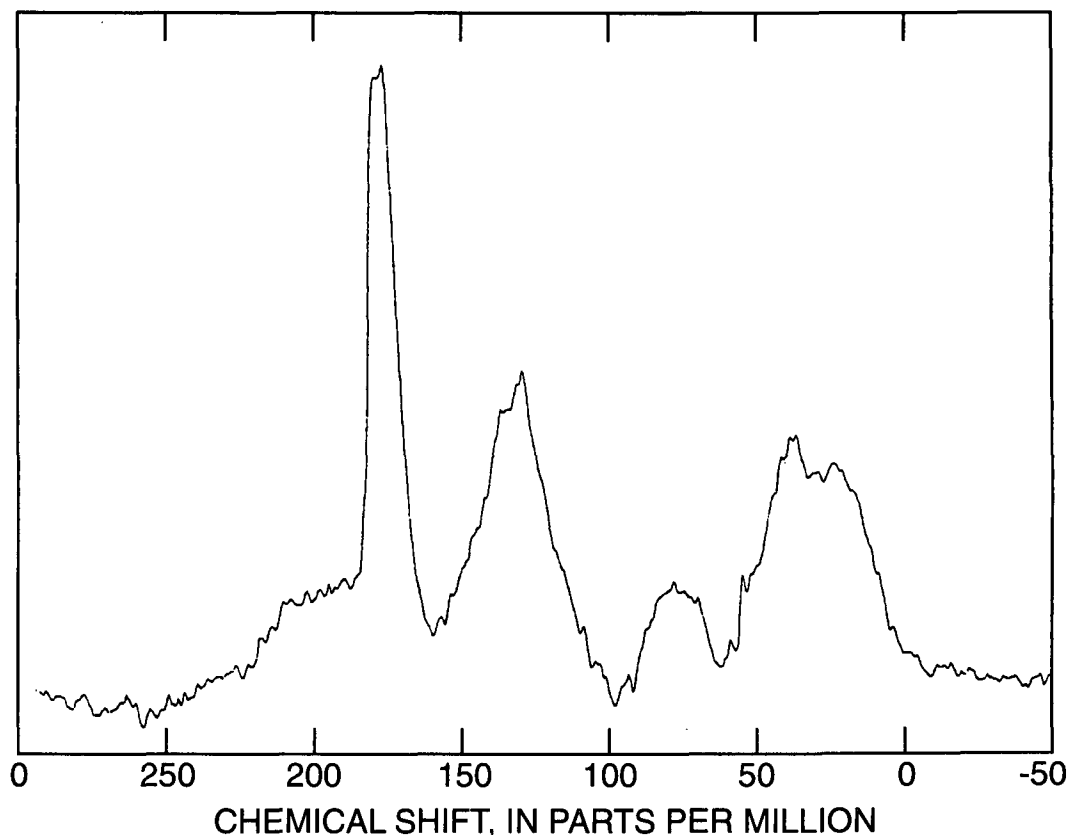


Figure E1. Carbon-13 nuclear magnetic resonance spectra for the hydrophobic acid fraction from the drainage ditch sample collected March 1996, Twitchell Island, California.

Suwannee sample is derived largely from lignin-containing plants. The Twitchell Island samples are more aromatic than even the Suwannee sample. The large amount of aromatic carbon associated with the Twitchell Island samples is of significance in this study

because of the enhanced reactivity of aromatic molecules with chlorine leading to the formation of DBP.

Intercomparison between the samples collected on Twitchell Island can be done by comparing data obtained from CPMAS ^{13}C -NMR analyses. Although

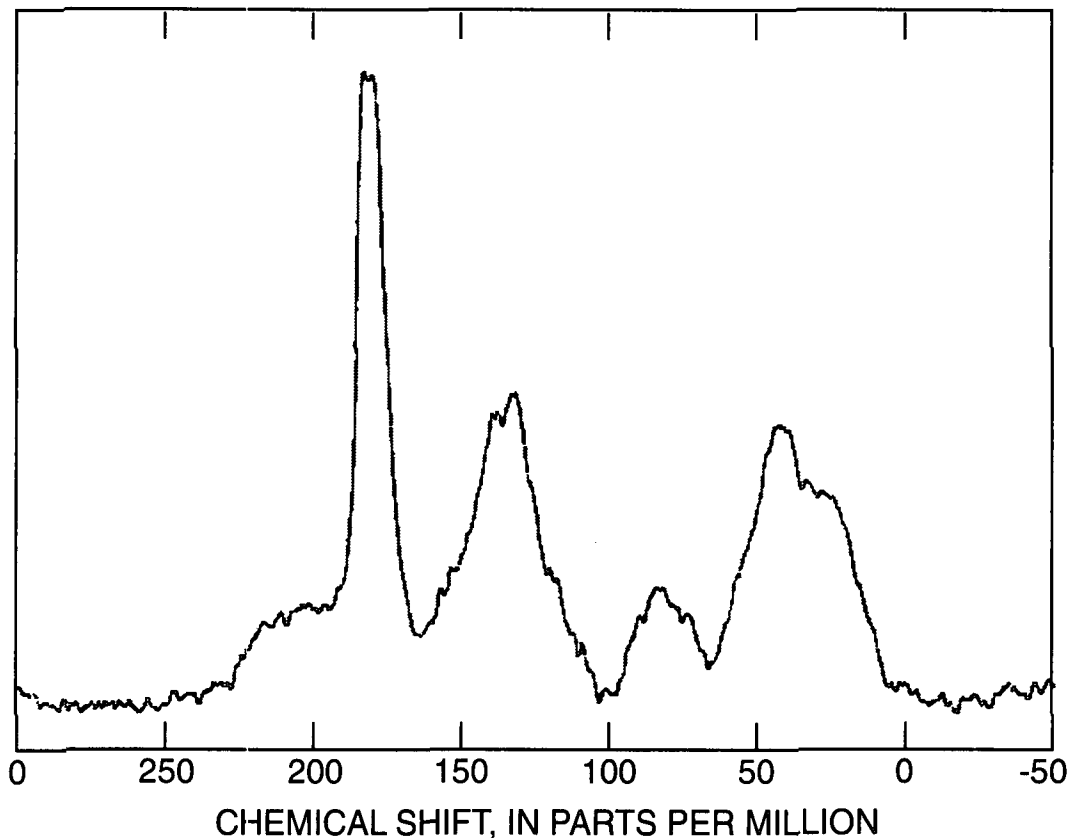


Figure E2. Carbon-13 nuclear magnetic resonance spectra for the hydrophobic acid fraction from piezometer 3 sample collected March 1996, Twitchell Island, California.

Table E1. Relative peak areas for carbon moieties in natural abundance, quantitative, liquid state carbon-13 nuclear magnetic resonance spectra for hydrophobic acid fractions from piezometer 3 and the drainage ditch sampling sites, Twitchell Island, California

[Values are in percent; ppm, parts per million]

Sample	Date	Aliphatic-I carbon (0-60 ppm)	Aliphatic-II carbon (60-90 ppm)	Anomeric carbon (90-110 ppm)	Aromatic carbon (110-160 ppm)	Carboxyl carbon (160-190 ppm)	Ketone carbon (190-230 ppm)
Piezometer 3	03/11/96	29.1	5.9	0.8	28.1	28.1	8.1
Ditch	03/11/96	28.7	5.3	0	28.4	28.3	9.4

these data are not quantitative, qualitative differences between the samples can be identified. Representative spectra are presented in figures E4 and E5, whereas integration data are presented in table E2. Note that the ketone region (190-230 ppm) has not been included in this table because of the presence of spinning side bands in this part of the CPMAS spectrum. In addition, the integration values in the aliphatic region of the CPMAS spectra are a much greater percent, whereas the aromatic and carboxyl regions are a much lower

percent relative to the data discussed above for the quantitative liquid state measurements. These differences in the spectra result from problems inherent in the CPMAS technique that are beyond the scope of this report. Interested readers are referred to the paper by Cook and others (1996) for a more detailed discussion of the difficulties in obtaining quantitative information by CPMAS ^{13}C -NMR. This technique is useful, however, for an intercomparison of samples from the same location.

