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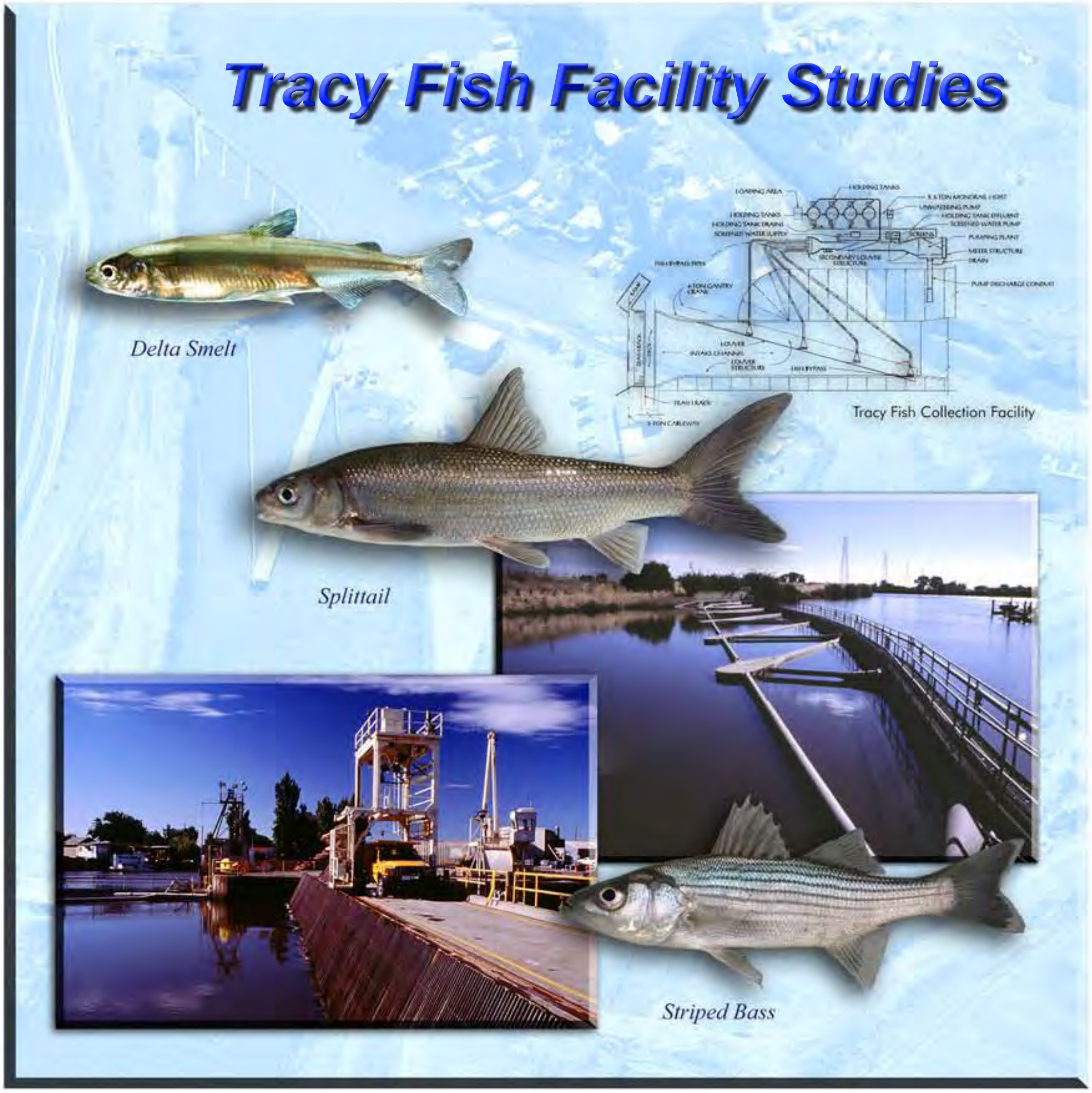

Composite Sampling and Analysis of Low Concentration Organic Compounds and Trace Elements in Surface Waters at the Tracy Fish Collection Facility, Tracy, California

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14. ABSTRACT

Monthly composite water samples for organic analyses (current use and persistent pesticides and hydrocarbons) were collected from late May 1999 through January 2000 from the intake channel at the Bureau of Reclamation's Tracy Fish Collection Facility (TFCF), Tracy California. When site power was uninterrupted, organic samples were pumped at a rate of 0.4-liter (L) per hour through a 1.0-micrometer pore-size disk filter and then extracted using solid phase extraction with XAD-2 Amberlite resin. During the organic sampling period, 2,642 L were pumped over 249 days. Filter disks and XAD columns were replaced monthly and then extracted and fractionated before analysis using high-resolution gas chromatography-low resolution mass spectrometry (HRGC-LRMS). These open scan LRMS data are generally described in this report and total ion chromatograms are included in electronic format for further mass spectra compound searching and identification. Frozen fractions from open scan analysis were later analyzed using quantitative methods for organic compounds using high resolution GC-high resolution MS (HRGC-HRMS) and liquid chromatography – tandem mass spectrometry (LC-MS/MS). These sensitive MS methods and the large volumes of water preconcentrated on filters and XAD columns allowed detection limits in the range of 0.010 to 0.100 nanograms per liter (ng/L). The HRMS and MS/MS data were summarized and compared with local agricultural chemical applications data from1997 and reported data from other studies. Several agricultural chemicals considered compounds of concern (Chlorpyrifos, Diazinon, Metolachlor, Trifluralin, and others) were detected at average concentrations from under 1 ng/L up to 120 ng/L (Metolachlor). Persistent and banned pesticides such as Aldrin, Chlordane, Lindane, and Mirex were mostly present at sub-ng/L concentrations, with some persistent analytes detected in the 1 – 10 ng/L range. Because of the dilution associated with composite sampling volumes, the average concentrations reported here may be much lower compared to actual short-term concentration spikes for detected organic compounds.

Trace metal composite sampling was also performed from May through November 1999 using a programmable peristaltic sampling pump that pumped 125 milliliters every 3 hours into sealed and clean high-density polyethylene containers. These samples were collected monthly, digested, and analyzed using inductively-coupled plasma – mass spectrometry (EPA method 6020A). The 1999 composite sample trace element data are presented and compared with 1997 discrete sampling and low-detection limit analysis of TFCF waters, along with other reported trace element data. Composite sample concentrations of all trace elements were below water quality guidelines except for mercury and possibly copper, and there were indications that contamination artifacts may have affected results.

15. SUBJECT TERMS

Tracy Fish Collection Facility, Tracy Fish Facility Improvement Program, TFCF, TFFIP, water quality, composite sampling, automated sampling pumps, solid phase extraction, XAD resin, organic compounds, herbicides, pesticides, chlorinated hydrocarbons, polyaromatic hydrocarbons, PAH, hydrocarbons, low resolution gas chromatography – mass spectrometry, GC-MS, open-scan GC-MS, AMDIS, mass spectra, compound identification, high resolution GC-MS, liquid chromatography – tandem mass spectrometry, LC-MS/MS, tandem mass spectrometry, sub-nanogram per liter, picogram per liter, ultra-trace concentrations, very low concentrations, trace elements, trace metals, inductively coupled plasma – mass spectrometry, ICP-MS

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Composite Sampling and Analysis of Low Concentration Organic Compounds and Trace Elements in Surface Waters at the Tracy Fish Collection Facility, Tracy, California

Volume 41

by

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COVER

Fish photography by René Reyes, Tracy Fish Collection Facility, Tracy, California.
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EXECUTIVE SUMMARY

This is the sixth report on water quality from the research project, *Chemical Monitoring and Assessment at the Tracy Fish Collection Facility*, funded as part of the Tracy Fish Facility Improvement Program (TFFIP). Started in 1989, the TFFIP was mandated and funded by the Central Valley Project Improvement Act of 1992 (CVPIA) (Reclamation, 2008) to investigate design and operational improvements for the Tracy Fish Collection Facility (TFCF). The purpose of this TFFIP research project is to develop a reliable reference or "baseline" water quality data set that combines historical water chemistry data and agricultural chemical application data (Craft *et al*., 2000a), validated semicontinuous measurement of general water quality variables (Craft *et al*., 2002; 2003; 2004; 2008), and chemical analysis data from discrete and composite water samples collected at the TFCF. A baseline water quality data set is important to the TFFIP because water quality has a direct influence on the health and stress responses of local fish populations (Portz *et al*., 2005) and impaired water quality may affect fish salvage survival.

This report is a summary of chemical analyses performed on composite (time integrated) water samples collected in 1999 and 2000 for organic compounds and trace elements. Included in the INTRODUCTION of this report is a description of the general water quality at the TFCF and the factors that influence the concentrations of organic compounds and trace elements in TFCF waters. This background is provided for the benefit of non-specialists and the general public.

Methods

Organic Composite Sampling

Composite samples for organic compounds were collected from the intake channel behind the trashrack at the TFCF using solid phase extraction (SPE). Composite sampling was performed with a programmable Infiltrex 300 sampling pump (Axys Analytical Services, Ltd. – Axys) that pumped channel water through a 1.0-micrometer (µm) pore-size in-line filter and then a flow-through SPE column (cartridge) containing pre-washed XAD-2 Amberlite resin (Dow Chemical). The Infiltrex unit pumped 0.4-liters per hour through the filter and SPE column and pumped volumes ranged from 59 L (in July) up to 634 L (in January) per month. These variable pumping volumes were caused by frequent summer power outages at the TFCF.

Open Scan, Low-Resolution Mass Spectrometry Methods

Once a month, the SPE column and filters were removed and shipped to Axys on ice. The filters and columns were rinsed with deionized water and then extracted using dichloromethane solvent in a Soxhlet extractor. The initial solvent extractions for each filter and XAD column were then fractionated (a clean-up procedure) using solvent exchange on a Florisil column into less polar (F1) and moderately polar (F2) fractions. These fractions were then analyzed using open scan high-resolution gas chromatography–low-resolution mass spectrometry (HRGC–LRMS).

After HRGC–LRMS analysis, the 30 largest peaks in each total ion chromatogram were identified using mass spectral data base search and matching methods. The 30 chromatogram peaks were background subtracted and reviewed manually using Automated Mass Spectral Deconvolution and Identification System (AMDIS), version 1.01, an application program designed to run with the National Institute of Science and Technology (NIST) mass spectrometry (MS) library of over 100,000 compounds with the NIST Mass Spectral Search Program (version 1.6d; Stein *et al*., 1998).

Quantitative High-Resolution Mass Spectrometry Methods

A portion of the original solvent extracts from the composite SPE columns and filters were archived and later analyzed by Axys using very specific quantitative analyses (Woudneh and Oros, 2006a; 2006b) for organic compounds with HRGC–high-resolution MS (HRGC–HRMS) and liquid chromatography-tandem mass spectrometry (LC–MS/MS). The sensitive MS methods coupled with significant preconcentration from composite sampling enabled detection limits (DLs) for many compounds in the range of 0.01 to 0.100 nanograms per liter (ng/L). All high-resolution methods used prepared calibration standards for individual compounds, and recoveries were calculated using isotopically labeled internal standards.

Extracts for two HRGC–HRMS methods were cleaned using an aminopropyl SPE column and a micro-silica column before instrumental analysis. One instrumental method was optimized for organonitrogen compounds, the other method for triazines, chlorinated, organophosphorus, and pyrethroid compounds. The capillary analytical column was coupled directly to the HRMS source. Carbamates were analyzed by LC–MS/MS without extract clean-up.

Chemical Compounds of Concern (COC) were selected by comparing agricultural chemical applications near the TFCF with toxicity for each compound (Craft *et al*., 2000a) to help evaluate the quantitative results. Quantitative data for COC analyses and other classes of compounds were summarized and compared to data published by the U.S. Geological Survey (MacCoy *et al*., 1995), the California Department of Pesticide Regulation (CDPR, 2008) for samples collected from the San Joaquin River near Vernalis, California, and the Regional Monitoring Program (RMP) and the San Francisco Estuary Institute (SFEI, 1997; 2006) for samples collected from San Francisco Bay and the San Joaquin and Sacramento Rivers near Suisun Bay.

Trace Element Methods

Trace metal composite sampling was performed from May through November 1999 using a Sigma programmable peristaltic sampling pump. These samples were collected monthly, digested, and analyzed using inductively coupled plasma–mass spectrometry (ICP–MS) following U.S. Environmental Protection Agency (EPA) method 6020A (EPA, 2008). These data are presented and compared with 1997 discrete sampling and low-detection limit analysis of TFCF waters (Craft *et al*., 2000a), along with trace element data from river samples and the San Francisco Bay and estuary reported by the RMP (SFEI, 1997; 2006).

Results for Organic Compounds

The filtration and SPE using an automated sampling pump successfully collected composite samples that provided data on a broad range of organic contaminants at the TFCF. Despite problems with power outages, the data presented here are thought to be temporally representative of the peak irrigation season and some of the winter dormant period.

Open Scan HRGC–LRMS Data

The open scan LRMS data provides a qualitative overview of all organic compounds present in TFCF waters, and these results are generally described in this report. The total ion chromatograms (TICs) from these analyses are also included here for further mass spectra compound searching and identification by other researchers. The electronic data for the open scan TICs are provided on the enclosed CD-R and total ion chromatograms are shown in Appendix 2. The HRGC–LRMS open scan data showed that petroleum derived compounds, including alkanes, PAHs, surfactants, and plasticizers, were common background contaminants in TFCF waters. These contaminants ranged in the 0–1,000 ng/L concentration range and were more frequently observed during rainy winter months.

Quantitative HRGS-HRMS and LC–MS/MS Data

High-resolution MS data are summarized in several report tables and Appendix 3. Many agricultural chemicals and other organic compounds were detected at average concentrations from under 1 ng/L up to 120 ng/L. These data show that both locally and regionally applied agricultural chemicals and persistent chemicals were present in TFCF waters most of the time during the sampling period, and most detected COCs and other current use pesticides showed dissolved phase > suspended phase concentrations.

Of the COC agricultural chemicals analyzed, only Aldicarb was not detected, and many compounds were detected in almost all composite samples including Chlorpyrifos, Diazinon, Metolachlor, and Trifluralin. Detected average concentrations for the COC list analyses ranged from tens of picograms per liter (pg/L) to over 100 ng/L, and Metolachlor was observed with the highest overall concentrations. Because of the dilution associated with composite sampling volumes, short-term concentrations (in spikes lasting from 1 day to several weeks) may have been much higher than reported averages for all detected organic compounds. Some agricultural compounds may have been present in TFCF waters at concentrations as high as 1,000 ng/L for short periods of time. Other non-COC agricultural chemicals were also detected in similar concentration ranges to the COC analytes. Some of these compounds were applied near the TFCF and others elsewhere in the San Joaquin River watershed.

There were no clear correlations between localized chemical applications from the 1997 data summary and the 1999 composite sample data. The lack of correlation is thought to be caused by the influence of basin-wide chemical applications, and perhaps changes in local applications during 1999. These results suggest the need for a re-evaluation of the COC analytes list using chemical application data from a much larger area in the south Delta, and including more recent monitoring data and agricultural practices.

Persistent chemicals such as Aldrin, Chlordane isomers and metabolites, Endrin, Lindane and other hexachlorocyclohexane (HCH) isomers, and Mirex were consistently detected in the composite samples in the < 10 ng/L to pg/L range of concentration. These data, along with recent reports of wildlife tissue concentrations of persistent chemicals (Greenfield *et al*., 2003; Davis *et al*., 2006; Fairey *et al*., 1997; Ohlendorf and Miller, 1984), showed that banned and restricted organic compounds remain a concern for water quality and fishery health in the Delta and San Francisco Bay.

Results for Trace Elements

The unfiltered composite trace element samples showed that chromium (Cr), nickel (Ni), and vanadium (V) were elevated above reported background averages, but well below regulated concentrations that indicate water quality problems. Elevated Cr, Ni, and V were also corroborated by data from the October 1997 discrete samples and others. The concentrations of copper (Cu) and zinc (Zn) in the composite samples were in the same concentration range, but higher than those reported by the RMP (SFEI, 1997; 2006), and almost all composite detections were higher than the discrete samples collected in October 1997. We would expect lower concentrations in the October 1997 samples as autumn is between the spring and summer peak irrigation season and before the winter rainy season when elevated runoff would be expected to mobilize trace elements. However, elevated aluminum (Al), iron (Fe), and Zn in unfiltered composites suggested either very elevated suspended particulates in 1999 TFCF waters, or possible contamination artifacts.