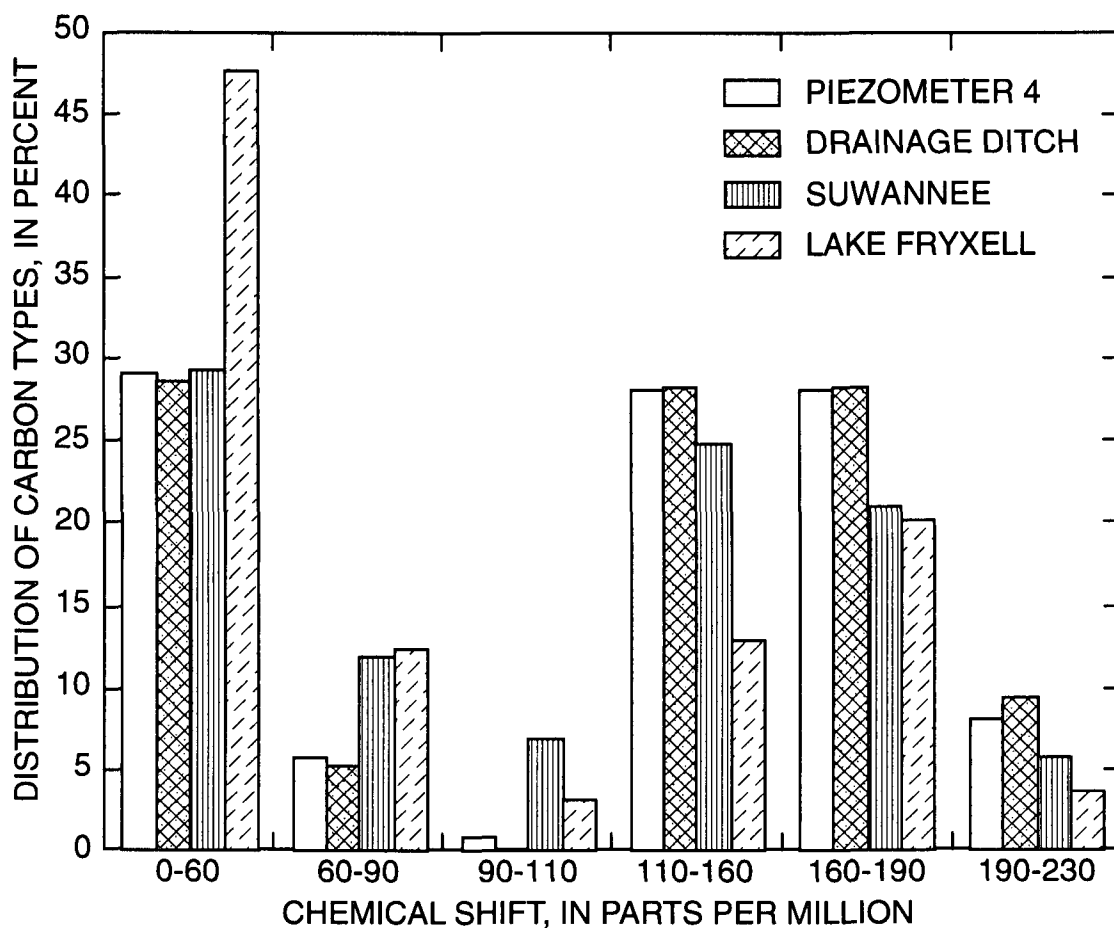


Figure E3. Comparison of quantitative carbon-13 nuclear magnetic resonance integration data for hydrophobic acid fraction data from samples from Twitchell Island, California; the Suwannee River, Georgia; and Lake Fryxell, Antarctica.

Differences between the HPOA and HPIA fractions are evident from a comparison of the spectra obtained for samples from piezometer 4 (figs. E4 and E5). The HPOA fraction has a more prominent peak in the aromatic carbon region (110-160 ppm) and a less prominent peak in the aliphatic-II region (60-90 ppm). The integration data in table E2 indicate that, for each

sample, the HPIA fractions have greater carboxyl, aliphatic-II, and aliphatic-I carbon contents and are less aromatic than the corresponding HPOA fractions. These differences are apparent in the bar graph comparison of the NMR data presented for piezometer 4 in figure E6. From the ^{13}C -NMR data, the major structural differences between the two fractions are that the

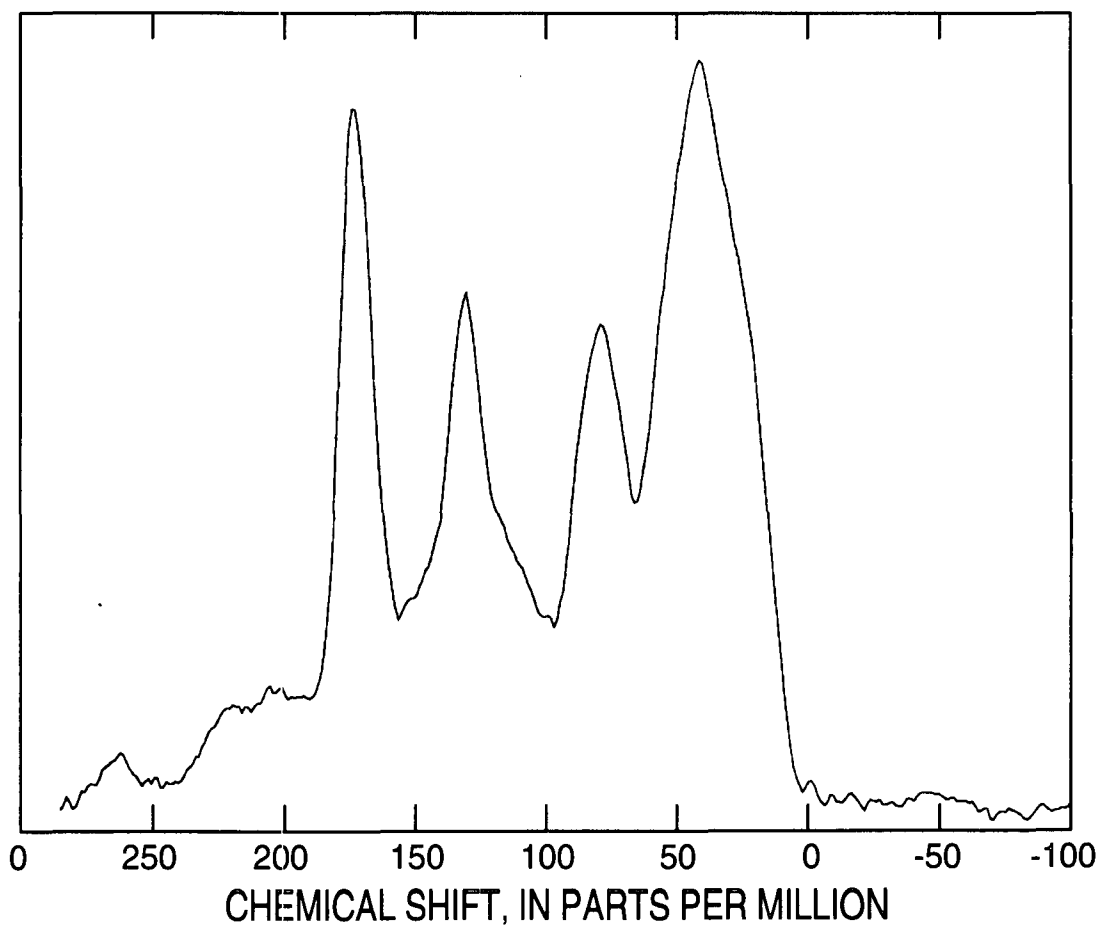


Figure E4. Carbon-13 nuclear magnetic resonance spectra for the hydrophobic acid fraction from piezometer 4 sample collected July 17, 1996, Twitchell Island, California.