Based on an assessment of both the 1999 composite samples and the October 1997 discrete sample results, the only elements suggesting water quality concern were silver (Ag), mercury (Hg), methylmercury (Me-Hg), Cu, and uranium (U). Ag was not detected in composites, but was elevated in the October 1997 discrete samples relative to the Toxic Reference Value (TRV) of 12 ng/L (Savannah River Site, 2008). Hg is a known problem Delta-wide based on elevated wildlife tissue concentrations, and while the October 1997 discrete samples did not indicate regulatory exceedence, the 1999 summer composite data suggested further study. Composite (and average) unfiltered Cu was close to regulated concentrations, so dissolved concentrations may have exceeded the California 4-day Fresh Water Aquatic Life guideline of 9.0 µg/L (SFEI, 2006). U was only detected in 1 composite sample very near the 5 µg/L DL, but we noted fairly elevated concentrations in all October 1997 discrete samples in the 7–10 µg/L range. This finding suggests that future trace element sampling should confirm and establish seasonal concentrations of U in south Delta waters.

Recommendations for Future Studies

General Composite Sampling

Given the power interruption issues that affected collection of samples, we recommend that any future composite sampling effort, for either organic compounds or trace elements, utilize an uninterruptable power supply as a backup, or that solar powered pumps be used.

We also suggest that a depth-integrating sample inlet be installed near mid-channel to improve sample representativeness for the entire channel.

Organic Sampling and Analyses

If future composite sampling for organic analyses is performed at the TFCF, we recommend that a full year of samples be collected to fully cover the dormant application and rainy season from February through May. Organic analyses should continue to utilize the highly sensitive HRGC–HRMS and LC–MS/MS methods for currently used pesticides, carbonates, and chlorinated compounds. Additional target analytes such as common polybrominated diphenyl ethers (PBDEs) should also be considered. Future sampling should plan to pump larger volumes for composites to enhance preconcentration and detection of compounds that were below detection, but were also likely present in TFCF waters in this study.

Trace Element Sampling and Analyses

Comparison of the unfiltered composite sample data with the discrete samples collected in October 1997 suggested that future sampling for trace elements at the TFCF should use more sensitive methods for ICP–MS analysis with detection limits for Ag, arsenic (As), cadmium (Cd), Cu, Hg, Ni, lead (Pb), selenium (Se), U, and Zn in the low ng/L range. EPA Method 1638 (EPA, 1996b) or a method that exceeds 1638 performance should be used for higher sensitivity and lower detection ICP–MS analysis. EPA Method 6020 (EPA, 2008), used for composite samples in this study, should *not* be used. Hg should be analyzed using EPA Method 1631 (Bloom, 1996; EPA, 1996c) and Me-Hg using the method of Bloom (1989) employing aqueous phase ethylation.

Because of the inherent dilution from compositing and lack of preconcentration, we recommend that composite sampling be replaced with discrete sampling using ultra-clean field sampling procedures (EPA, 1996a) and contamination reduction protocols. Lab selection should be a careful process and significant experience with ultra-trace analytical methods and adequate facilities are essential. A minimum schedule should include monthly collection at mid-month during mid-tide, but biweekly sampling would establish a better baseline data set of reliable ultra-trace data. Discrete samples should be collected from a single station in the channel behind the trash rack at the TFCF using a depth-integrating manifold. Samples should only be filtered and preserved under clean room or semi-clean room conditions by the analysis lab, and field blanks, random duplicates, and spikes should included as quality assurance (QA) blind samples.

INTRODUCTION

The Tracy Fish Collection Facility

The Tracy Fish Collection Facility (TFCF) is the Bureau of Reclamation (Reclamation) fish salvage facility at the head of the intake canal for the C.W. “Bill” Jones Pumping Plant (BJPP – formerly Tracy Pumping Plant), that removes entrained fish from the Old River, a distributary of the San Joaquin River (SJR), before the water is pumped into Reclamation’s Delta Mendota Canal (DMC). Both the TFCF and the BJPP were built in the early 1950s as part of Reclamation’s Central Valley Project (CVP), a large water diversion infrastructure project that enabled agricultural expansion throughout most of the Central Valley of California.

The TFCF and BJPP are located approximately 8 kilometers (km) (4 miles [mi]) northwest of Tracy, California, in the southern riverine estuary region of the Sacramento-San Joaquin River Delta (south Delta) that flows into San Francisco Bay in northern California (see map in Figure 1). California's Department of Water Resources (CDWR) and Department of Fish and Game (CDFG) operate a similar salvage and pumping operation as part of the California State Water Project (SWP) directly to the north of the TFCF at Clifton Court Forebay (CCF). The SWP facility includes the Harvey O. Banks Pumping Plant (BPP), the John E. Skinner Delta Fish Protective Facility (SDFPF), and the California Aqueduct. Before the CVP and SWP diversion systems were implemented, SJR water flowed north unimpeded into San Francisco Bay. Much of the SJR is now recycled by being diverted south in the DMC and other State and Federal irrigation canals (Liston *et al*., 1993).

This report is the sixth in a series from the research project, *Chemical Monitoring and Assessment at the Tracy Fish Collection Facility*, funded as part of the Tracy Fish Facility Improvement Program (TFFIP). Started in 1989, the TFFIP was mandated and funded by the Central Valley Project Improvement Act of 1992 (CVPIA) to investigate design and operational improvements for the TFCF (Reclamation, 2008). The purpose of this TFFIP research project was to develop a reliable reference or “baseline” water quality data set that combined historical water chemistry data and agricultural chemical application data (Craft *et al*., 2000a), validated semicontinuous measurement of general water quality variables (Craft *et al*., 2002; 2003; 2004; 2008), and chemical analysis data from discrete and composite water samples collected at the TFCF. A baseline water quality data set is important to the TFFIP because water quality has a direct influence on the health and stress responses of local fish populations (Portz *et al*., 2005).

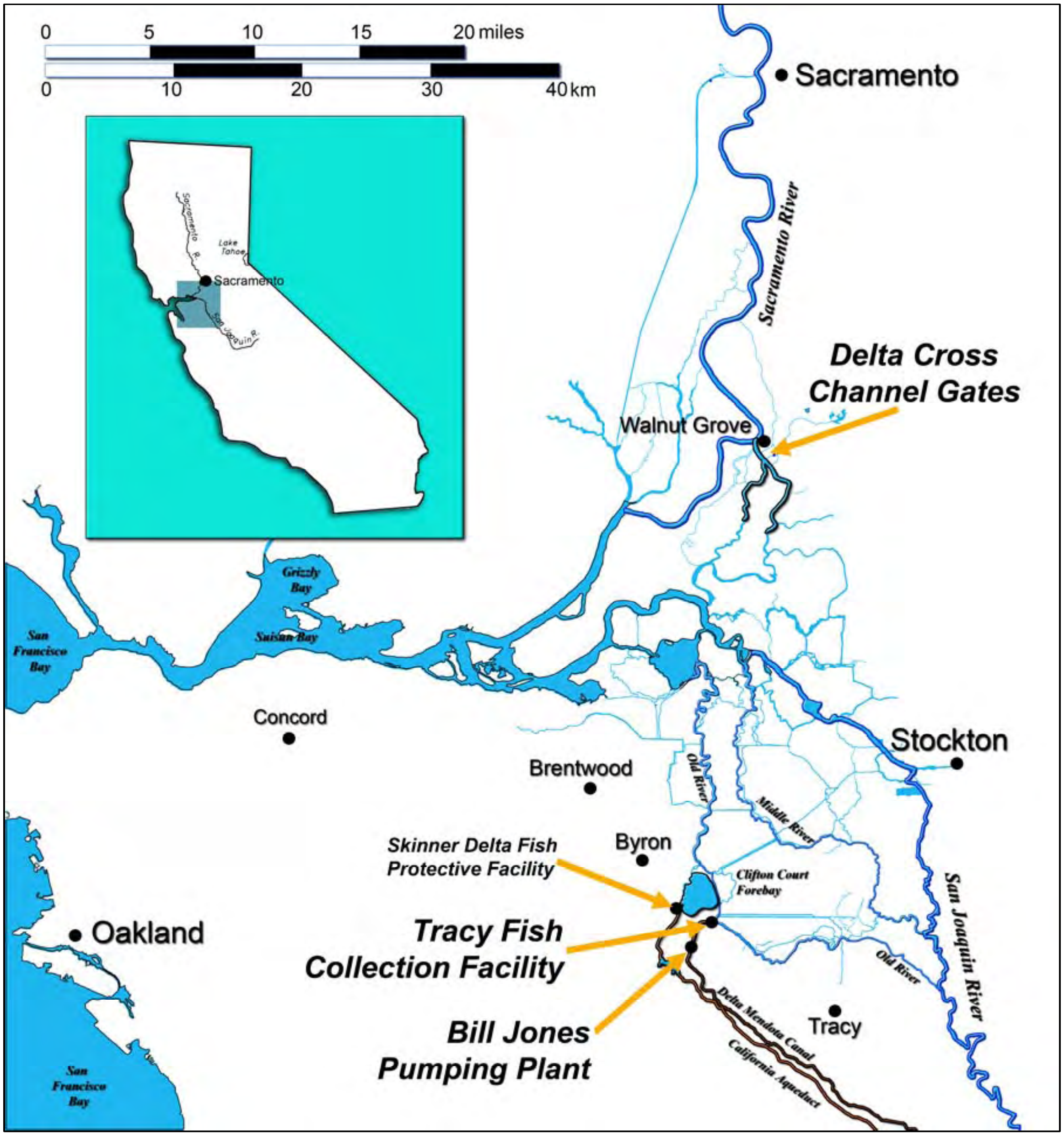


FIGURE 1.—Map showing the location of the Tracy Fish Collection Facility in the south Delta region of the Central Valley of California.

In April 1999, a multiprobe (sonde) was installed in the intake channel of the TFCF behind the trash rack as part of this project. The sondes have been measuring fundamental water quality variables water temperature (T, in degrees Celsius, °C), pH, electrical conductivity (EC, measured in µS/cm), dissolved oxygen (DO, measured in milligrams per liter, mg/L), oxidation-reduction or redox potential (Eh, in millivolts, mV), and turbidity (measured in nephelometric turbidity units, NTU), at 30-min intervals since April 1, 2000. Sonde data are posted for public download on the TFFIP Tracy research website: http://www.usbr.gov/pmts/tech_services/tracy_research/.

A composite sampling study was performed from May 1999 through January 2000 to collect water from the intake channel of the TFCF upstream of the primary louvers (see Figure 2 aerial photograph). Composite samples were collected for analysis of organic compounds and trace elements, and this report summarizes the analytical results from this effort.

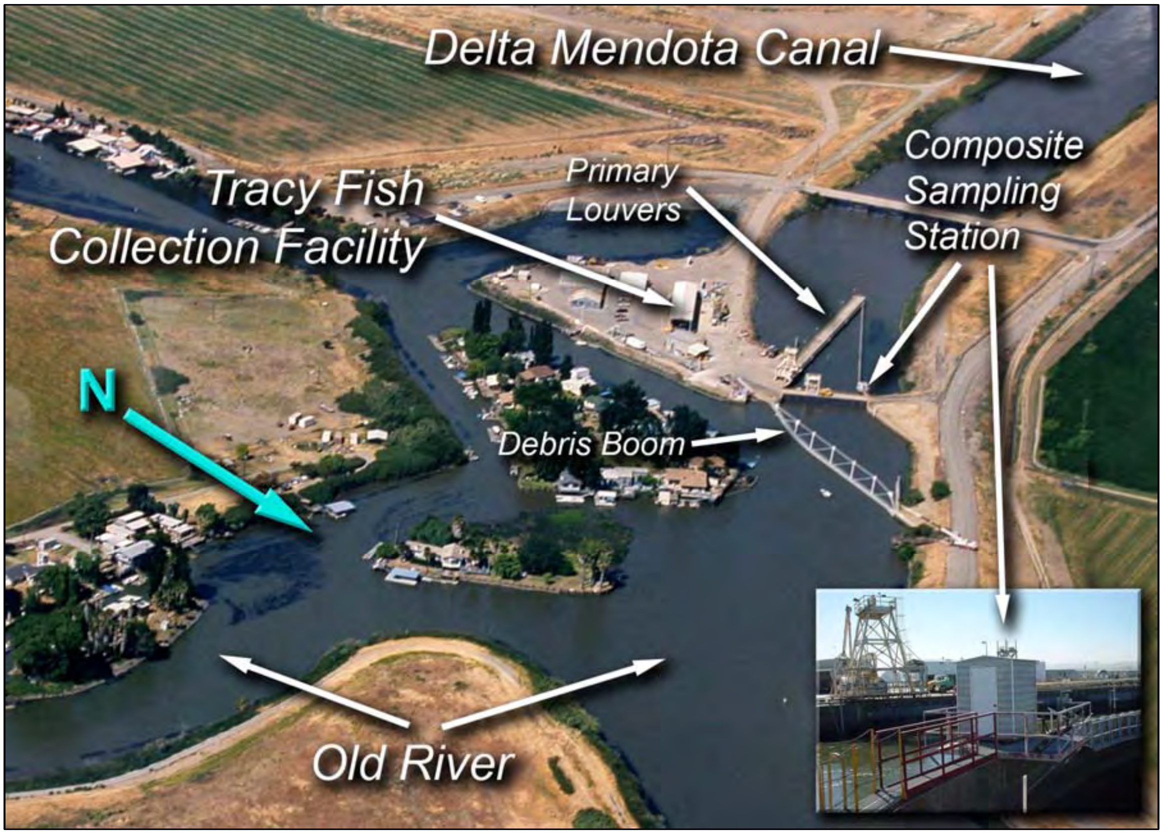


FIGURE 2.—Aerial photograph showing the Tracy Fish Collection Facility and the location used for the composite sampling. The calibration shed used to house the composite sampling pumps is shown in the inset. Reclamation photographs.

Water Quality Defined

Water quality is a general term that refers to the quantity of dissolved and suspended constituents present in water. Legally, water quality may refer to the concentrations of specific contaminants or toxicants that are regulated based on the toxicity of the contaminant and the intended use of the water. Generally, lower overall concentrations suggest “good” water quality, while higher concentrations suggest “impaired” water quality. Dissolved and suspended constituents in surface water are primarily caused by the interaction of precipitation water with rock and soil, biotic waste and decay, and the discharge or runoff of contaminants and waste chemicals. Chemical compounds may also be introduced to surface waters by atmospheric transport.

Here, dissolved refers to detected constituents in water having passed through a filter membrane with a specific pore size. Suspended is often defined as “total” minus dissolved; however, in this study, suspended fractions for organic composite samples were determined directly from extraction of filter membranes. Pore sizes used to define dissolved and suspended may vary depending on the analytical method and the sampling methods used for a given water. The U.S. Environmental Protection Agency (EPA) and many state regulatory agencies define dissolved as constituents detected in water having passed a 0.45-micrometer (µm) pore size filter. Some of the trace element data reported here (Craft *et al*., 2000a) used total and dissolved as defined by 0.45-µm filtration; however, the in-line filter used to collect composite samples for organic analyses was a 1.0-µm filter.

Water quality can be described by the constituents that fall into broad and sometimes overlapping classes or concentration ranges (Hem, 1970). These terms can be somewhat arbitrary and so are defined here as: fundamental variables (T, pH, EC, Eh, DO, turbidity), the major constituents (major ions, or majors), trace constituents, and ultra-trace constituents. Table 1 provides an outline of the different concentration classes, associated chemical properties or compounds, and concentration units and ranges for constituents reported in south Delta surface waters (Craft *et al*., 2000a; 2008).

Ultra-trace Constituents

Ultra-trace constituents are the subject of this report and usually refer to analytes in water below the microgram per liter (µg/L) concentration range. They may range from 5,000 – 10,000 nanograms (10^{-9} g) per liter (ng/L, or 5–10 µg/L) down to picograms (10^{-12} g) per liter (pg/L, below 1 ng/L) concentrations. The ultra-trace compounds that impair water quality include toxic inorganic trace elements and manmade organic compounds. Many of the ultra-trace compounds are deleterious to aquatic organisms but are usually present at very low and sub-lethal concentrations. These low concentrations are important; however, because they represent chronic stressors to fish and may have population and reproductive effects even at very low concentrations (Colborn and Carroll, 2007).

TABLE 1.—Summary of water quality terms used in this report to describe different concentration classes of properties and compounds, and approximate concentration ranges observed at the Tracy Fish Collection Facility.