HPIA fraction is less aromatic than the fulvic acid and has a greater amount of carboxyl and heteroaliphatic carbon. On the basis of the greater aromatic carbon content of the HPOA fractions, this fraction of the DOC is expected to be more of a factor with regard to the generation of DBP.

A comparison of the differences between different sites for a given sampling date (figs. E7 and E8) shows that there are few differences in the composition of either the HPOA or HPIA fractions. The similarities in composition for the isolates from the piezometer samples reflect similarities in the source materials, for

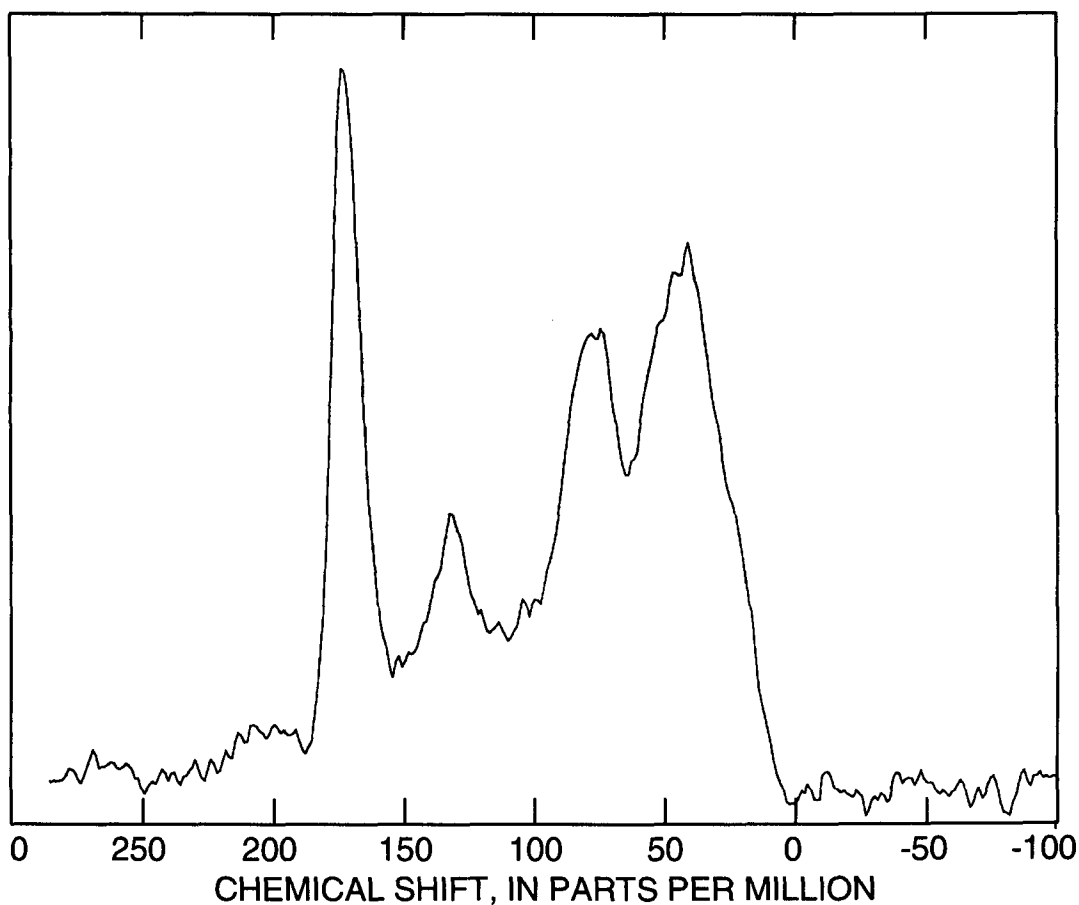


Figure E5. Representative carbon-13 nuclear magnetic resonance spectra for the hydrophilic acid fraction from piezometer 4 sample collected July 17, 1996, Twitchell Island, California.

Table E2. Relative peak areas for carbon moieties in natural abundance cross polarization magic angle spinning carbon-13 nuclear magnetic resonance for hydrophobic acid and hydrophilic acid fractions from selected surface and soil waters on Twitchell Island, California

[Values are in percent. ppm, parts per million]

Sample	Date	Aliphatic-I carbon (0-60 ppm)	Aliphatic-II carbon (60-90 ppm)	Anomeric carbon (90-110 ppm)	Aromatic carbon (110-160 ppm)	Carboxyl carbon (160-190 ppm)
Hydrophobic acid fractions						
Piezometer 4	03/11/96	36.4	17.2	8.1	22.2	16.2
Ditch	03/11/96	36.6	16.8	6.9	23.8	15.8
Piezometer 1	07/17/96	37.8	16.2	6.3	23.4	16.2
Piezometer 2	07/17/96	37.8	16.2	6.3	23.4	16.2
Piezometer 4	07/17/96	38.2	16.4	6.4	21.8	17.3
Ditch	07/18/96	44.1	18	6.3	18.9	12.6
Pump	07/17/96	36.9	16.2	6.3	25.2	15.3
Piezometer 1	09/04/96	32.4	18	5.4	27	17.1
Piezometer 2	09/04/96	36.6	16.1	7.1	24.1	16.1
Piezometer 4	09/04/96	37.2	18.6	7.1	23	14.2
Piezometer 1	11/13/96	42.3	17.1	6.3	19.8	14.4
Piezometer 2	11/13/96	40.5	17.7	5.4	22.5	14.4
Ditch	11/13/96	44.1	15.3	6.3	20.7	13.5
Lysimeter 2	01/02/97	40.9	18.2	6.4	19.1	15.4
Piezometer 1	01/02/97	39.6	18	6.3	20.7	15.3
Piezometer 2	01/02/97	40	18.2	7.3	19.1	15.4
Ditch	01/03/97	43.8	18.8	6.2	18.8	12.5
Hydrophilic acid fractions						
Piezometer 4	03/11/96	40.2	22.3	7.1	13.4	17
Ditch	03/11/96	40.7	23	7.1	13.3	15.9
Piezometer 2	07/17/96	40	20	6.4	14.5	19.1
Piezometer 4	07/17/96	36.8	21	6.1	15.8	20.2
Ditch	07/17/96	40.4	19.3	6	14.6	19.3
Pump	07/17/96	42	23.2	6.2	14.3	14.3
Piezometer 2	09/04/96	35.6	19.1	6.1	19.1	20
Piezometer 4	09/04/96	37.5	20.4	7.1	16.1	18.8
Piezometer 1	11/13/96	46.4	21.4	6.2	12.5	13.4
Piezometer 2	11/13/96	40.2	20.5	6.2	16.1	17
Ditch	11/13/96	47.8	21.7	6.1	10.4	13.9
Lysimeter 2	01/02/97	49.5	23.4	5.4	8.1	13.5
Piezometer 1	01/02/97	44.6	23.2	6.2	10.7	15.2
Piezometer 2	01/02/97	42.4	21.2	6.2	13.3	16.8
Ditch	01/03/97	41.6	26.5	6.2	11.5	14.2

example, the peat soils, and in the processes leading to the generation of DOC from these soils. These similarities suggest that dissolved organic matter of similar composition and reactivity would be obtained from other fields that have similar soils and land use. The compositional similarity of the samples collected from

the drainage ditch and at the pump location to those samples obtained from the piezometers confirms one of the original hypotheses of this study, that the nature of the soil organic matter exerts a strong influence on the chemical composition and reactivity of the organic matter transported off the island.

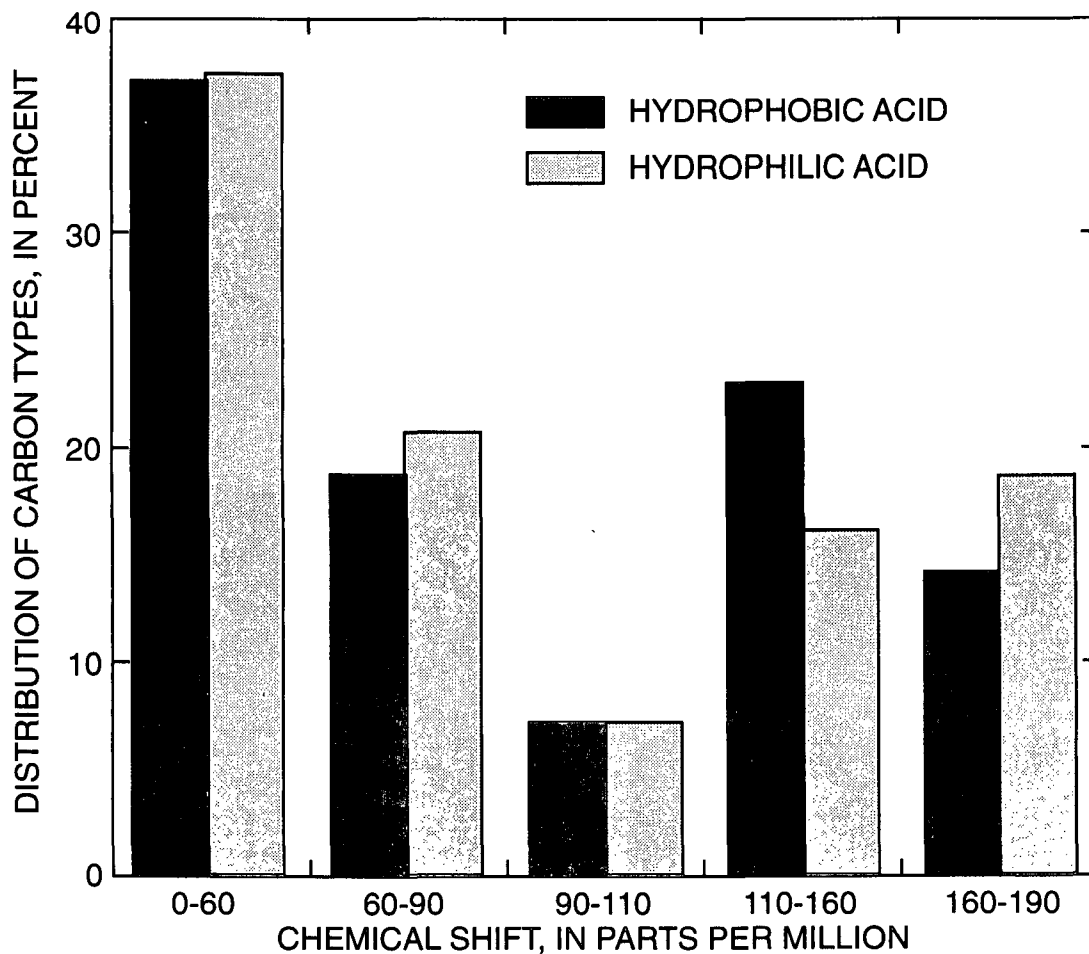


Figure E6. Comparison of carbon-13 nuclear magnetic resonance data for hydrophobic and hydrophilic acid fractions from piezometer 4 sample collected July 17, 1996, Twitchell Island, California.

Finally, samples of the peat soils also were characterized by CPMAS ^{13}C -NMR (fig. E9). In general, the soil samples were observed to be more aliphatic and to contain greater amounts of carbohydrates, as evidenced by the aliphatic-II peak compared to the HPOA

fractions from the lysimeters and the piezometers. The soil samples also contained significantly less carboxyl content than the dissolved HPOA fractions. These results suggest that the aromatic organic acids are removed from the peat at a faster rate than other

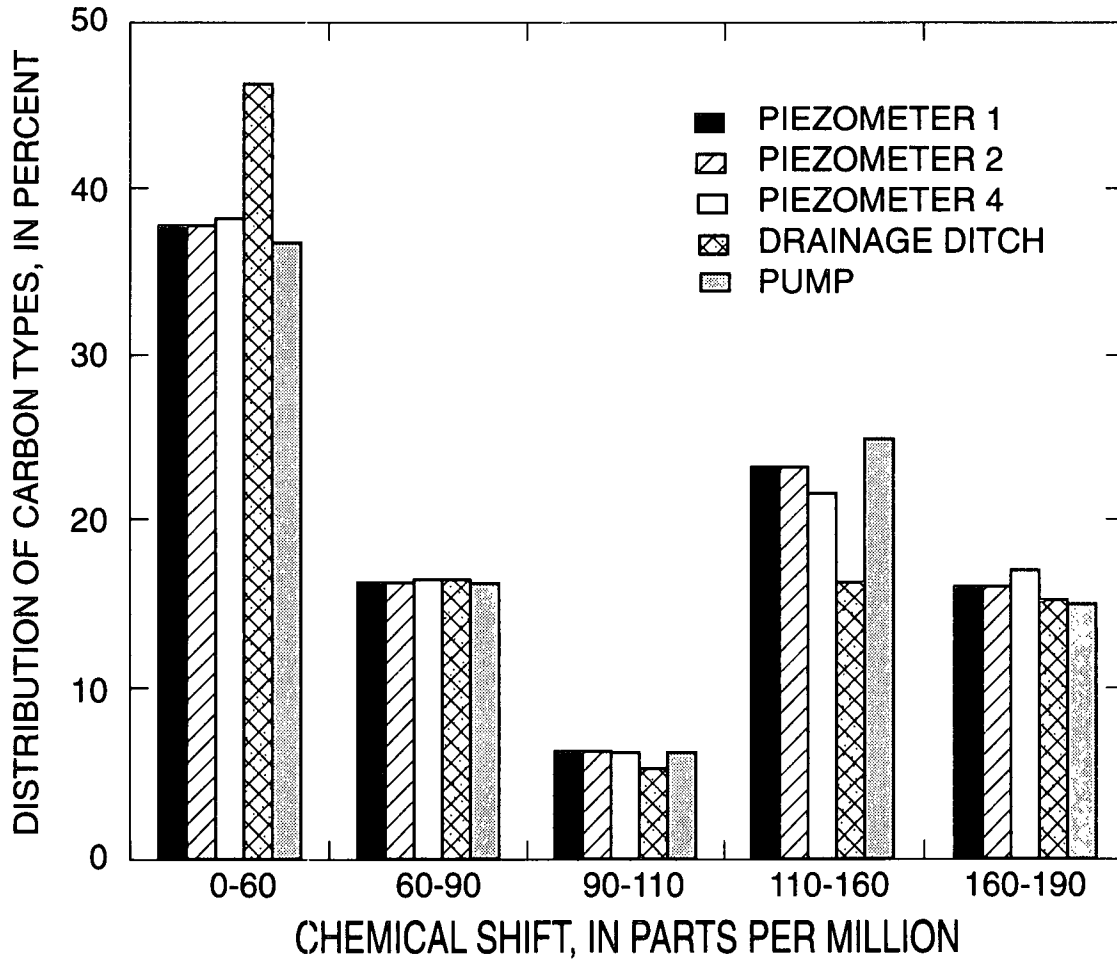


Figure E7. Comparison of carbon-13 nuclear magnetic resonance data for hydrophobic acid fraction from piezometers 1, 2, and 4, drainage ditch, and pump samples collected July 17, 1996, Twitchell Island, California.

components of the peat and that the aliphatic and carbohydrate (probably cellulose) rich fractions of the peat organic matter are selectively preserved.