Class	Property or Constitient	Approximate Ranges
Fundamental Variables	T	5–25 °C
	pH	6.5–8.5 s.u.
	Eh	200–500 mV
	DO	3.0–12.0 mg/L
	EC	100–1100 µS/cm
	Turbidity	0–50 NTU with short–term spikes > 200 NTU
Major Constituents	Calcium – Ca^{2+}	20–100 mg/L
	Magnesium – Mg^{2+}	2–50 mg/L
	Sodium – Na^{+}	20–200
	Potassium – K^{+}	<1–10 mg/L
	Chloride – Cl^{-}	15–800 mg/L
	Sulfate – SO_4^{2-}	20–150 mg/L
	Carbonate – CO_3^{2-}	0–10 mg/L
	Bicarbonate – HCO_3^{-}	30–130 mg/L
	Total Dissolved Solids – TDS	150–1,200 mg/L
	Silicon – Si, or silica – SiO_2	1–10 mg/L
	Total or Dissolved Organic Carbon – TOC/DOC	1–10 mg/L
Trace Constituents	Nitrogen – N	<10 mg/L unfiltered
	Nitrate – NO_3^{-}	400–1,200 µg/L dissolved
	Nitrite – NO_2^{-}	0–10 µg/L dissolved
	Ammonia – NH_3	50–200 µg/L dissolved
	Organic N	800–2,300 µg/L unfiltered
	Phosphorus – P	120–250 µg/L unfiltered
	Orthophosphate – PO_4^{3-}	70–140 µg/L filtered
	Organic P	70–90 µg/L filtered
	Trace Elements	
	Aluminum – Al	10–1,000 µg/L
	Iron – Fe	10–1,000 µg/L
	Manganese – Mn	10–1,000 µg/L
Ultra-Trace Constituents	Toxic Trace Elements	< 5,000 nanograms (10^{-9} g) per liter – ng/L
	Arsenic – As	down to picograms (10^{-12} g) per liter – pg/L
	Cadmium – Cd	
	Copper – Cu	
	Chromium – Cr	
	Lead – Pb	
	Mercury – Hg	
	Selenium – Se	
	Vanadium – V	
	Zinc – Zn	
	Organic Compounds	
	Hydrocarbons – PAHs	
	Solvents – Surfactants	
	Adhesives – Coatings	
	Plasticizers	
	Flame Retardants	
	PCBs	
	Feedstock Chemicals	
	Pharmaceuticals	
	Herbicides	
	Pesticides	
	Fungicides	

Ultra-trace contaminants in water may be present in dissolved form or adsorbed onto suspended particulate matter in water, and both forms may be transported and mixed in Delta waters. Some trace elements and organic chemical classes favor the dissolved phase, such as organophosphorus herbicides like Diazinon, and trace elements such as selenium (Se). Adsorbed contaminants will eventually settle and deposit in stream and lake bottom sediments. Examples include the cationic trace elements cadmium (Cd), copper (Cu), and lead (Pb), or pyrethroid insecticides such as Permethrin. However, high stream flows and storm events can disturb sediments and re-introduce adsorbed ultra-trace contaminants to the water column and aquatic biota (Kratzer, 1998; Hoffman and Taylor, 1998; Thompson *et al*., 2000).

Analysis of ultra-trace compounds in water poses poses difficulties from contamination during sampling, sample filtration and other preparative procedures prior to analysis, and the limited detection sensitivity of instrumentation. These issues are partially overcome during field sampling using ultra-clean sampling protocols (EPA, 1996b). In the laboratory, highly sensitive analytical methods may be employed along with contamination control using air filtration, clean room facilities, and statistical blank correction. Ultra-trace compounds may also be detected at much lower concentrations using pre-concentration techniques such as composite sampling with solid phase extraction (SPE), as applied in this study for organic compound analyses.

Factors Affecting Surface Water Quality at the Tracy Fish Collection Facility

Because of the extensive re-use of water by the CVP and SWP, surface water quality in the Central Valley is affected by complex interactions of hydrology, mixing, and inputs from natural and human activities.

Natural and Artificial Hydrology

Natural hydrologic influences include basin-wide spring snowmelt runoff and seasonal winter rains, which vary year to year because of snowpack variability in different segments of the Sierra Nevada and the areal distribution and frequency of winter rains. Waters near the TFCF are also influenced by daily ebb and flood tides. Artificial hydrologic influences include extensive pumping, diversion, storage, and re-use of basin surface waters by the CVP and SWP for irrigation agriculture, municipal, and industrial uses.

Another major artificial hydrologic influence on TFCF water quality is the seasonal installation (usually in April and May) and removal (usually in September through November) of temporary channel barriers in the south Delta flow channels (California Department of Water Resources – CDWR, 2007). The temporary barriers are embankments of piled rocks across the Old River, Middle River, and Grant Line Canal that retard inflows and mixing from the SJR. The SJR (by way of the Old River) is a primary source water for the TFCF; however, operation of the Delta Cross Channel (DCC) gates (Figure 1) near Walnut Grove, California, during temporary barrier installation allows for significant southerly transport and mixing of lower concentration Sacramento River water into the south Delta (Reclamation, 2007; State of California, 1999; Craft *et al*., 2000a, Craft *et al*., 2008).

Contaminant Transport Mechanisms

Localized storm runoff, usually during the winter rainy season, may dissolve contaminants or transport contaminants on suspended matter from agricultural fields and urban areas (Orlando *et al*., 2003; Bergamaschi *et al*., 1999). These seasonal inflows contribute organic agricultural chemicals, trace elements, nutrients, turbidity, vegetative debris, and organic carbon into local waters. Irrigation during the agricultural growing season will similarly dissolve and mobilize contaminants associated with basin soils and agricultural chemical applications, with contaminant sources at irrigation return flow outlets to local canals and streams. Pollutants may also enter surface waters from contaminated groundwater along natural discharge zones, a problem near hazardous waste sites and landfills.

Atmospheric transport is another important contaminant source. Atmospheric transport of volatile organic compounds and pesticides is enhanced during aerial field spraying and by fog (McConnell *et al*., 1998; Seiber and Woodrow, 2000). Sulphur and N compounds from fossil fuel burning are transported by winds adsorbed on atmospheric particulates and dissolved in water vapor. Trace elements are transported in smelter, powerplant, and cement kiln aerosol emissions (Kanare, 1999), and Hg readily forms a gas as well as adsorbing on atmospheric particulates (Sorenson, 1990; United Nations Environmental Program – UNEP, 2003).

The Need for Composite Sampling Methods

The complex runoff, tidal, and water re-use hydraulics that produce the water quality observed at the TFCF underscore the need for accurate measurements that are representative with respect to spatial and temporal hydrologic processes. Further, the high variability in sources of water during tidal cycles requires the use of composite sampling techniques able to integrate the changes over time by incremental sampling throughout the hours of the day.

Ultra-Trace Contaminants, Sources, and Processes

The widespread agricultural activity and urban populations, coupled with the extensive mixing and transport of water across the Delta from tides, diversions, pumping, and re-use, assures that all waters in the Central Valley contain chemical contaminants from both agricultural and urban influences.

Ultra-Trace Organic Constituents

The major source of ultra-trace organic contaminants at the TFCF is local and basin-wide agricultural activity that mostly occurs during winter (dormant season chemical applications) and during irrigation periods from April through October. The 42,000 mi^2 (10.9 million hectare – ha) Central Valley of California is one of the most intensively farmed and productive agricultural areas in the world, and is home to over 5 million people. Irrigation return flows affect Central Valley water quality in 1,512 mi (2,430 km) of natural streams and rivers, and almost 19,821 mi (34,200 km) of agricultural channels (Umbach, 2008). Around 7 million acres (2.83 million hectares – ha) in the Central Valley are under irrigated cultivation, and the region produced $12 billion in crops and livestock during 2002 (State of California, 2003). This agricultural productivity requires annual application of around 100 million lbs (45.4 million kg) of pesticide active ingredients, along with their formulation additives (usually organic surfactants, adjuvants, and sticking agents) (State of California, 1992). Varying localized chemical contaminants enter TFCF waters by way of irrigation return flows along the Grant Line, Fabian, Bell, Victoria, and North Canals, Tom Paine Slough, Paradise Cut, and the Old and Middle Rivers.

Urban and highway runoff is another important source of organic contaminants to surface waters in the Central Valley, especially during winter storm events. Urban runoff contributes petroleum based hydrocarbon contaminants and byproducts of fuel burning, such as saturated hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, fuel additives, and industrial solvents to surface waters (Ross and Oros, 2004; Oros *et al*., 2007). Urban areas are also an increasing non-point source of insecticides such as pyrethroids (Permethrin, Bifenthrin, Cyfluthrin) and herbicides such as 2,4-D and Glyphosate in surface runoff (Weston *et al*., 2004; Budd *et al*., 2007). Ultra-trace organic pharmaceutical compounds and their metabolic byproducts are introduced from treated sewage outfalls (Loraine and Pettigrove, 2006), landfills, fuel storage, and transport spills contribute other organic solvents and waste products into groundwater that eventually reach surface waters.

Ultra-trace Elements

Since the implementation of the 1970 Clean Water Act and hazardous waste site remediations, contamination of Delta waters from trace element point sources has been reduced, but several trace elements remain a concern for water quality. Elemental contaminants generally come from mining, refining, smelting, metalworking, fossil fuel burning (especially coal), cement manufacturing, pigment manufacturing and paint breakdown, semiconductor manufacturing and waste, battery manufacture and disposal, and electroplating. Erosion of natural ultramafic (low silica volcanic) rocks in the Central Valley has contributed to higher than background levels of chromium (Cr), nickel (Ni), mercury (Hg), and vanadium (V) in Delta waters (Hornberger *et al*., 1999, Ganguli *et al*., 2000). Atmospheric transport is also important to the distribution of smelter, cement kiln, and coal-fired powerplant aerosols containing Hg and other toxic trace metals.

Historical gold and silver mining in the Sacramento and American River watersheds represents another important trace element source to the Central Valley. Abandoned mines and precious metals refinery sites are ongoing sources of silver (Ag), Cd, Cu, iron (Fe), manganese (Mn), mercury (Hg), Pb, and zinc (Zn) to Delta waters (Saiki *et al*., 1995; Hornberger *et al*., 1999; Prokopovich, 1984). Hg is of special concern because it can impair water quality at very low aqueous concentrations on the order of < 10 ng/L (Eisler, 1987; Tuttle and Thodal, 1998; Thompson *et al*., 2000). Generally, atmospheric sources of Hg dominate background concentrations in undisturbed ecosystems, and coal burning is the dominant current Hg source to the environment (United Nations Environment Program, UNEP, 2003). In the San Joaquin Valley, the New Idria mine near Pinnacles National Monument is a notable inoperative Hg mine that contributes Hg to tributaries of the SJR (Ganguli *et al*., 2000).

Trace metals such as Cd, Cu, Zn, Ni, and Hg are often adsorbed on soil particles that can become re-suspended and mobilized in snowmelt waters, storm runoff, and irrigation return flows. The relative distribution between adsorbed and dissolved forms of metals may also be influenced by changes in pH, salinity, organic carbon, and redox potential in stagnant or anaerobic waters and sediments. Changes in irrigation drainage and water project management practices, hydraulic modifications, and dredging can also mobilize trace elements sequestered over time in river and canal sediments.

Selenium is another problem trace element for the Delta and San Francisco Bay Estuary (Estuary). The marine sedimentary geology of the SJR basin contains soils with elevated concentrations of salts along with Se and boron (B). Irrigation, a lack of natural drainage caused by impervious clay layers, and a dry climate have combined to promote soil salinization in the SJR Valley, especially the western reaches such as the Panoche Creek alluvial fan. Se is soluble (as selenate) and soil salinization enhances concentration in irrigation return flows. Because Se also bioaccumulates, it is a serious concern for Delta wildlife and human health, especially in agricultural drains and reservoirs and wetlands subject to evaporation concentration such as Kesterson Wildlife Refuge. The CDFG has posted ongoing public health warnings regarding Se for consumption of bluegill (*Lepomis macrochirus*), largemouth bass (*Micropterus salmodes*), and ducks and coots in the San Joaquin Valley (Presser and Luoma, 2007).

Persistent Chemicals and Bioaccumulation

Persistent chemicals are toxic compounds that are chemically very stable, resist breakdown in the environment, and tend to accumulate in biota. They may include both organic compounds and trace elements. Persistent chemicals of concern include banned or restricted chlorinated pesticide compounds like DDT (with its metabolic breakdown byproducts DDE and DDD), chlordane and its isomers and metabolites, aldrin, dieldrin, PAHs (SFEI, 2006; Oros *et al*., 2007), polybrominated biphenyl ethers (PBDEs – widely used in fire retardants), phthalates (used as plasticizers), polychlorinated biphenyls (PCBs – formerly widely used in electrical transformers), and trace elements Hg, Ni, Cr, and Se (San Francisco Estuary Institute – SFEI, 2006; Leatherbarrow *et al.*, 2005; Davis, 2004; Davis *et al*., 2007).

Benthic organisms tend to accumulate the persistent compounds, especially the lipid soluble compounds like chlorinated organic compounds and methylmercury (Me-Hg), as they feed in and filter sediments. Higher trophic level organisms who eat the contaminated benthic fauna further accumulate the toxins in their tissues as they grow and age (Fairey *et al*., 1997; Pereira *et al*., 1996; Brown, 1997). Similarly, phytoplankton and zooplankton become contaminated with persistent toxins from the water column that bioaccumulate in the aquatic and fishery food chain. This process has been called bioconcentration, bioaccumulation, or biomagnification. As the higher trophic level organisms die, the bioconcentrated toxins are then re-released and recycled into the environment, thus contributing to their persistence.

Endangered Delta fish, such as the delta smelt (*Hypomesius transpacificus*) have tissue concentrations reported above the California Elevated Data Level for Ni and Zn, with Hg above the 0.6 mg/kg fish consumption advisory level. Elevated concentrations of Cu, Cr, PCBs, napthalenes, chlordane, toxaphene, DDE, DDD, and nonachlor have also been reported for delta smelt (Bennett *et al*., 2001). The California Environmental Protection Agency (CEPA) has issued draft fish consumption guidelines for Hg in the fish of the SJR and south Delta, and noted elevated tissue concentrations of PCBs in fish collected from the Port of Stockton (Gassel *et al*., 2007).

Previous Studies

Regional Monitoring Programs

In the Estuary, environmental sampling and analysis monitoring has been coordinated by the Regional Monitoring Program (RMP), established in 1993 by the San Francisco Regional Water Quality Control Board (Thompson *et al*., 2000), and overseen by the SFEI. The RMP relies on participation of many state and federal cooperators and monitors algal productivity, sediments and water for toxic compounds, and well as integrative bioassay testing using amphipods and bivalves. The RMP includes a sampling station at the entrance to Suisun Bay on the SJR, and has identified PCBs, DDTs, dieldrin, and trace elements Cr, Hg, and Ni as contaminants of concern for the Estuary. The RMP currently monitors a large suite of ultra-trace organic compounds and trace elements (SFEI, 2006).

Monitoring water quality and assessment of trends for the Delta has also been a long-term activity of the Interagency Ecological Program (IEP), a governmental body that coordinates research and archives environmental data (IEP, 2008). The IEP is composed of state and federal wildlife and resource management agencies such as Reclamation, U.S. Geological Survey (USGS), National Oceanic and Atmospheric Administration's National Marine Fisheries Service (NMFS), U.S. Fish and Wildlife Service (FWS), U.S. Army Corps of Engineers (COE), CDWR, CDFG, and other state and local water resource agencies and irrigation districts. Notably, the USGS has performed and published many studies measuring ultra-trace concentrations of current use agricultural chemicals in the Delta and Estuary as part of the National Water Quality Assessment Program (NAWQA) and other water quality assessment programs.

Compounds of Concern for the Tracy Fish Collection Facility

Table 2 provides a list of toxic agricultural chemicals applied in large quantities in the near vicinity of the TFCF (Craft *et al*., 2000a) during 1997. This list represents compounds of concern (COC) likely to be present at elevated concentrations during the agricultural season, and that are deleterious to aquatic life at lower concentrations (see the METHODOLOGY section for details of the selection process). Based on literature review and issues identified by the RMP, we also included the trace elements Cd, Cu, Cr, Hg, Ni, Pb, Se, V, and Zn in the COC list. Subsequent data and discussions in this report will reference this COC list.