It is interesting to compare the spectra for soil samples collected from depths in the soil profile that have different redox conditions. The lysimeters were 6 to 18 in. below the surface. At this depth, the soils are

exposed to oxygen and are classified as oxidized. The piezometers, on the other hand, were below the water table at a depth of 54 to 72 in. in a reduced zone with little oxygen. Exposure of the peat soils to oxygen results in accelerated rates of peat oxidation, a mechanism that is largely responsible for the subsidence of soils on the peat islands as a result of wetland drainage

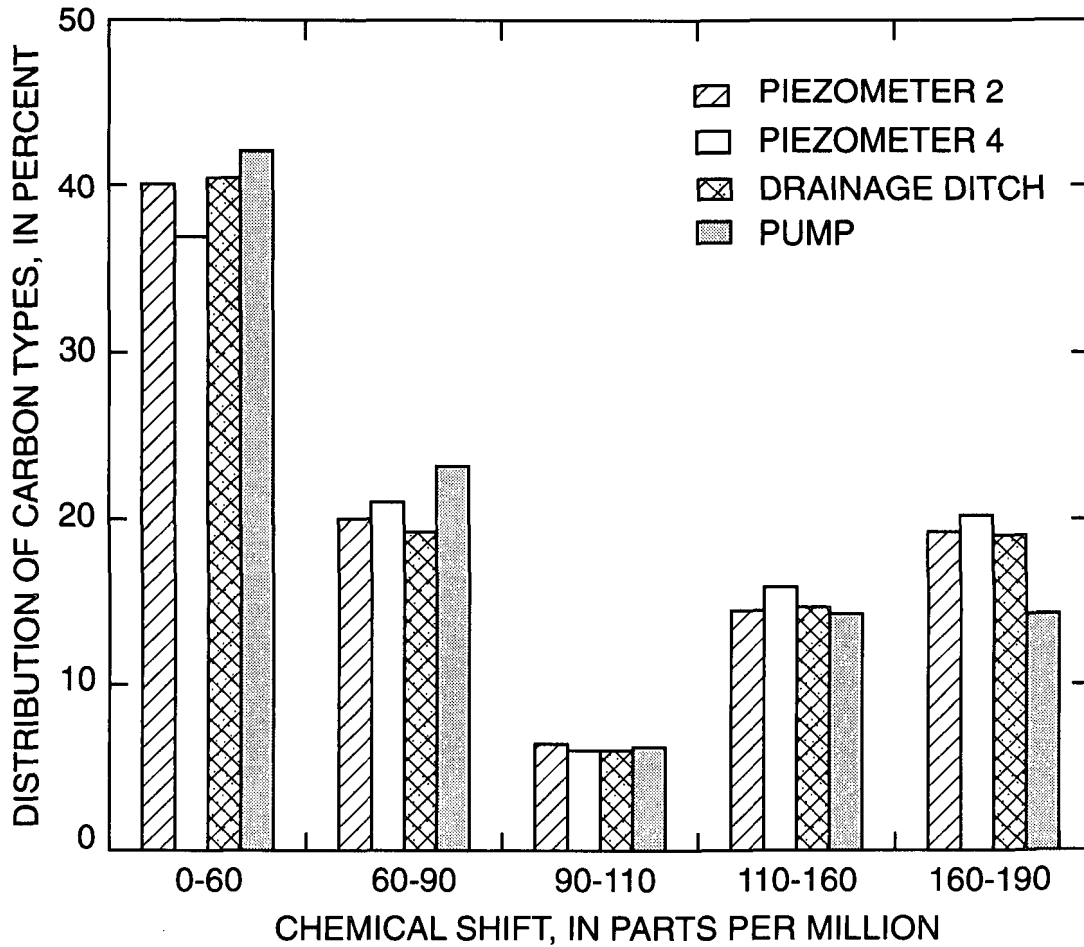


Figure E8. Comparison of carbon-13 nuclear magnetic resonance data for hydrophilic acid fraction from piezometers 2 and 4, drainage ditch, and pump samples collected July 17, 1996, Twitchell Island, California.

and subsequent cultivation. CPMAS ^{13}C -NMR spectra for soil samples collected near lysimeters 2 and 4 are compared with those from piezometers 2 and 4 in figures E9 and E10. As expected, the shallow samples are similar to each other, as are the deeper samples. Differences between the shallow and deep soils can be attributed to enhanced degradation of the shallow soils.

The lysimeter samples are less aromatic and have less aliphatic II carbon associated with carbohydrates than the piezometer samples. The shallow samples also are enriched in carboxyl content and aliphatic I carbon. These results are consistent with greater degradation rates for the aromatic, and to a lesser extent, carbohydrate moieties in the oxidized soils compared to the

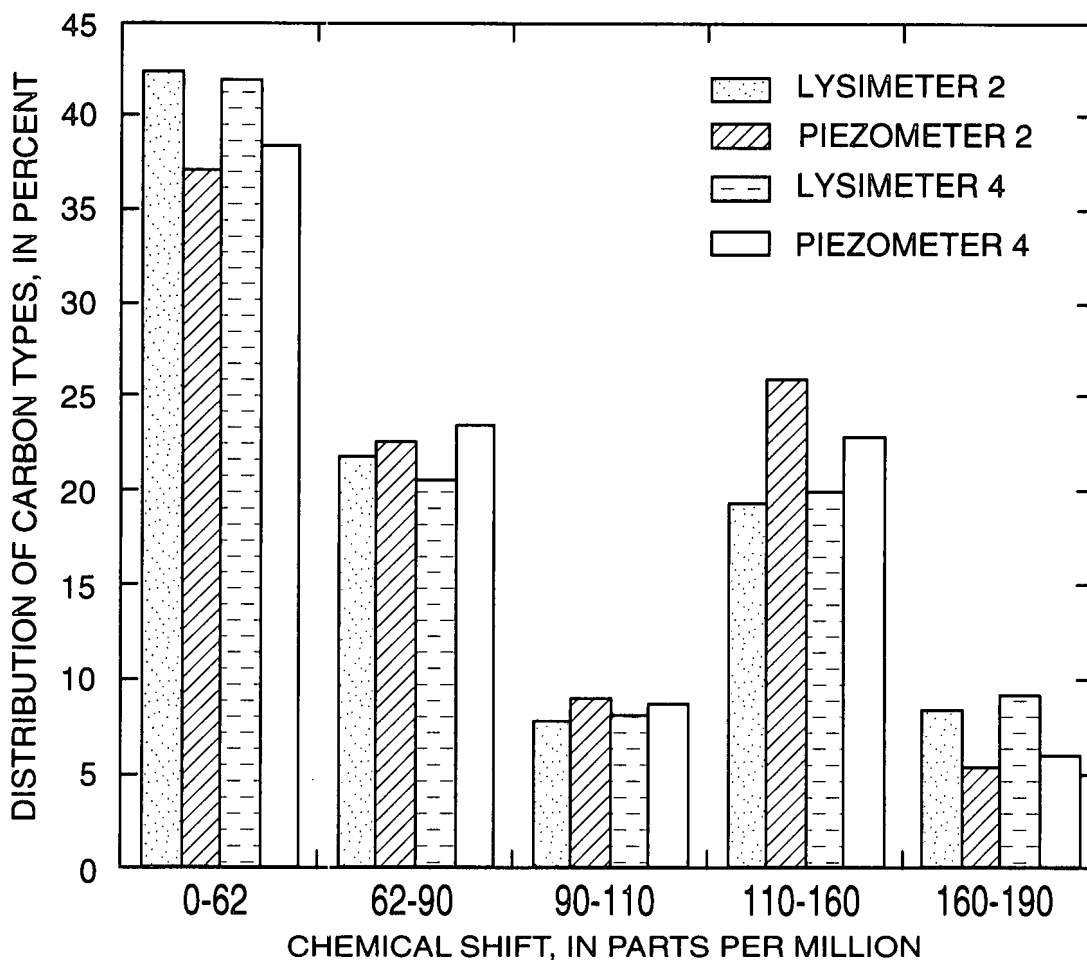


Figure E9. Comparison of carbon-13 nuclear magnetic resonance data for soil samples taken near lysimeters 2 and 4 and piezometers 2 and 4, Twitchell Island, California.