TABLE 2.—Agricultural chemicals of concern for the water quality at the Tracy Fish Collection Facility (TFCF), including purpose, chemical class, amounts applied near the TFCF, and local acreage applied. (Craft et al., 2000).

Chemical Name	**Purpose or Source**	**Chemical Class**	**1997 Local Applications, equivalent kg**	**1997 Acreage Applied**
Aldicarb	insecticide	carbamate	1,756	365
Bromoxynil	herbicide	aromatic nitrile	274	557
Carbofuran	insecticide	carbamate	1,790	4,190
Chlorpyrifos	insecticide	organophosphorus	8,734	9,730
Desmedipham	herbicide	phenyl carbamate	3,450	4,100
Diazinon	insecticide	organophosphorus	604	609
Esfenvalerate	insecticide	pyrethroid	671	2,940
Fenbutatin-oxide	insecticide	organo-tin	111	232
Fonofos	insecticide	organophosphorus	5,592	1,130
Metam-sodium	insecticide	carbamate	4,234	28
Metolachlor	herbicide	chloracetanilide	3,405	2,850
Oryzalin	herbicide	dinitroaniline	624	174
Oxyfluorfen	herbicide	diphenyl ether	1,461	2,490
Permethrin	insecticide	pyrethroid	724	659
Phosmet	insecticide	organophosphorus	1,244	1,700
Trifluralin	herbicide	dinitroaniline	51,643	13,300
Cadmium – Cd	mining – batteries	trace metal	–	–
Copper – Cu	mining – electrical	trace metal	–	–
Chromium – Cr	mining – metals	trace metal	–	–
Mercury – Hg	mining – coal	trace metal	–	–
Nickel – Ni	mining – metals	trace metal	–	–
Lead – Pb	mining – batteries	trace metal	–	–
Selenium – Se	marine geology	trace element	–	–
Vanadium – V	mining – metals	trace metal	–	–
Zinc – Zn	mining – metals	trace metal	–	–

METHODOLOGY

Overview of Organic Analyses

Composite filters and XAD column samples for organic analyses were analyzed in two fundamentally different but complementary ways. XAD-2 columns and filters for each monthly composite sample were extracted, fractionated (a sample clean-up procedure), and intially analyzed using high-resolution gas chromatography–low-resolution mass spectrometry (HRGC–LRMS) in full scan (open scan) mode. This is a *semi-quantittive* or *qualitative* method of analysis that nonetheless provides good survey identification of almost all organic compounds in TFCF water. Unfractionated and archived column and filter extracts were later analysed for a broad range of current use pesticides using quantitative high-resolution methods. Archived composite sample extracts were cleaned prior to analysis for chlorinated, organophosphorus and pyrethroid pesticides, PCBs and hydrocarbons (also called multiresidue pesticides), and organonitrogen (ON) pesticides using high-resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS). Archived extracts were also analyzed for carbamate pesticides using liquid chromatrography–tandem mass spectrometry (LC–MS/MS).

Analytical Laboratory and Quality Assurance Program

All organic analyses were performed by Axys Analytical Services, Ltd, Sidney, British Columbia, Canada (Axys). Axys also produced the composite sampling equipment for organic sampling used in this study and assisted with field installation. Axys specializes in ultra-trace organic analyses and used controlled facility access, semi-clean room procedures, and filtered laboratory air to minimize background contaminants. The lab operates under an ISO 17025 quality system (International Organization for Standardization/International Electrotechnical Commission; ISO/IEC, 2005. Axys is also accreditated by the National Environmental Laboratory Accreditation Conference (NELAC, 2008).

Composite Sampling for Organic Compounds

Composite sampling for organic compounds used SPE with an Axys Infiltrex 300 programmable sampler. The Infltrex system (Figure 3a) employed a high capacity 1.0-µm pore-size glass fiber disc filter (Whatman GF/C) in a 298-cm stainless steel filtration stack (upper right inset, Figure 3a), and 55 g of Amberlite XAD-2 macroreticular resin (Sigma Aldrich) packed in a 30 x 2.0 cm PTFE (polytetrafluoroethylene) Teflon® column (lower inset, Figure 3a). Suspended particulate organic compounds were collected on the filter, and dissolved organic compounds on the XAD-2 column. Figure 3b shows a plumbing and controller block diagram for the Infiltrex SPE system.

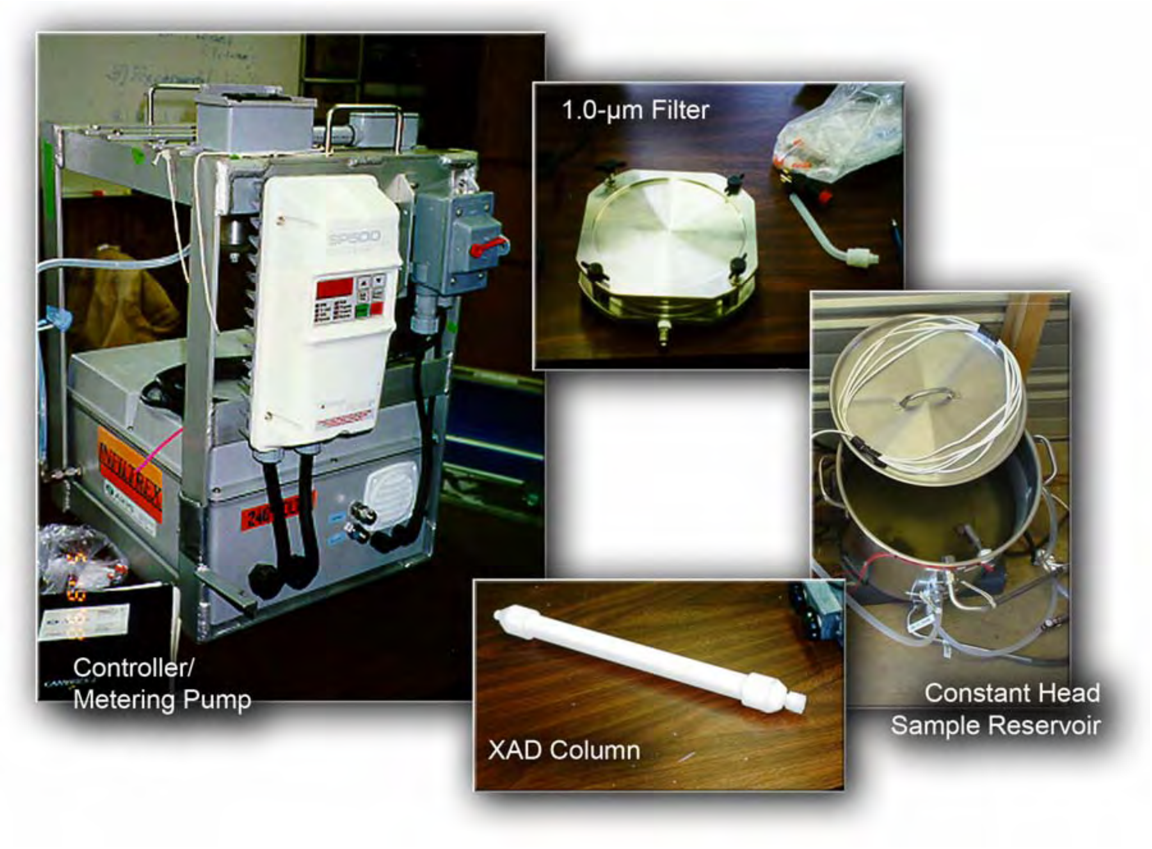


FIGURE 3a.—Infiltrex 300 automated sampling pump, the in-line filter, and the Teflon® XAD-2 column used for organic composite sampling using solid phase extracton (SPE) at the Tracy Fish Collection Facility. The controller unit and SPE metering pump are seen on the left. The high capacity 1.0-µm pore-size disk filter is shown in the upper right inset, the XAD-2 column in the lower inset, and the constant head sample reservoir in the right inset. Reclamation photographs by Lee Mao.

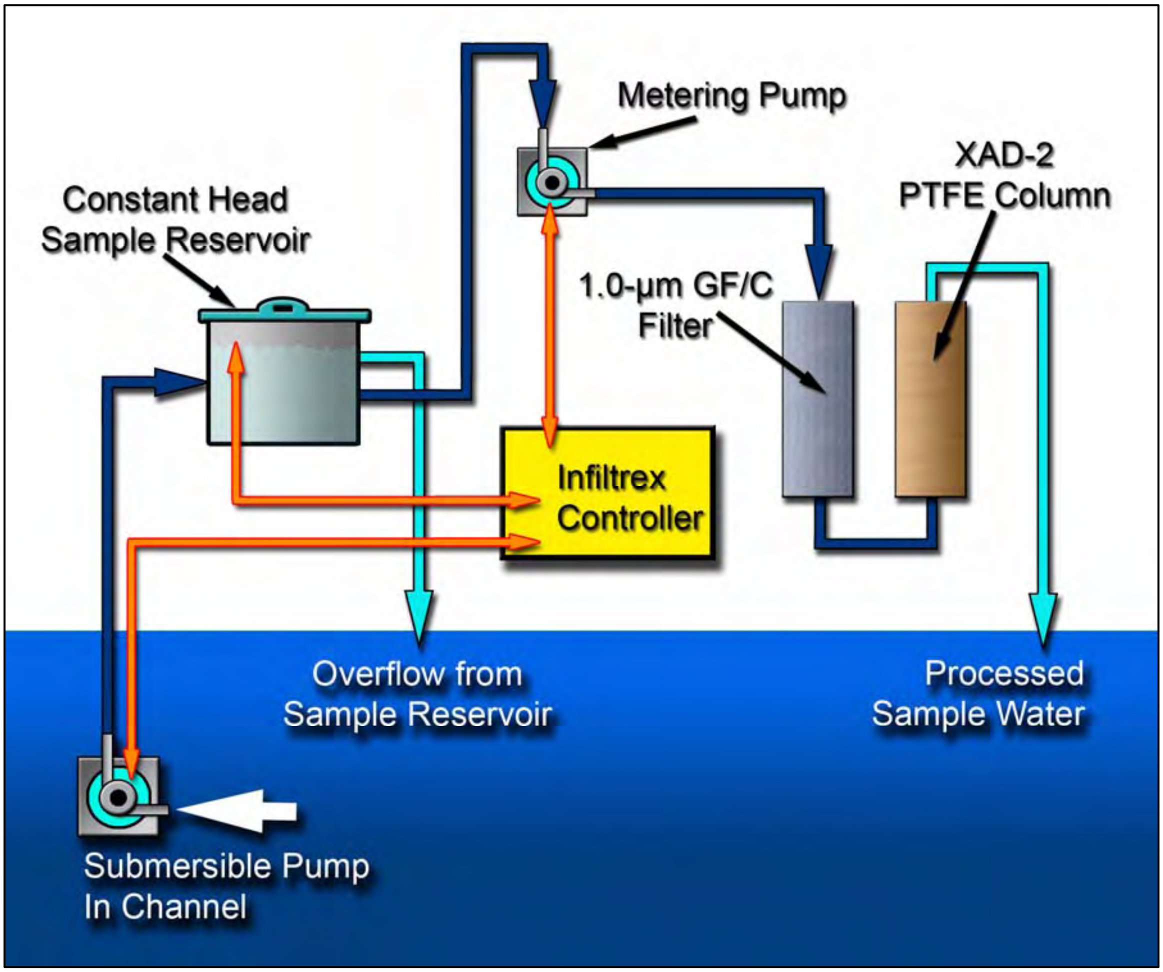


FIGURE 3b.—Block diagram of Infiltrex 300 pump and solid phase extraction (SPE) system used for collecting organic composite samples.

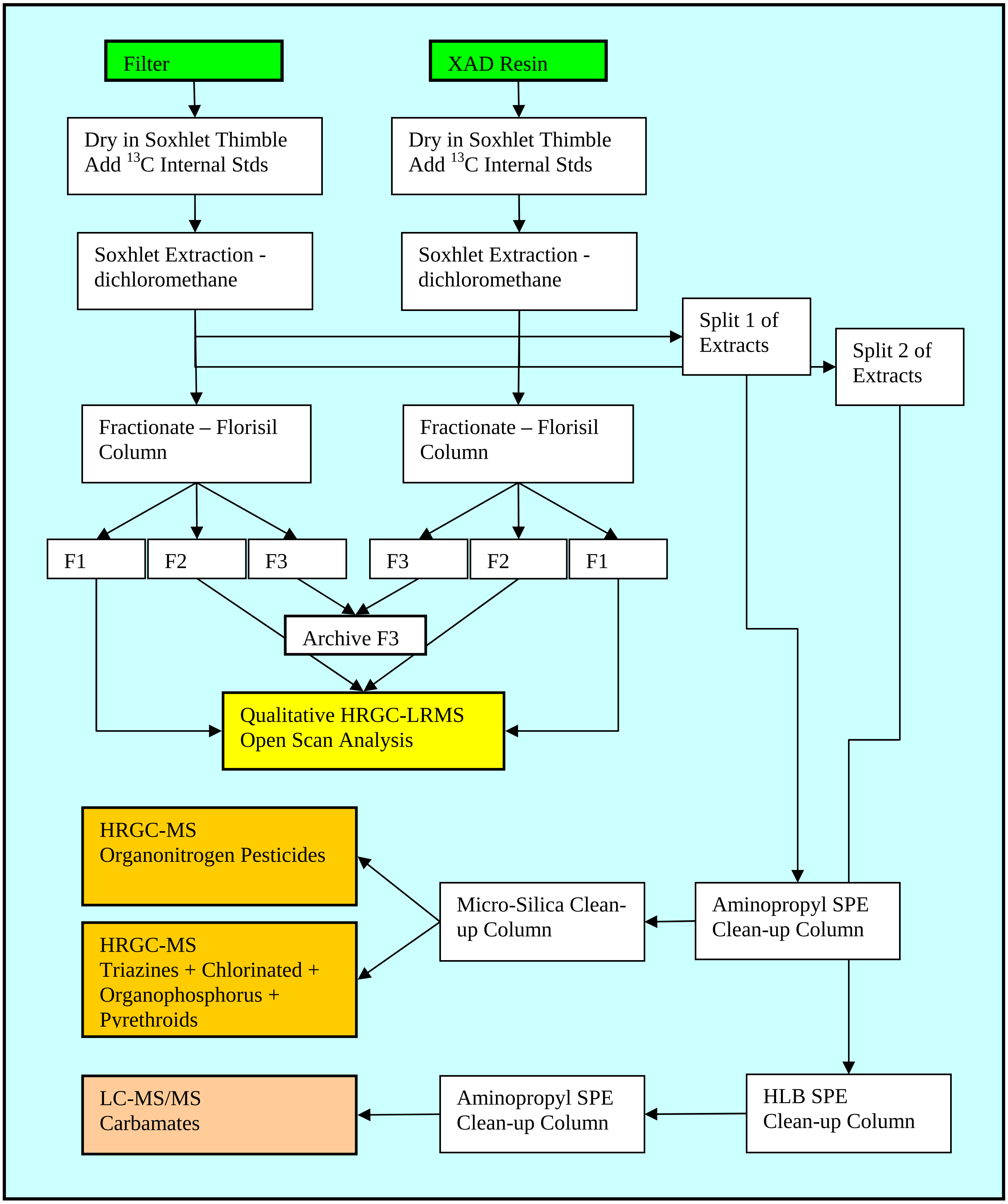


FIGURE 4.—Diagram showing the extraction and fractionation steps for processing of the inline filters and XAD resin for the open-scan high-resolution gas chromatograph–low-resolution mass spectrometry (HRGC–LRMS) analysis, and later high-resolution and quantitative HRGC–HRMS and liquid chromatography–tandem mass spectromertry (LC–MS/MS) analyses.

A submersible well pump located at mid-depth in the channel supplied water through a 12.7-mm (½-in) Teflon®- FEP (fluorinated ethylene propylene) hose to a 5-L stainless steel constant head sampling reservoir located adjacent to the sampler (Figure 3a right). The submersible feed pump was triggered by the water level in the constant head sampling reservoir such that the tank was continuously refilled and flushed. Channel samples were collected near the concrete channel wall and were not depth integrated; however, the channel immediately behind the louvered trash rack at the TFCF is a turbulent mixing zone. The Infiltrex 300 sampler was programmed to sample 0.4 L each hour by pumping water at 100 mL/min for 3.5 min every hour from the sampling reservoir through the filter and a pre-cleaned XAD resin column (Figure 3a inset). A calibrated flow meter on the sampler was used to determine the volume of water sampled and pumping events data were stored by the Infiltrex and regularly downloaded from the sampler. The sampler recorded date and time of sample cycles, flow rates, volume pumped, and pump times. Approximately 300 L/month were collected over a 9 month period.

Because of TFCF power upgrades and repairs undertaken during most of this study, intermittent power outages occurred causing system resets on the Infiltrex pump controller. These power interruptions, most numerous during July 1999, reduced the volumes pumped through the filter and XAD-2 column. While these interruptions affected the temporal representativeness of the composite sampling during July, the volumes pumped each month by the Infiltrex were sufficient for significant preconcentration of analytes. Volumes of water pumped for each monthly composite sample are summarized in Appendix 3, Table A3-1. Field quality assurance (QA) included analysis of XAD-2 column and filter field blanks, and all columns were shipped on ice in coolers to Axys under legally defensible chain of custody procedures and documentation.

Extraction of Composite Sample Columns and Filters

Figure 4 provides a general flow chart describing the sample preparation for both open scan LRMS and quantitative HRMS and MS/MS analytical methods.

XAD-2 resin was removed and transferred from the SPE column using 5–25 mL of deionized (di) water into a fritted Soxhlet thimble. Residual water was removed by aspiration, and the dried resin was then spiked with an aliquot of internal standards (a suite of ^{13}C-isotopically labeled compounds) and then extracted 14–16 hr with dichloromethane. The extract was cooled to room temperature, dried over sodium sulphate and then concentrated to 0.5 mL. Filter samples were air dried 16 hr at room temperature and placed in Soxhlet thimbles over anhydrous sodium sulphate, and then spiked with internal standard and extracted under the same conditions used for the XAD-2 resin. The solvent was then changed to hexane in preparation for chromatographic clean-up procedures. A subsample (approximately 1/3) of each extract was archived for later analysis and the remaining was passed through a Florisil column for preliminary clean-up and separation by polarity into three fractions: F1 (non- polar), F2 (moderately polar), and F3 (polar).

Qualitative Open Scan HRGC–LRMS Analysis

Fractionation for HRGC–LRMS Open Scan Analyses

Extracts from filters and XAD resin were cleaned and fractionated using a Florisil column (2.1 percent deactivated). Extracts were applied to the column, which was first eluted with hexane followed by 15:85 dichloromethane-hexanes. These 2 eluants were combined to create the less polar fraction (F1). The column was then eluted with 1:1 dichloromethane-hexane followed by dichloromethane, and these two eluates were combined to create the moderately polar fraction (F2). Polar compounds were eluted with 1:1 dichloromethane-methanol as fraction F3.

The F1 and F2 fractions were concentrated and activated Cu was added to remove sulphures. The fractions were then transferred to autosampler vials and an aliquot of ^{13}C-labeled PCB 153 (2,2',4,4',5,5'-hexachlorobiphenyl) recovery standard was added. The autosampler vial was capped for qualitative open scan analysis of pesticides by HRGC–LRMS. The F3 fraction was concentrated to 10 mL, transferred to a glass ampoule, cooled to -30 °C and then sealed for archival storage. The F3 fractions were not analyzed in this study.

Qualitative Open Scan HRGC/LRMS Instrumental Analyses

Extract fractions F1 and F2 collected from the Florisil clean-up column were analysed using a Finnigan Incos 50-B system quadrupole mass spectrometer with a Varian 3400 gas chromatograph equipped with a 60-m, 0.25-mm id, 0.1-µm film DB-5 capillary column. 1.0 µL of the sample extract was injected. The temperature program for the GC was: 50 °C for 1.1 min, an increase of 11.5 °C /min to 150 °C, an increase of 3 °C /min to 250 °C, and then an increase of 50 °C /min to 320°, held for 11 min. We used splitless/split injection with 2 min for splitless, injector temperature 280 °C, and helium carrier at an inlet pressure such that ^{13}C-labeled PCB 153 eluted in the range 37.1 to 37.3 min (typically 170 kilopascals [kPa]).

The MS was operated in electron impact mode using continuous scan mode, scanning from 40 to 600 amu at the rate of one scan/s. Reference retention times were determined using an n-alkane series standard (even n-alkanes, C-12 to C-36) and a chlorinated pesticide and PCB calibration standard run immediately prior to the sample batch. MS data were acquired by a Prolab GC–MS data system and converted to Hewlett-Packard ChemStation format data files (*.D format) and preliminary review using HP ChemStation software (G1701AA version 3.00).

HRGC–LRMS Open Scan Data Analysis

For each fraction, the 30 largest peaks detected between 9 and 50 minutes in the integrated total ion chromatogram (TIC) were selected for mass spectral data analysis. The detected component peaks were background subtracted and reviewed manually using Automated Mass Spectral Deconvolution and Identification System (ADMIS), version

1.01, an open source program designed to run with the National Institute of Science and Technology (NIST) MS library of over 100,000 compounds with the NIST Mass Spectral Search Program (version 1.6d) (Stein *et al*., 1998). For each of the ten sample components subjected to a library search, the candidate spectral matches were evaluated and, where applicable, the name of the most likely candidate was selected as an inferred compound. When no reasonable library match was found, the spectra were manually interpreted. Unidentified components were classified by compound type. Compounds identified solely by mass spectra were considered unconfirmed inferences. Confirmation of an inferred compound identification would require analysis of a sample of the authentic compound and comparison to MS and retention time data.

Reverse AMDIS searches of the open scan data were performed targeting 23 current use pesticides. This list was based on HRGC–LRMS determination of chromatographic retention times for pesticide standards, including Eptam, Pebulate, Molinate, Dimethoate, Simazine, Carbofuran (on the TFCF COC list), Atrazine, Fonofos (COC), Diazinon (COC), Methyl-parathion, Carbaryl, Thiobencarb, Metalochlor (COC), Dacthal, Chlorpyrifos (COC), Cyanazine, Diuron, trans-chlordane, cis-chlordane, Methidathion, Napropramide, p,p'-DDE, and p,p'-DDT. Other COC analytes were reverse-searched including Trifluralin, Phosmet, Permethrin, Desmedipham, Aldicarb, and Bromoxynil.

Quantitative High-Resolution Organic Methods

Quantitative analyses for organic compounds involved three instrumental methods. Two of the methods used the same sample extract clean-up procedures and instrumental approach with HRGC–HRMS: one method for triazines, chlorinated, organophosphorus, and pyrethroid pesticides (also called multiresidue pesticides), and one method for organonitrogen (ON) compounds. The third method was for carbamate pesticides and used analysis with liquid chromatography – tandem mass spectrometry (LC–MS/MS) as the high-resolution MS technique.

Extract Clean-up for HRGC–HRMS Analyses

The unfractionated archive extracts from the initial Soxhlet extractions were prepared prior to quantitative HR analyses using aminopropyl SPE and microsilica column clean-up procedures. The aminopropyl SPE clean-up column (1g aminopropyl bonded silica, NH2 cartridge, Varian) was preconditioned by eluting with 1:2:1 ethyl acetate:acetonitrile:toluene (two column volumes, ~6 mL). A 1-mL extract subsample was loaded on the column in 1:2:1 ethyl acetate:acetonitrile:toluene, followed by a 1-mL rinse of the extract container with the same 1:2:1 solvent mixture. Eluate was collected in a centrifuge tube. The SPE column was then eluted with an additional 11 mL of the 1:2:1 solvent, and subsequently concentrated to 1 mL by rotary evaporation. Sample residue was transferred to a centrifuge tube with hexane and concentrated to 100 µL using a gentle stream of nitrogen. The 100-µL aliquot from the aminopropyl SPE column clean-up was diluted to 1 mL with hexane and then used for the micro-silica column clean-up.

The micro-silica column was dry packed (10% deactivated, 0.75 g) and rinsed with hexane until the column was completely wetted (typically 5–10 mL). The first clean-up extract was loaded onto the micro-column followed by a 500-µL hexane rinse and then two 300-µL rinses with 1:9 methanol-dichloromethane rinses. The micro-silica column was then eluted with 5 mL of 1:9 methanol-dichloromethane. Eluent was collected in a round bottom flask, and then 5 mL of acetone and ~1 mL of iso-octane were added before concentration to 1 mL by rotary evaporation. The evaporate was transferred to a centrifuge tube with hexane, and then concentrated to 300 µL under a gentle stream of nitrogen before transfer to a microvial. An aliquot of recovery standard was added to each extract and the final volume was adjusted to 400 µL with toluene. The microvial was then capped for instrumental analysis.

Quantitative HRGC–HRMS Instrumental Analyses

Post-clean-up samples for pesticides relied on two different HRGC–HRMS instrumental methods for analysis of different compounds classes: one optimized for the multiresidue pesticides (organophosphorus, triazines, pyrethroids, and chlorinated compounds), and one optimized for ON compounds. All of these analysis methods were performed using a micromass Autospec Ultima HRMS equipped with an Aglient 6890 HRGC equipped with Agilent and micromass software. A DB-17 MS analytical column (30-m length, 0.25-mm i.d., 0.25-µm film thickness, or equivalent) was coupled directly to the HRMS source. The HRMS was operated at a static (8,000 amu) mass resolution (10% valley) in the electron ionization, positive ion mode using multiple ion detection (MID). The MID method acquires two characteristic ions for each target analyte and surrogate standard. A splitless/ split injection sequence was used with 1.0–2.0 µL injected. Appendix 1, Tables A1-1 and A1-4 provide instrumental conditions used for the two quantitative HRGC–HRMS methods. The list of analytes, chromatographic relative retention times, and characteristic mass fragments for the two HRGC–HRMS methods may be found in Appendix 1, Tables A1-2 (multiresidue pesticides) and A1-5 (ON pesticides)

Initial calibration was performed using a minimum of five calibration solutions of target compounds that covered the working concentration range of the instrument. The initial calibration was used to determine response factors for target analytes and ^{13}C-labeled standards. Calibration was verified at the beginning and end of the batch run using a mid-level calibration solution (CAL/VER, also called CCV – continuing calibration verification). The mean relative response factors (RRF) from the mid-level calibration run at the beginning and end of the sample batch were used for the quantification of target analytes. Appendix 1 details the calibration standards, surrogtate standards, and ^{13}C-labeled standards used for the multiresidue pesticides (Table A1-3), and ON pesticides (Table A1-6) quantification.

Target concentrations were determined with respect to either a labeled surrogate or the internal standard. Mean relative response factors (RRF), determined from either a multi-level initial calibration series or a mid-level calibration standard run at the beginning and end of the samples, were used to convert raw peak areas in sample chromatograms to final concentrations. For target compounds quantified against the labeled standard added at the beginning of the analysis procedure, the results were recovery corrected based on the method of quantification. Surrogate recoveries were determined similarly against the recovery (internal) standard and were used as general indicators of overall analytical quality. Results for analytes quantified using the recovery standards were not recovery corrected. Blank correction was not applied.

Analysis for Carbamates by LC–MS/MS

A split from the original Soxhlet extraction of filters and XAD-2 was gravimetrically split into two portions after homogenizing with a vortex mixer: one split for analysis by LC–MS/MS, and one split for backup. Splits were quantitatively spiked with surrogate standards summarized in Appendix 1, Table A1-8. No further clean-up was performed for carbamate analyses prior to quantitation.

Carbamates were analyzed using a Waters 2695 HPLC (high performance liquid chromatograph) coupled to a micromass Quattro Ultima MS/MS using the micromass MassLynx v.4.0 software. Extract injection volume was 20 µL onto a Waters Sunfire C18 LC column (3.5 µm i.d., 4.6-mm o.d. x 30 mm), eluted using a two-solvent program with formic acid buffer in HPLC-grade water and HPLC-grade acetonitrile. Chromatographic conditions applied for the LC are summarized in Appendix 1, Table A1-7. Positive electrospray ionization [(+)ESI] was used in the MS and the MS was operated using unit mass resolution in multiple reaction monitoring (MRM) mode. The (+) ESI parameters for each carbamate target analyte are summarized in Appendix 1, Table A1-8.

Carbamate Quantification

Analytes were quantified using calibration standards and surrogate standards. The surrogate standard methanol solution contained 200 ng of $^{13}C_6$ Carbofuran, 100 ng of d3-Methomyl, 100 ng of d3-Oxamyl, and 10 ng of d10-Diazinon. A 10-µL aliquot of surrogate standard solution was spiked into each extract before analysis. The recovery standard solution contained $^{13}C_3$-Atrazine prepared at a nominal concentration of 2,750 ng/mL in methanol. A 20-µL aliquot of recovery standard solution was added to each sample extract prior to instrumental analysis. Spiked recovery was determined for the batch using the spiking solution containing the carbamate analytes detailed in Appendix 1, Table A1-9.

A series of five calibration solutions containing analytes, surrogate standard, and recovery standard were used to establish the initial calibration of the analytical instrument and quantify samples. Appendix 1, Table A1-10 details the standard concentrations used for carbamate analyses. A mid-level calibration solution was analyzed at the beginning and end of each batch to bracket samples. The mean RRTs determined from the mid-level calibration solution were used for quantification of sample results.

Trace Elements

Composite Sampling for Trace Elements

Composite samples were collected for trace elements for 7 months from May through November 1999 using a Sigma Model 900 Max automated sampling pump (Figure 5). The pump was programmed to deliver a 60-mL/min flow rate through a 0.9-m (3-ft) length of 9.53-mm (3/8-in) ID Teflon® FTE tubing, collecting 125 mL every 3 hr. into 1 of 24 1-L high density polyethylene (HPDE) sample bottles. Samples were pumped from the channel at mid-depth near the concrete channel wall and were not depth integrated. The trace element composite samples were also affected by TFCF power outages.

Each month, filled sample bottles were combined and mixed to create the composite sample. Subsamples were split from the composite to create submission samples and QA blind samples (duplicates and field spikes). Pre-cleaned HPDE subsample bottles were filled and then preserved with ultra-clean nitric acid (Ultrex) at 4 mL/L. Blind QA blanks were created on site using DI water (American Chemical Society – ACS type III). All samples were collected, processed, and delivered to the analytical laboratories under legally defensible chain of custody procedures and documentation. All preserved samples were analyzed within EPA recommended holding time.

Analytical Methods for Trace Elements

Trace metal composite subsamples were submitted to Quanterra Incorporated, West Sacramento, California, for analysis following Environmental Protection Agency (EPA) Method 6020-A (EPA, 2008) for total metals by inductively coupled plasma–mass spectrometery (ICP–MS). Laboratory QC reports summarized laboratory blanks, initial calibration verification (ICV) and continuing calibration verification (CCV) standards, laboratory control samples (LCS), random batch duplicates, spike recoveries, and duplicate spike recoveries. Mercury composite subsamples were submitted to CalTest Analytical Laboratory, Napa, California, for Hg analysis following EPA Method 245.2 (EPA, 1983) by cold vapor atomic absorption spectrophotometry. Field QA was identical to that for the ICP–MS samples. Laboratory QC reports summarized laboratory blank, laboratory control sample (LCS), random batch duplicates, spike recoveries and duplicate spike recoveries. Data were reviewed and quality validated by the Reclamation Mid-Pacific Regional Office, Environmental Monitoring Branch, MP-157, Sacramento, California.

FIGURE 5.—Hach/Sigma programmable sampling pump used to collect monthly composite samples at the Tracy Fish Collection Facility for trace elements. Photographs ©Hach/Sigma, Inc., 2008, used with permission.

Comparative ultra-trace element data from Craft *et al*., (2000a) were collected using ultra-clean field sampling procedures (Craft *et al*., 2000b; EPA, 1996a) and analyzed by Frontier Geosciences, Inc., Seattle, Washington (FGS). The analytical lab provided pre-cleaned samples bottles and samples were filtered under semi-clean room conditions with statistical blank correction applied to results. High sensitivity ICP–MS analyses were performed for trace elements using FGS-developed methods providing ng/L-range detection limits (EPA, 1996b). Ultra-trace Hg and Me-Hg were analyzed using FGS-developed methods (adopted by EPA as method 1631) involving oxidation, purge and trap, thermal desorption, followed by cold-vapor atomic fluorescence spectrometry (EPA, 1996c) for total Hg, and the method of Bloom (1989) using aqueous phase ethylation for Me-Hg prior to method 1631.

Compounds of Concern and Agricultural Chemical Applications

We developed the COC list (Table 2) of 16 agricultural chemicals by relational comparison of agricultural chemical applications in the vicinity of the TFCF with the toxicity scores of the chemicals. See Table 3 for the criteria used to assign toxicity scores for agricultural chemicals. The most toxic agricultural chemicals with the greatest locally applied amounts were selected as compounds of concern (Craft *et al*., 2000a).