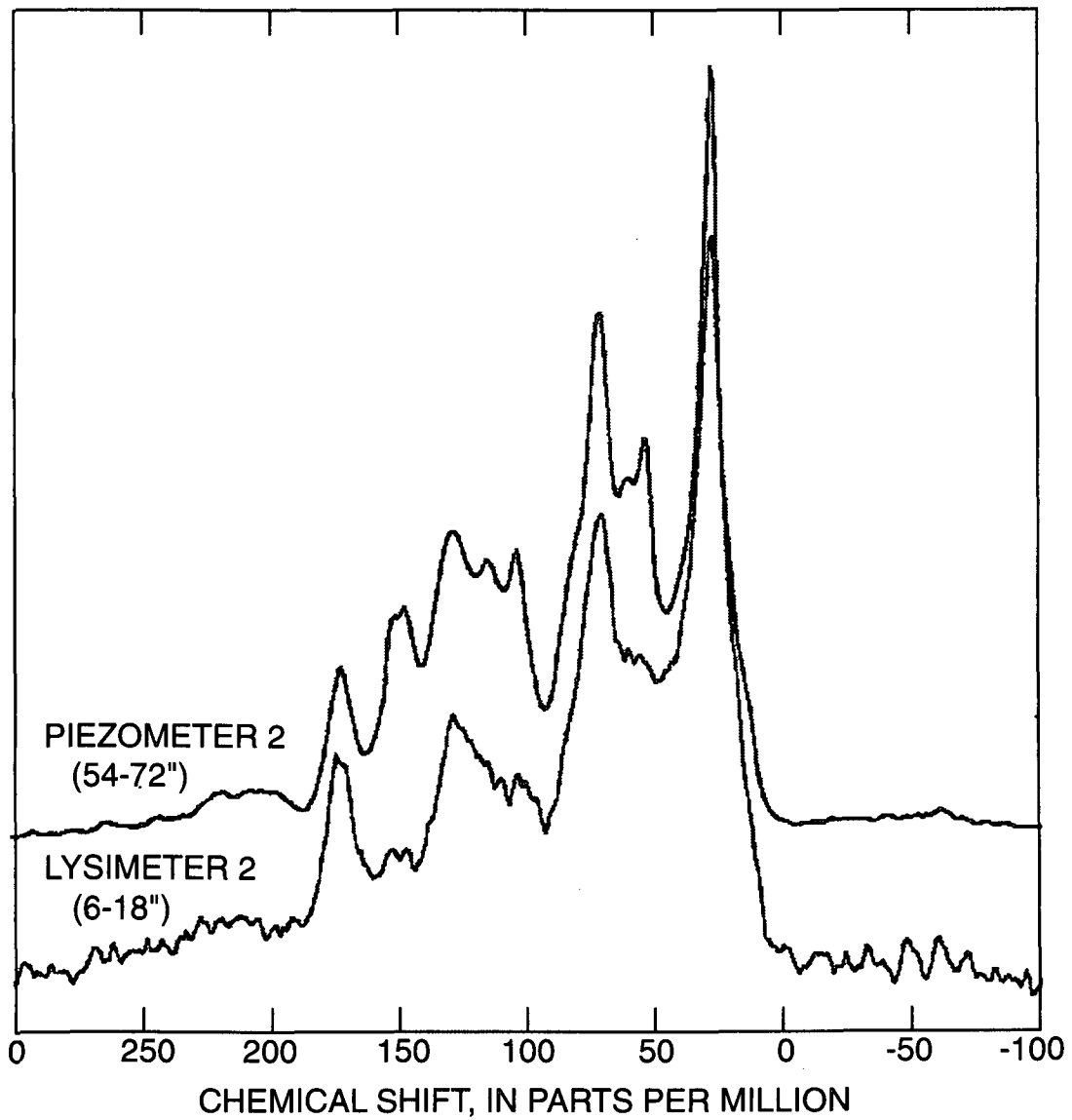


Figure E10. Carbon-13 nuclear magnetic resonance spectra for soil samples taken near piezometer 2 and lysimeter 2, Twitchell Island, California.

reduced soils. Carboxyl groups are a product of microbial oxidation and also are consistent with a greater degree of oxidation of the shallow soils.

More detailed examination of the aromatic region of the NMR spectra for the soils indicates that the region of the spectra associated with aromatic phenols (140-160 ppm), such as tannins and lignin phenols, is depleted at a faster rate than the aromatic moieties that do not have hydroxyls associated with them (110-140 ppm). Associated with the loss of aromatic phenols is the loss at about 57 ppm of what is likely to be methoxy ethers. A model for degradation that would account for this difference involves the oxidation of aromatic phenols with the subsequent opening of the aromatic ring, resulting in lower aromatic carbon and increased carboxyl and aliphatic carbon content.

APPENDIX F: PRELIMINARY DATA FOR WETLAND-HABITAT PONDS

In addition to the primary study of DOC and THM precursors released from peat soils under agricultural production, soil water from three wetland-habitat test ponds were sampled by the USGS and samples were analyzed by the DWR Bryte Laboratory for the same parameters discussed in appendix A. The test ponds were designed to evaluate the effects of different wetland habitats on land subsidence in the Delta. Microbial oxidation of peat soil is the primary cause of currently observed land subsidence in the Delta (Deverel and others, 1998). Implementation of wetland habitats is being tested to evaluate how these treatments

affect subsidence compared to nonwetland land uses (for example, drained pastures, agriculture). As part of this study, three test ponds also were monitored for potential effects of the wetlands on water quality, in particular DOC and THM precursor release.

Two of the three wetland-habitat test ponds consisted of 30-ft square enclosures, and the third test pond was a small (about 100 ft²) spring-fed pond (TwitPiz5) in a subsidence mitigation test area being maintained by DWR. One of the enclosed test ponds is flooded continuously (TwitPiz6) with about 1 to 1.5 ft of water maintained above land surface. This flooded pond has been in operation for about 4 years, and results have indicated that shallow flooding decreases subsidence rates by a factor of about four and also encourages the growth of cattails that contribute biomass back to the system. The second enclosed pond is a reverse-flooding treatment pond (TwitPiz7) that is intentionally flooded to a depth of about 1 ft above land surface from early spring until mid-July. Winter precipitation kept this pond moist to very wet (for example, standing water) during the later part of December 1996 and through February 1997.

Stainless-steel piezometers were installed in each test pond to sample water from 0.5 to 1.5 ft below land surface. In August 1996, surface water in the ponds also was analyzed. Samples were collected from the open-water and continuously flooded ponds for the September and November 1996 samplings. Results of these analyses are presented in tables F1 through F4.