TABLE 3.—Criteria from the Farm Chemicals Handbook (Meister and Sine, 2002) and 96-hr LC_{50} concentration ranges used to assign relative toxicity scores to 96-hour LC_{50} data for agricultural chemicals.

Toxicity Score	Meaning	FCH Designation	LC_{50} Concentration Range
1	non-toxic	PNT	>100,000 µg/L
2	slightly toxic	ST	10,000 to 100,000 µg/L
3	moderately toxic	MT	1,000 to 10,000 µg/L
4	toxic	HT	100 to 1,000 µg/L
5	very toxic	W-IT	<100 µg/L

Raw data for 1997 agricultural chemical applications were obtained from the Office of the Agricultural Commissioner, San Joaquin County, California. This data set is the same used for regulatory reporting to state and federal agencies and included 83,875 records. Information included in the database included landowner, location (township, range, section), agricultural chemical formulation names, associated EPA and safety codes, amounts applied, dates applied, application method, as well as crop name and acreage treated.

Chemical application records in the near vicinity of the TFCF were queried by selecting only township-range quadrangles T1S-R4E, T1S-R5E, and T1S-R6E. These quadrangles represent an approximate rectangle 29.3 X 5.8 km starting at the TFCF and striking east (and upstream) to include the branch point of the SJR and the Old River. This 27,000 ha

(67,700 acre) rectangle includes crop land adjacent to the Old River, the branching point of the Old and Middle River and the Middle River in T1S-R5E, Grant Line Canal, Fabian and Bell Canal, Victoria Canal, North Canal, the Clifton Court Forebay intake, and northern extremes of Paradise Cut and Tom Paine Slough where they enter the Old River.

RESULTS AND DISCUSSION

Several investigators have reported ultra-trace analyses of water and sediment in the Delta and Estuary for current-use agricultural chemicals, other organic compounds, and trace elements (Kinsey *et al*., 2005; Brown *et al*., 2004; Panshin *et al*., 1998; Dubrovsky *et al*., 1998). We compared the summary organic compounds results from this study with data published by the California Department of Pesticide Regulation (CDPR, 2008), and the USGS (MacCoy *et al*., 1995). Trace element data comparisons will refer to data published by the RMP (Leatherbarrow *et al*., 2005; SFEI, 1997; SFEI, 2006), and ultra-trace samples collected by Craft *et al*. (2000a).

Data Interpretation Issues

Composite Sample Concentration and Dilution

All composite sample data presented here are reported as *average* monthly concentrations. Trace element composite samples did not have any preconcentration and were diluted up to 30 L each month. Organic analyses represented the preconcentration and dilution associated with pumping sample volumes from 59 L (July) up to 634 L (December). These sample volumes (and high-resolution MS) produced very low detection limits (DLs) for organic compounds (in the tens of pg/L range). However, the composite sample volumes also suppressed higher concentration and short duration spikes by dilution. These shorter duration, higher concentration spikes were reported by others with methods having much higher DLs (MacCoy *et al*., 1995). Because of composite sample dilution, monthly organic compound averages reported here were much lower compared with data reported by others (Panshin *et al*., 1998; Dubrovsky *et al*., 1998; Kinsey *et al*., 2005). These investigators all used much shorter sampling periods and lower SPE sampling volumes.

The reason for this apparent discrepancy in reported concentrations is the episodic manner agricultural chemicals are applied on fields, and the way they are eventually transported from fields and mixed in local waters.

To illustrate, let us assume that Diazinon is applied to a local field along the Old River upstream of the TFCF, and that the field is then irrigated. The irrigation water will dissolve some of the applied Diazinon, which will be transported over time into the Old River by way of the irrigation return flows. This will create a pulse or wave of increasing then decreasing Diazinon concentrations flowing past the TFCF in a roughly Gaussian manner. Therefore, a measured average Diazinon concentration of 10 ng/L from a composite sample representing 720-L preconcentration (1 L/hour pumped through an SPE column for 30 d), represents a total monthly quantity of 7,200 ng (7.2 µg) of Diazinon collected on the SPE column.

If the Diazinon pulse completely passed in only one hour (not likely), the 1-hr concentration would have to be 7,200 ng/L, or 7.2 µg/L, to still have a monthly average of 10 ng/L. A 1-d pulse would have an hourly average of 300 ng/L, a factor of 30 times higher than the monthly average, but only for 24 hr. A 3-d pulse would require an average hourly concentration of 100 ng/L; a 7-d pulse an hourly average concentration of 43 ng/L. Because these pulses are Gaussian and not a square wave, the actual maximum concentration associated with a pulse would be much higher than the averages we report. Assuming you were fortunate enough to collect a discrete sample at the peak, maximum concentrations could be multiple orders of magnitude higher than the averages reported here. Data from MacCoy *et al*. (1995) suggest that spikes of higher concentrations for organic compounds lasting from 1 day to a week are not uncommon in the south Delta.

Sample Representativeness

Composite samples in this study were not collected from center channel or with depth-integrating sample intakes. Because of possible channelizing and stratification of suspended materials and inherent heterogeneity, suspended samples (including the unfiltered trace element composite samples) were not likely representative of the entire channel. Dissolved organic compounds samples, however, may have been more representative of the entire channel because of turbulence and mixing as Old River water passed beneath a trash boom and then through a louvered trash rack before being sampled. Temporal representation for the organic composite sampling, except for the month of July, should be considered reliable, even given TFCF power interruptions.

Qualitative Open Scan HRGC–LRMS Data

The LRMS total ion chromatograms (TICs), and full MS data for all nine composite samples (4 TICs per sample for suspended F1, suspended F2, dissolved F1, and dissolved F2 fractions), and calibration and QC TICs are included on the enclosed Appendix 2 CD-ROM. TICs are saved in Hewlett-Packard ChemStation format that are compatible with AMDIS/NIST library searches. An example of the open scan chromatograms are presented in Figure 6a for the June 1999 composite samples, and the printed version of Appendix 2 provides a guide to the TIC file names (Tables A2-1 and A2-2) on the CD-ROM, along with figures showing the complete set of open-scan TICs (Figures A2-1 and A2-2). Note that the files on the CD-ROM require the AMDIS software, which is available as an open source program. AMDIS may be down loaded at http://chemdata.nist.gov/mass-spc/amdiss/.

The AMDIS NIST MS library search routines on the LRMS data allowed examination of each peak on a TIC; however, the scope of this study permitted only a preliminary evaluation of the LRMS data. AMDIS library searches were performed for each composite TIC for the 30 greatest TIC abundance peaks.

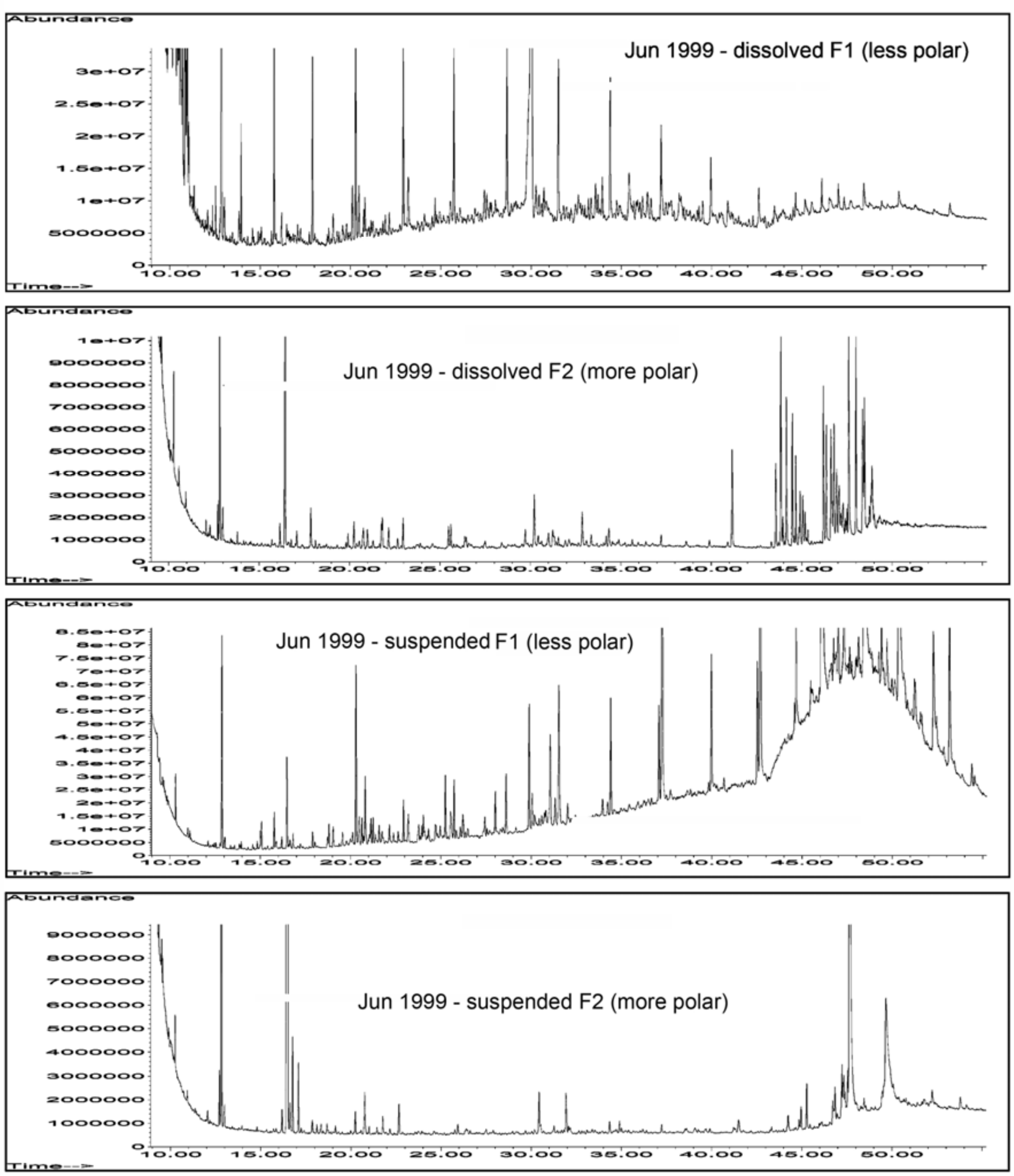


FIGURE 6a.—Open scan high-resolution gas chromatography–low-resolution mass spectrometry (HRGC–LRMS) total ion chromatograms (TICs) for the June 1999 composite samples. The top 2 chromatograms are for dissolved F1 (less polar) and F2 (more polar) fractions and the bottom 2 chromatograms are for the suspended F1 and F2 fractions.

We found mostly saturated hydrocarbons in the less polar dissolved F1 fractions, and other petroleum-related hydrocarbons, PAHs, and linear chain alkyl benzenes (from surfactants) in the F2 fractions (both suspended and dissolved). The average concentrations of these petroleum-related compounds ranged from the tens of ng/L up to several µg/L range, and suggest year round influence from urban petroleum usage and fossil fuel burning reaches the more remote rural regions in the Central Valley. Hydrocarbons and other petroleum related compounds are ubiquitous background contaminants in TFCF waters.

The prominent regular peaks from 15 to 40 min RRT shown in Figure 6a (dissolved F1 fraction TIC for June 1999) indicated a clear set of regularly spaced peaks for the homologous series of normal alkanes, hydrocarbons that are associated with human petroleum fuel usage. These prominent peaks were seen in all dissolved F1 fraction chromatograms, but were very prominent in the June, July, and October samples (seen in the Appendix 2 chromatograms arranged by month). Another observation is that the F1 fraction hydrocarbons show that C27–C29 chain hydrocarbons dominated. Odd over even predominance ratio (OEP) in chain length suggests that waters at the TFCF were mostly influenced by natural processes despite the significant human inputs to the ecosystem (Scanlan and Smith 1970; Tan and Heit, 1981; Lipiatou and Saliot, 1992). This is not to say that Delta water quality was unaffected by pollution, but rather that the distribution of hydrocarbons and their ratios showed a system dominated by natural organic breakdown processes, and that the south Delta water was not severely polluted.

An example of a 4-ring PAH identified using AMDIS may be seen in Figure 6b (right hand data). AMDIS search output identified 1-methylpyrene from a peak seen in a prominent cluster of peaks from RT = 30–40 min in the January 2000 suspended F2 fraction TIC chromatogram (see Appendix 2 TIC). These results are supported by Oros *et al*. (2007) suggesting rainwater runoff mobilization of PAHs during winter storm events. We also observed hydrocarbons associated with fossil fuel usage such as pristane (2,6,10,14-tetramethylpentadecane, $C_{19}H_{40}$) and phytane (2,6,10,14-tetramethylhexadecane, $C_{20}H_{42}$) were more frequently observed in the open scan data during the winter months.

Linear chain alkyl benzene surfactants, which are widely used in a variety of health and beauty products, detergents, industrial fluids, and other consumer products, were also clearly observed in the open scan data. Figure 6b (left hand data) shows an AMDIS identification of 1-ethyldecylbenzene, found in a prominent cluster of peaks from RT = 15 to 30 min on the July 1999 suspended F1 fraction chromatogram. Other compounds consistently identified in the suspended F2 fraction chromatograms included some PCB congeners, lindane (gamma HCH, or hexachlorocyclohexane), p’p’-DDE and p,p’-DDT. However, of the COC list compounds, only Trifluralin was consistently observed above the qualitative DLs associated with LRMS data.

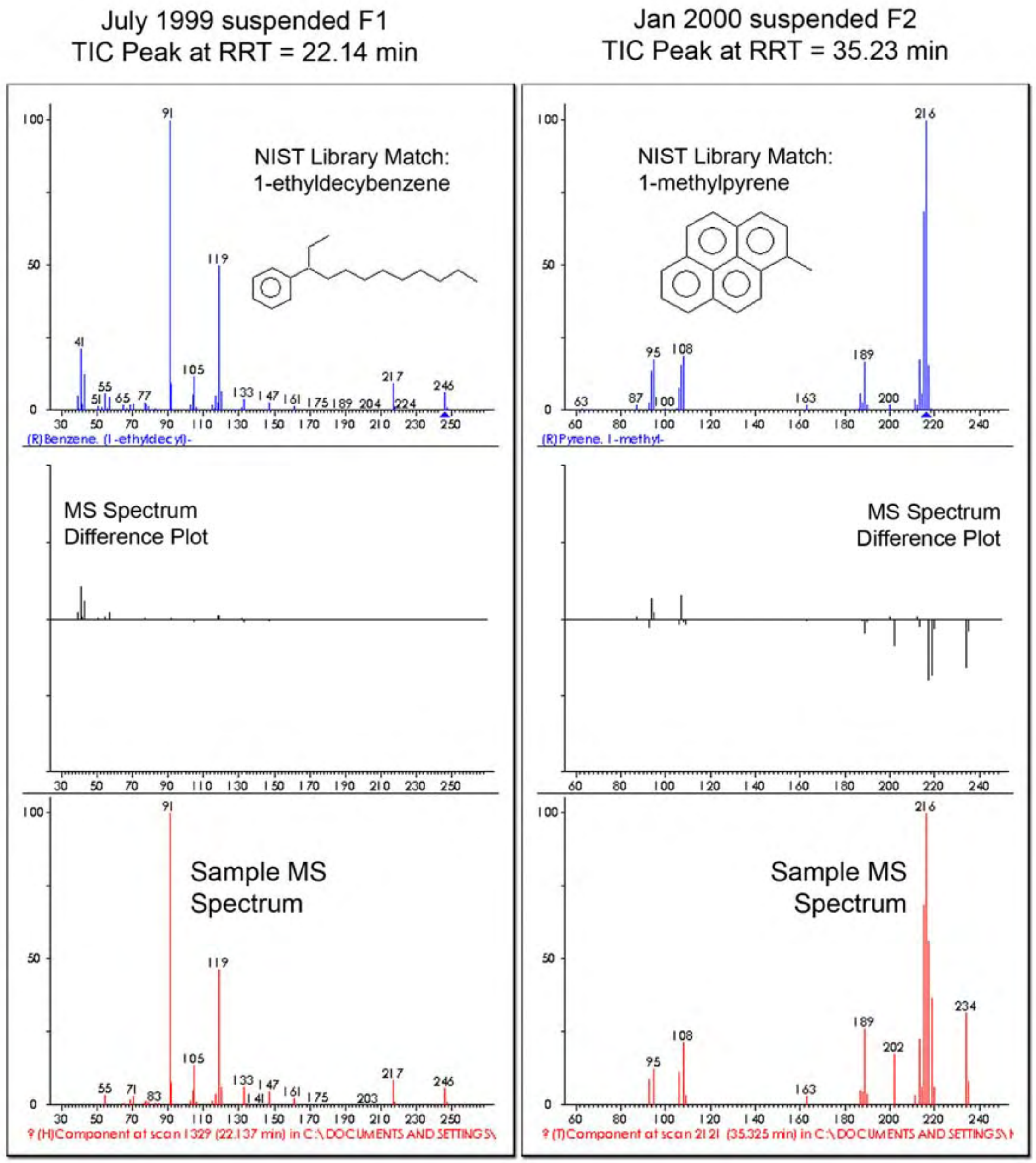


FIGURE 6b.—Examples of compounds inferred by library searches of full scan mass spectrometry (MS) data using Automated Mass Spectral Deconvolution and Identification System (AMDIS) and National Institute of Standards and Technology (NIST) MS library for selected peaks in the July 1999 F1 and January 2000 F2 filter extracts.