Table F1. Field parameters measured for samples from piezometers and surface-water samples, Twitchell Island, California

[$\mu\text{S/cm}$, microsiemens per centimeter; $^{\circ}\text{C}$, degrees Celsius; mg/L , milligrams per liter; na, not analyzed; TwitPiz, piezometer; TwitSur, surface water. Samples are from the California Department of Water Resources]

Site	Date	Time	Specific conductance ($\mu\text{S/cm}$)	pH, water, field (standard units)	Temperature, water ($^{\circ}\text{C}$)	Dissolved oxygen (mg/L)
TwitPiz6	03/21/96	11:05 am	4,700	6.4	20.3	na
TwitPiz7	03/21/96	12:45 pm	4,660	6.6	27.5	na
TwitPiz5	04/11/96	11:00 am	4,670	6.2	17.7	na
TwitPiz6	04/11/96	11:45 am	6,630	6.3	15.0	na
TwitPiz7	04/11/96	12:35 pm	9,900	6.5	17.5	na
TwitPiz5	05/28/96	11:25 am	4,24	6.0	21.6	na
TwitPiz6	05/28/96	11:55 am	1,165	6.4	21.3	na
TwitPiz7	05/28/96	11:55 am	1,470	6.5	19.9	na
TwitPiz5	06/20/96	11:25 am	409	6.0	21.0	na
TwitPiz6	06/20/96	12:25 pm	974	6.3	21.7	na
TwitPiz7	06/20/96	12:04 pm	1,781	6.4	20.2	na
TwitPiz5	07/17/96	10:11 am	522	5.6	21.7	na
TwitPiz5	07/17/96	10:11 am	522	5.6	21.7	na
TwitPiz6	07/17/96	10:18 am	1,001	6.1	21.7	na
TwitPiz6	07/17/96	10:18 am	1,001	6.1	21.7	na
TwitPiz7	07/17/96	10:21 am	1,913	6.3	21.3	na
TwitPiz7	07/17/96	10:21 am	1,913	6.3	21.3	na
TwitPiz5	08/16/96	10:11 am	522	5.8	21.7	na
TwitPiz6	08/16/96	10:18 am	1,001	6.1	21.7	na
TwitPiz7	08/16/96	10:21 am	1,913	6.3	21.3	na
TwitPiz5	09/04/96	10:13 am	563	6.87	22.1	na
TwitPiz6	09/04/96	10:20 am	1,112	6.39	20.6	na
TwitPiz5	10/23/96	10:20 am	830	6.47	15.7	na
TwitPiz5	10/23/96	10:20 am	550	5.94	16.7	na
TwitPiz6	10/23/96	10:32 am	489	6.07	14.4	na
TwitPiz5	11/13/96	10:50 am	615	5.93	15.6	na
TwitPiz6	11/13/96	10:25 am	1,302	6.00	12.5	na
TwitPiz5	01/02/97	na	na	na	na	na
TwitPiz6	01/02/97	na	na	na	na	na
TwitPiz6	01/02/97	na	na	na	na	na
TwitPiz7	01/02/97	na	na	na	na	na
TwitSur5	09/04/96	10:15 am	933	6.94	20.3	na
TwitSur6	09/04/96	10:20 am	293	6.63	16.5	na
TwitSur5	11/13/96	10:53 am	824	6.40	13.6	na
TwitSur6	11/13/96	10:44 am	557	6.33	12.1	na
TwitSur6	01/02/97	na	na	na	na	na
TwitSur7	01/02/97	na	na	na	na	na

Table F2. Results for speciation of trihalomethane formation potential and associated parameters for piezometer and surface-water samples collected at piezometer locations, Twitchell Island, California

[CHCl₃, chloroform; CHCl₂Br, bromodichloromethane; CHBr₂Cl, chlorodibromomethane; CHBr₃, bromoform; TwitPiz, piezometer; TwitSur, surface water; na, not analyzed; <, less than. Values in micrograms per liter, except ultraviolet absorbance, which is in per centimeter units. Trihalomethane formation potential determined using dose-based method, unless otherwise noted in Method column. Samples from the California Department of Water Resources]

Site	Date	CHCl ₃	CHCl ₂ Br	CHBr ₂ Cl	CHBr ₃	Dis-solved organic carbon	Trihalo-methane formation potential	Ultra-violet absorbance	Halo-acetic acid 1	Halo-acetic acid 2	Halo-acetic acid 3	Halo-acetic acid 4	Halo-acetic acid 5	Halo-acetic acid 6	Method
TwitPiz6	03/21/96	1,500	190	20	20	10.4	1,730	0.759	na	na	na	na	na	na	
TwitPiz7	03/21/96	4,900	300	60	60	39.3	5,320	2.540	na	na	na	na	na	na	
TwitPiz5	04/11/96	1,400	200	20	20	10.1	1,640	.769	na	na	na	na	na	na	
TwitPiz6	04/11/96	3,600	420	50	50	27.9	4,120	1.960	na	na	na	na	na	na	
TwitPiz7	04/11/96	9,800	680	90	90	85.4	10,660	4.240	na	na	na	na	na	na	
TwitPiz5	05/28/96	1,200	180	20	20	10.6	1,420	.814	na	na	na	na	na	na	
TwitPiz6	05/28/96	7,100	610	120	120	77.3	7,950	5.730	na	na	na	na	na	na	
TwitPiz7	05/28/96	15,100	2,800	410	250	171.4	18,560	12.300	na	na	na	na	na	na	
TwitPiz5	06/20/96	1,400	220	29	20	11.7	1,669	.857	na	na	na	na	na	na	
TwitPiz6	06/20/96	6,500	620	100	100	67.0	7,320	5.040	na	na	na	na	na	na	
TwitPiz7	06/20/96	21,100	2,700	330	300	207.9	24,430	13.340	na	na	na	na	na	na	
TwitPiz5	07/17/96	1,100	240	44	0	8.3	1,384	.686	na	na	na	na	na	na	
TwitPiz6	07/17/96	6,800	630	0	0	59.1	7,430	4.860	na	na	na	na	na	na	
TwitPiz7	07/17/96	18,200	2,000	0	0	155.6	20,200	15.700	na	na	na	na	na	na	
TwitPiz5	08/16/96	1,100	250	48	0	9.0	1,398	.718	na	na	na	na	na	na	
TwitPiz6	08/16/96	11,900	800	0	0	99.8	12,700	7.890	na	na	na	na	na	na	
TwitPiz7	08/16/96	1,900	2,400	290	0	172.0	22,590	11.720	na	na	na	na	na	na	
TwitPiz5	09/04/96	970	270	66	<20	8.4	1,306	.629	na	na	na	na	na	na	
TwitPiz6	09/04/96	9,300	510	<80	<80	94.5	9,810	na	na	na	na	na	na	na	
TwitPiz5	10/23/96	560	270	96	<10	6.8	926	.556	na	na	na	na	na	na	Reactivity-based

Table F2. Results for speciation of trihalomethane formation potential and associated parameters for piezometer and surface-water samples collected at piezometer locations, Twitchell Island, California—Continued

Site	Date	CHCl ₃	CHCl ₂ Br	CHBr ₂ Cl	CHBr ₃	Dis-solved organic carbon	Trihalo-methane formation potential	Ultra-violet absorbance	Halo-acetic acid 1	Halo-acetic acid 2	Halo-acetic acid 3	Halo-acetic acid 4	Halo-acetic acid 5	Halo-acetic acid 6	Method
TwitPiz5	11/13/96	490	230	94	<10	5.8	814	0.433	na	na	na	na	na	na	
TwitPiz5	11/13/96	320	200	99	<10	5.8	619	.433	na	na	na	na	na	na	Reactivity-based
TwitPiz6	11/13/96	12,000	890	<150	<150	132.0	12,890	8.78	na	na	na	na	na	na	
TwitPiz6	11/13/96	10,000	800	<180	<180	132.0	10,800	8.78	na	na	na	na	na	na	Reactivity-based
TwitPiz5	01/02/97	na	na	na	na	na	na	na	na	na	na	na	na	na	
TwitPiz6	01/02/97	2,700	180	<30	<30	35.2	2,880	1.26	na	na	na	na	na	na	
TwitPiz6	01/02/97	2,600	210	<30	<30	35.2	2,810	1.26	<30	<30	<30	<30	1,600	2,300	Reactivity-based
TwitPiz6	01/02/97	na	na	na	na	na	na	na	na	na	na	na	na	na	
TwitPiz7	01/02/97	na	na	na	na	na	na	na	na	na	na	na	na	na	
TwitSur5	09/04/96	1,300	370	110	<10	14.8	1,780	.607	na	na	na	na	na	na	
TwitSur6	09/04/96	270	71	19	<10	3.7	360	.092	na	na	na	na	na	na	
TwitSur5	10/23/96	1,400	350	92	<20	16.3	1,842	.662	na	na	na	na	na	na	
TwitSur5	10/23/96	1,200	410	120	<20	16.3	1,730	.662	na	na	na	na	na	na	Reactivity-based
TwitSur6	10/23/96	220	120	63	<10	3.6	403	.135	na	na	na	na	na	na	
TwitSur6	10/23/96	140	130	98	13	3.6	381	.135	na	na	na	na	na	na	Reactivity-based
TwitSur5	11/13/96	1,200	350	81	<20	15.7	1,631	.666	na	na	na	na	na	na	
TwitSur5	11/13/96	930	340	91	<20	15.7	1,361	.666	na	na	na	na	na	na	Reactivity-based
TwitSur6	11/13/96	430	170	56	<10	6.2	656	.291	na	na	na	na	na	na	
TwitSur6	11/13/96	280	170	73	<10	6.2	523	.291	na	na	na	na	na	na	Reactivity-based
TwitSur6	01/02/97	na	na	na	na	na	na	na	na	na	na	na	na	na	
TwitSur7	01/02/97	na	na	na	na	na	na	na	na	na	na	na	na	na	

Table F3. Mineral data for piezometer and surface-water samples, Twitchell Island, California

[Values are in milligrams per liter; °C , degrees Celsius; TwitPiz, piezometer; TwitSur, surface water; na, not analyzed. Samples are from the California Department of Water Resources]

Site	Date	Hardness as CaCO ₃	Calcium, dis- solved	Magnesium, dis- solved	Sodium, dis- solved	Potassium, dis- solved	Alkalinity, lab, as CaCO ₃	Sulfate, dis- solved	Chloride, dis- solved	Bromide	Solids, residue at 180°C	Boron, dis- solved
TwitPiz6	03/21/96	32	6	4	68	1.6	43	6	87	0.3	248	0.2
TwitPiz7	03/21/96	63	12	8	46	1.9	68	12	63	.46	270	.4
TwitPiz5	04/11/96	28	6	3	67	1.5	44	6	88	.3	229	.2
TwitPiz6	04/11/96	76	14	10	91	2	64	13	139	.58	379	.4
TwitPiz7	04/11/96	121	35	8	100	8.4	176	32	87	1.54	568	.7
TwitPiz5	05/28/96	32	6	4	70	1.8	42	6	95	.33	261	.2
TwitPiz6	05/28/96	156	31	19	134	1.4	143	25	194	1.09	693	.9
TwitPiz7	05/28/96	354	94	29	240	7.2	632	38	110	5.47	1,390	.9
TwitPiz5	06/20/96	34	7	4	76	2.1	44	5	105	.38	284	.2
TwitPiz6	06/20/96	136	28	16	130	1.2	132	18	193	1	647	.8
TwitPiz7	06/20/96	288	76	24	228	6.5	499	66	189	4.14	1,370	1.7
TwitPiz5	07/17/96	36	8	4	81	2.5	44	5	120	.41	302	.2
TwitPiz6	07/17/96	123	26	14	129	0.6	116	18	185	.95	606	.7
TwitPiz7	07/17/96	367	91	34	297	5.9	677	52	193	4.64	1,620	2.0
TwitPiz5	08/16/96	34	7	4	87	2.4	42	5	125	.46	287	.2
TwitPiz6	08/16/96	173	38	19	131	0	170	32	185	1.02	756	1.3
TwitPiz7	08/16/96	258	64	24	236	4.8	533	48	171	3.32	1,210	1.5
TwitPiz5	09/04/96	40	8	5	91	2.8	45	4	138	.49	310	.2
TwitPiz5	10/23/96	43	9	5	94	2.8	36	4	144	.53	336	.2
TwitPiz5	11/13/96	43	9	5	95	2.6	36	5	141	.55	319	.2
TwitPiz6	11/13/96	204	52	18	129	1.4	224	29	177	1.34	817	1.1
TwitPiz5	01/02/97	na	na	na	na	na	na	na	na	na	na	na
TwitPiz6	01/02/97	517	113	57	112	8.8	26	433	202	.21	1,110	.2
TwitPiz6	01/02/97	na	na	na	na	na	na	na	na	na	na	na
TwitPiz7	01/02/97	na	na	na	na	na	na	na	na	na	na	na
TwitSur5	09/04/96	88	17	11	146	4.8	96	4	218	.67	486	.2
TwitSur6	09/04/96	60	11	8	29	1	58	12	40	.14	151	<.1
TwitSur5	10/23/96	88	17	11	139	4	95	4	207	.69	484	.2
TwitSur6	10/23/96	92	17	12	68	1.1	60	25	102	.39	309	.0
TwitSur5	11/13/96	78	15	10	131	4	91	5	197	.64	434	.2
TwitSur6	11/13/96	88	14	13	68	3.6	68	17	111	.39	290	.1
TwitSur6	01/02/97	na	na	na	na	na	na	na	na	na	na	na
TwitSur7	01/02/97	na	na	na	na	na	na	na	na	na	na	na

Table F4. Iron, manganese, and nitrogen species (as N) for piezometer and surface-water samples, Twitchell Island, California

[All measurements are in milligrams per liter; TwitPiz, piezometer; TwitSur, surface water; na, not analyzed; <, less than. Samples are from the California Department of Water Resources]

Site	Date	Nitrate, dissolved (as N)	Nitrite plus Nitrate, dissolved (as N)	Nitrogen, ammonia, dissolved (as N)	Iron	Manganese, dissolved
TwitPiz6	03/21/96	0	na	na	na	na
TwitPiz7	03/21/96	0	na	na	na	na
TwitPiz5	04/11/96	0	na	na	na	na
TwitPiz6	04/11/96	.3	na	na	na	na
TwitPiz7	04/11/96	.5	na	na	na	na
TwitPiz5	05/22/96	1.7	na	na	na	na
TwitPiz6	05/22/96	11	na	na	na	na
TwitPiz7	05/22/96	34	na	na	na	na
TwitPiz5	07/17/96	<.1	0	0.44	2.53	0.04
TwitPiz6	07/17/96	.2	.02	.78	30	.268
TwitPiz7	07/17/96	2.5	.02	4.40	27.2	1.61
TwitPiz5	08/16/96	<.1	0	.56	3.29	.054
TwitPiz6	08/16/96	<.1	0	.30	60	1.05
TwitPiz7	08/16/96	<.1	.02	3.60	65.8	1.68
TwitPiz5	09/04/96	.2	.03	.54	3	.038
TwitPiz6	09/04/96	na	na	na	na	na
TwitPiz5	10/23/96	<.1	.02	.67	3.07	.059
TwitPiz5	11/13/96	3.8	na	.07	2.99	.054
TwitPiz6	11/13/96	.9	na	1.40	39.2	.714
TwitPiz5	01/02/97	na	na	na	na	na
TwitPiz6	01/02/97	58	13	.93	na	na
TwitPiz6	01/02/97	na	na	na	na	na
TwitPiz7	01/02/97	na	na	na	na	na
TwitSur5	09/04/96	<.1	.01	.02	.383	.025
TwitSur6	09/04/96	<.1	.03	.03	.113	.017
TwitSur5	10/23/96	<.1	.02	.12	.567	.069
TwitSur6	10/23/96	<.1	.02	.02	.731	.044
TwitSur5	11/13/96	<.1	na	.05	.722	.052
TwitSur6	11/13/96	<.1	na	.00	1.44	.092
TwitSur6	01/02/97	na	na	na	na	na
TwitSur7	01/02/97	na	na	na	na	na

State of California
The Resources Agency
Department of Water Resources
Division of Planning and Local Assistance

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Compendium of
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and
San Francisco Bay Area

August 1998



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Governor
State of California

Douglas P. Wheeler
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