Quantitative HRMS and MS/MS Data

The complete summary tables for the HRMS and MS/MS data are in Appendix 3, Tables A3-1 (for dissolved data), and A3-2 (for suspended data). The quantitative HRGC–HRMS data showed that except for Aldicarb, Permethrin, and Phosmet, the COCs were consistently detected in all composite samples.

Compounds of Concern

Table 4a summarizes concentrations for the agricultural COC list, and Tables 4b (USGS data) and 4c (CDPR data) summarize the COC analytes from the SJR station at Vernalis, California, that were analyzed by others (MacCoy *et al*., 1995; CDPR, 2008). Figures 7a–7f provide plots of dissolved and suspended data for COCs detected for each composite sample with a plot of local agricultural applications from the 1997 data summary (Craft *et al*., 2000a). While there were probably differences in local agricultural practices between the 1997 and 1999 agricultural seasons, the 1997 data were thought to represent typical conditions generally applicable to the 1999 analytical results. Several agricultural COCs were not analyzed using the HRMS or MS/MS methods, including Bromoxynil, Desmedipham, Esfenvalerate, Fenbutatin-Oxide, Oryzalin, and Oxyfluorfen. Of the COCs analyzed, only Aldicarb was not detected in this study.

The carbamate insecticide Carbofuran (Figure 7a) ranged from 0.120 to 8.46 ng/L in 8 of 9 dissolved samples but was undetected in suspended samples. There was no apparent relationship between local applications and the months when Carbofuran was detected. Given the likely local application in June and widespread basin applications, the below detection limits (DL) found in June for suspended and dissolved Carbofuran appears to be anomalous. Table 4b suggests that Carbofuran was only detected by the USGS around 3 percent of the time above a DL of 31 ng/L. The higher detections were in March and April ranging from 58 to 105 ng/L, and June and July concentrations were only slightly above the DL. The USGS data suggested 1- to 2-week spring Carbofuran pulses with concentrations > 100 ng/L occurring rarely (< 0.5 percent of the time) for very short periods (1 d or less). The CDPR data (Table 4c), with similar DLs to the USGS, showed only 3.8 percent detections above 30 ng/L with very few detections of Carbofuran above 90 ng/L.

The organophosphorus pesticide Chloryprifos (Figure 7b) was detected in all composite samples with dissolved concentrations dominating from 0.574 to 38.0 ng/L compared to 0.027–0.597 ng/L for suspended samples. A metabolite, Chlorpyrifos-oxon, was observed in 5 of 9 dissolved samples ranging from 0.005 to 0.139 ng/L. Maximum Chlorpyrifos concentration was observed in June for both dissolved and suspended fractions. There was no clear correlation between 1997 applications and observed concentrations. The USGS (Table 4b) only observed dissolved Chlorpyrifos qualitatively around 1 percent of the time (no detections above the DL), and the CDPR only reported concentrations above 5 ng/L in 2.5 percent of samples. The CDPR detected values are corroborative of the data we report; however, we found that Chlorpyrifos was fairly common in TFCF waters, and was likely present at much higher spiking concentrations for short periods. Average dissolved Chlorpyrifos concentrations above 10 ng/L (as seen in May, June, and September) suggest that TFCF water was often above the 41 ng/L 4-day Fresh Water Aquatic Life water quality guideline. During June, transient concentrations of Chlorpyrifos may have exceeded the 0.083 ng/L 1-hour Fresh Water Aquatic Life water quality guideline (EPA, 1999; SFEI, 2006).

TABLE 4a.—Concentration ranges from this study for suspended and dissolved fractions and fish toxicity scores for Tracy organic compounds of concern (COC) analytes and several metabolite compounds. A fish toxicity score of 0 is “nontoxic” while a score of 5 is “very toxic.” NA – not analyzed this study, “<” represents analyzed, but not detected at < detection limit range.

			Dissolved		**Suspended**	
Compound	**Chemical Class**	**Avg Fish Tox Score**	**Range, ng/L**	**n of 9 Detected**	**Range, ng/L**	**n of 9 Detected**
Aldicarb	carbamate	4.3	< 0.011–0.113	0	< 0.011–0.113	0
Bromoxynil	aromatic nitrile	5.0	NA	-	NA	-
Carbofuran	carbamate	5.0	0.120–8.46	8	< 0.011–0.113	0
Chlorpyrifos	organophosphorus	5.0	0.574–38.0	9	0.027–0.597	9
Chlorpyrifos- Oxon	metabolite	-	0.005–0.139	5	< 0.002–0.023	0
Desmedipham	phenyl carbamate	4.0	NA	-	NA	-
Diazinon	organophosphorus	4.3	0.646–7.70	8	0.002–0.117	8
Diazinon-Oxon	metabolite	-	0.014–0.229	8	<	0
Esfenvalerate	pyrethroid	5.0	NA	-	NA	-
Fenbutatin-oxide	organo-tin	5.0	NA	-	NA	-
Fonofos	organophosphorus	5.0	0.013–4.43	9	0.010–0.066	8
Metam-sodium	carbamate	4.0	NA	-	NA	-
Metolachlor	chloracetanilide	3.5	0.307–120	8	0.029–1.01	9
Oryzalin	dinitroaniline	4.0	NA	-	NA	-
Oxyfluorfen	diphenyl ether	5.0	NA	-	NA	-
Permethrin	pyrethroid	5.0	<	0	0.033	1
Phosmet	organophosphorus	4.0	0.103–0.308	2	< 0.011–0.152	0
Trifluralin	dinitroaniline	4.3	0.260–24.5	9	0.013–0.254	9

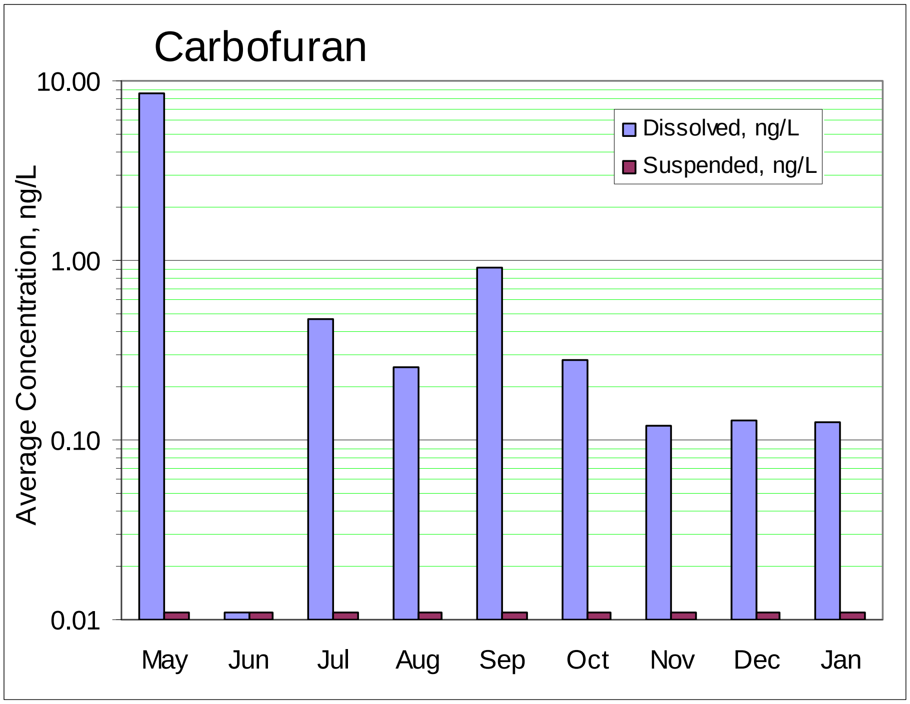
TABLE 4b.—Summary of percentiles for Tracy compounds of concern (COC) analytes analyzed using solid phase extraction (SPE) and gas chromatography–mass spectrometry (GC–MS) by the U.S. Geological Survey from their sampling station on the San Joaquin River, Vernalis, California (MacCoy et al., 1995). Negative values should be read as “below detection limit” with inverse values representing the concentration in ng/L at the detection limit (DL). For example, Metolachlor had a reported DL of 47 ng/L. Data are rounded to 2 significant figures.

	Carbofuran	**Chlorpyrifos**	**Diazinon**	**Fonofos**	**Metolachlor**	**Trifluralin**
Samples	640	640	640	410	293	410
Percentiles	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
0.5th Percentile	-31	-35	-38	-25	-47	-60
1st Percentile	-31	-35	-38	-25	-47	-60
2.5th Percentile	-31	-35	-38	-25	-47	-60
5th Percentile	-31	-35	-38	-25	-47	-60
16th Percentile	-31	-35	-38	-25	-47	-60
Median	-31	-35	-38	-25	-47	-60
84th Percentile	-31	-35	57	-25	38	-60
95th Percentile	17	-35	160	-25	59	-60
97.5th Percentile	32	-35	250	-25	71	-60
99th Percentile	60	20	370	-25	110	-60
99.5th Percentile	83	23	570	-25	120	-60

TABLE 4c.—Summary of percentiles for Tracy compounds of concern (COC) analytes in µg/L analyzed by other agencies and archived by the California Department of Pesticide Regulation (CDPR, 2008) for sampling station 39-17 – San Joaquin River at Vernalis, California. Aldicarb (n = 11), Esfenvalerate (n = 14), Permethrin (n = 55), and Phosmet (n = 155) were analyzed but not detected. Bromoxynil, Fenbutatin-oxide, Metam-Sodium, Oryzalin, and Oxyfluorfen were not analyzed or reported from this source.

Carbofuran		**Chlorpyrifos**		**Diazinon**	
Analyzed	825	Analyzed	836	Analyzed	862
Detected	31	Detected	21	Detected	219
Not Detected	794	Not Detected	815	Not Detected	643
Percent Detected	3.80	Percent Detected	2.50	Percent Detected	25.4
Percentiles	µg/L	Percentiles	µg/L	Percentiles	µg/L
0.5th Percentile	-0.030	0.5th Percentile	-0.005	0.5th Percentile	-0.004
1st Percentile	-0.030	1st Percentile	-0.005	1st Percentile	-0.004
2.5th Percentile	-0.030	2.5th Percentile	-0.005	2.5th Percentile	-0.004
5th Percentile	-0.030	5th Percentile	-0.005	5th Percentile	-0.004
16th Percentile	-0.030	16th Percentile	-0.005	16th Percentile	-0.004
Median	-0.030	Median	-0.005	Median	-0.004
84th Percentile	-0.030	84th Percentile	-0.005	84th Percentile	0.050
95th Percentile	-0.030	95th Percentile	-0.005	95th Percentile	0.130
97.5th Percentile	0.044	97.5th Percentile	0.005	97.5th Percentile	0.218
99th Percentile	0.070	99th Percentile	0.010	99th Percentile	0.325
99.5th Percentile	0.089	99.5th Percentile	0.020	99.5th Percentile	0.503

Fonofos		**Metolachlor**		**Trifluralin**	
Analyzed	844	Analyzed	360	Analyzed	672
Detected	2	Detected	80	Detected	6
Not Detected	842	Not Detected	280	Not Detected	666
Percent Detected	0.200	Percent Detected	22.2	Percent Detected	0.900
Percentiles	µg/L	Percentiles	µg/L	Percentiles	µg/L
0.5th Percentile	-0.050	0.5th Percentile	-0.015	0.5th Percentile	-0.006
1st Percentile	-0.050	1st Percentile	-0.015	1st Percentile	-0.006
2.5th Percentile	-0.050	2.5th Percentile	-0.015	2.5th Percentile	-0.006
5th Percentile	-0.050	5th Percentile	-0.015	5th Percentile	-0.006
16th Percentile	-0.050	16th Percentile	-0.015	16th Percentile	-0.006
Median	-0.050	Median	-0.015	Median	-0.006
84th Percentile	-0.050	84th Percentile	0.053	84th Percentile	-0.006
95th Percentile	-0.050	95th Percentile	0.088	95th Percentile	-0.006
97.5th Percentile	-0.050	97.5th Percentile	0.113	97.5th Percentile	-0.006
99th Percentile	-0.050	99th Percentile	0.128	99th Percentile	-0.003
99.5th Percentile	-0.050	99.5th Percentile	0.143	99.5th Percentile	0.008



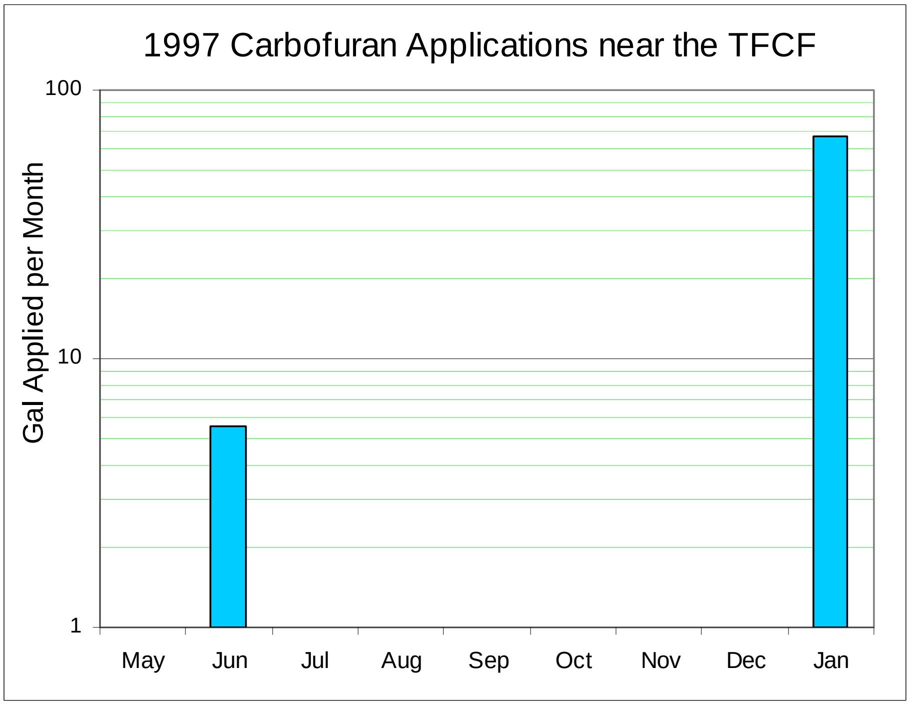
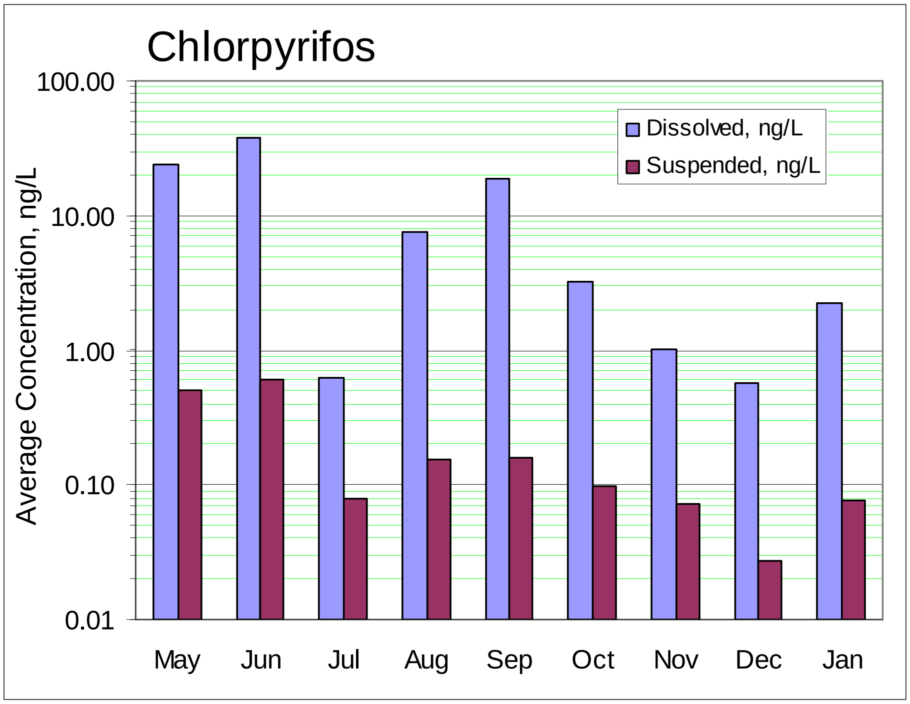


FIGURE 7a.—Average dissolved and suspended concentrations of the carbamate insecticide Carbofuran for the 1999–2000 study period (top graph). Values of 0.011 indicate non-detected (refer to Appendix 3, Tables A3-1 and A3-2 for estimated detection limits for each sample). Concentrations are plotted on a logarithmic scale. Bottom, 1997 Carbofuran formulation applications near the Tracy Fish Collection Facility (TFCF). Another local application (393 gal [1,488 L]) of Carbofuran formulation was observed in March 1997. English units are used in the lower graph of agricultural chemical applications because of common usage by the agricultural community, local governments, and water districts (1 gal = 3.84 L).



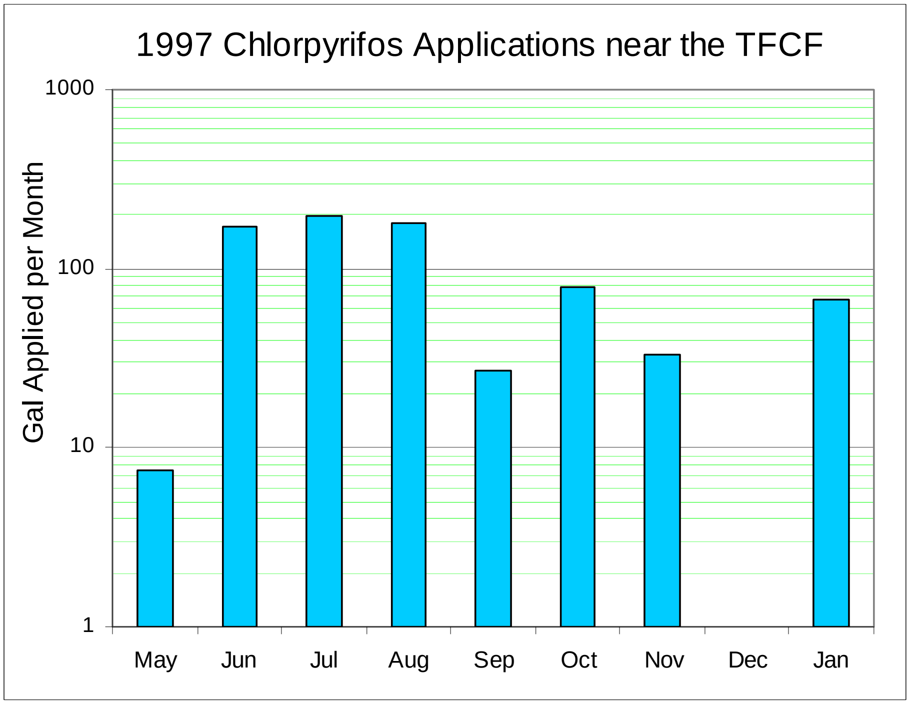


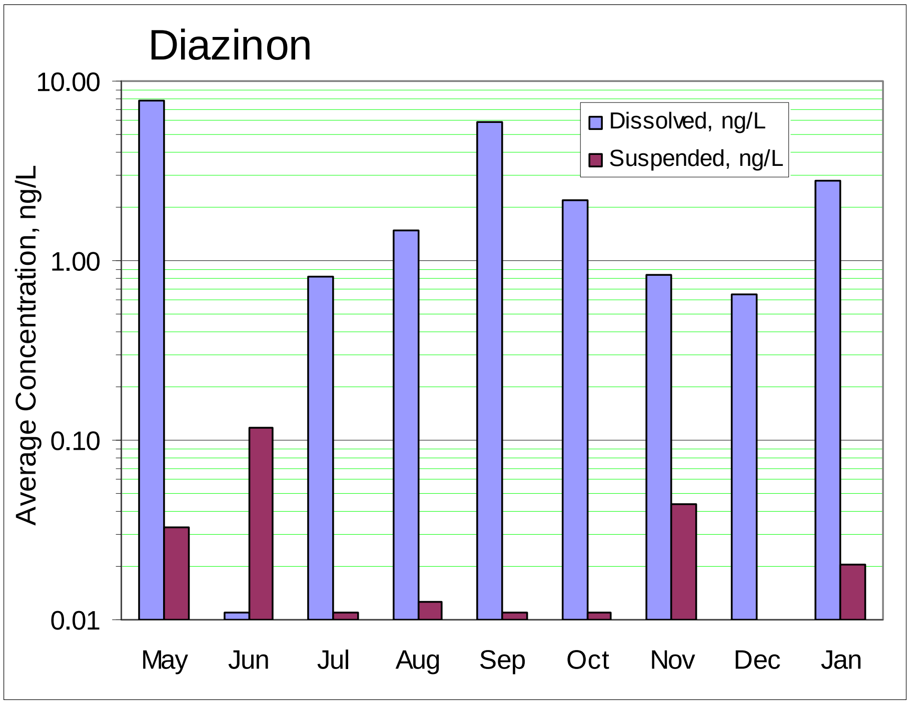
FIGURE 7b.—Average dissolved and suspended concentrations of the organophosphate insecticide Chlorpyrifos for the 1999–2000 study period (top graph). Concentrations are plotted on a logarithmic scale. Bottom, 1997 Chlorpyrifos formulation applications near the Tracy Fish Collection Facility (TFCF). Local applications of Chlorpyrifos also occurred in 1997 during in February (16 gal [61 L]), March (1,480 gal [5,602 L]) and April (36 gal [136 L]). English units are used in the lower graph of agricultural chemical applications because of common usage by the agricultural community, local governments, and water districts (1 gal = 3.84 L).

Diazinon (Figure 7c), an organophosphorus pesticide COC, was observed in 8 of 9 dissolved samples ranging from 0.646 to 7.70 ng/L, and 8 of 9 suspended samples ranging from 0.002 to 0.117 ng/L. Given the maximum suspended Diazinon in June of 0.117 ng/L, the dissolved non-detection (ND) observed during June was again thought to be an anomaly. No correlation with local applications was observed. We also observed a Diazinon metabolite, Diazinon-oxon in 8 of 9 dissolved samples that ranged from 0.014 to 0.229 ng/L. Diazinon was more frequently observed by both the USGS (Table 4b) and CDPR (Table 4c) with maximum concentrations reported for ~ 1-d periods above 500 ng/L. The USGS data, with a DL of 38 ng/L, showed winter maxima with 2- to 3-weak pulses and maximum concentrations of 527–714 ng/L, and August maxima ranging from 100 to 250 ng/L. The CDPR data (DL = 5 ng/L, n = 862) similarly showed detections in 50–84 percent of samples, suggesting that Diazinon was often above the average concentrations reported here. CDPR data also suggested short-term maxima for Diazinon that were two orders of magnitude higher than the average values reported here.

Fonofos (Figure 7d) was observed in all dissolved samples ranging from 0.013 to 4.43 ng/L and in 8 of 9 suspended samples at much lower concentrations of 0.010–0.066 ng/L. The maximum Fonofos concentration was observed in June, and no correlation with local application applications was observed. However, there were large local applications in March (> 2,000 lbs [> 907 kg]) and April (> 1800 lbs [> 816 kg]) in spring of 1997. Fonofos was not observed by the USGS (DL = 25 ng/L, n = 410) and only detected in 0.2 percent of samples reported by the CDPR (DL = 50 ng/L, n = 844). The data reported here show that Fonofos was fairly common, though at generally lower concentrations compared to Diazinon and Chlorpyrifos.

Of the organic COCs, the chloracetanilide herbicide Metolachlor had the highest observed maximum concentration, 120 ng/L for the May dissolved sample. There were local applications in February, March, and April 1997, suggesting that similar local spring applications may have accounted for the May maximum. Except for another anomalous June dissolved non-detection, Metolachlor data showed a downward concentration trend from the May maximum with a December minimum dissolved value of 0.307 ng/L. Suspended Metolachlor was around one-tenth of dissolved concentrations, ranging from 0.029 to 1.01 ng/L. Table 4b USGS data (DL = 47 ng/L, n = 293) and Table 4c CDPR data (DL = 15 ng/L, n = 360) corroborate the May maximum, though the average May data suggested much higher temporary concentration spikes than maxima reported elsewhere. The USGS data showed a fairly broad detection peak from February through September, with 1- to 3-d spikes of higher concentrations. Despite the lower DL of 15 ng/L, the CDPR data only reported 22.2 percent detections.

The dinitroaniline herbicide Trifluralin was the COC with the greatest amount of 1997 local applications: around 52,000 kg formulation equivalent applied over 13,300 acres near the TFCF. There was g*eneral* correspondence (but again, no clear correlation) between the



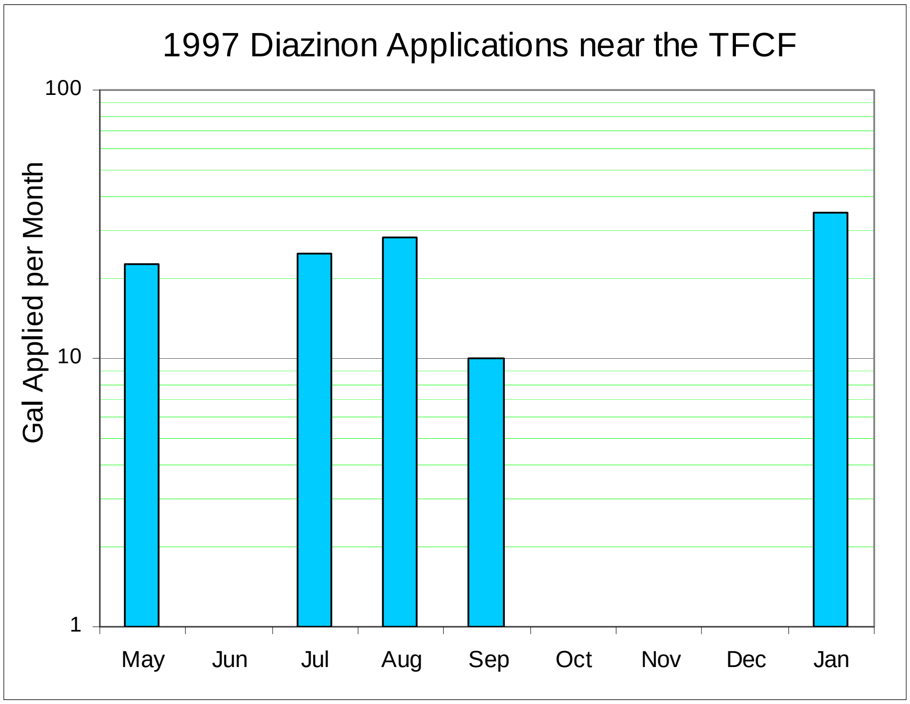
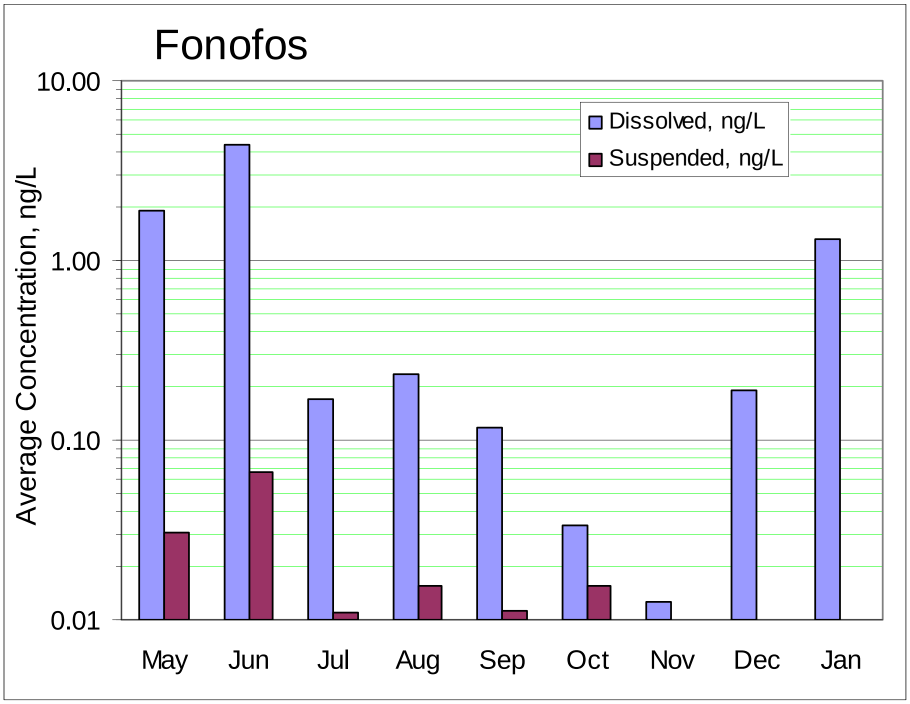


FIGURE 7c.—Average dissolved and suspended concentrations of the organophosphate insecticide Diazinon for the 1999–2000 study period (top graph). Values of 0.011 indicate non-detected (refer to Appendix 1, Table A1-1 for estimated detection limits for each sample). Concentrations are plotted on a logarithmic scale. Bottom, 1997 Diazinon formulation applications near the Tracy Fish Collection Facility (TFCF). English units are used in the lower graph of agricultural chemical applications because of common usage by the agricultural community, local governments, and water districts (1 gal = 3.84 L).



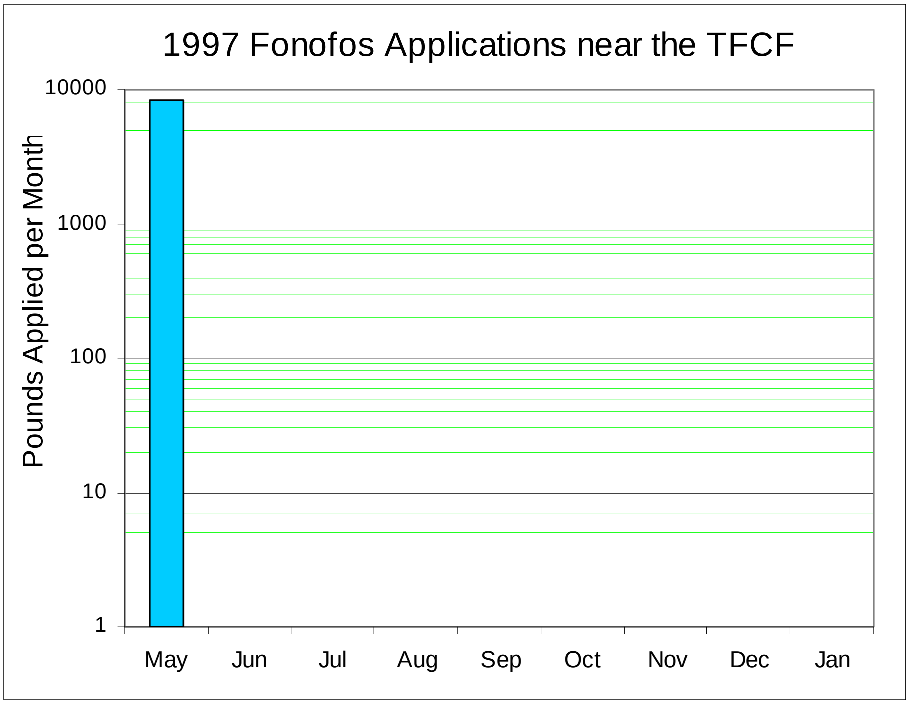
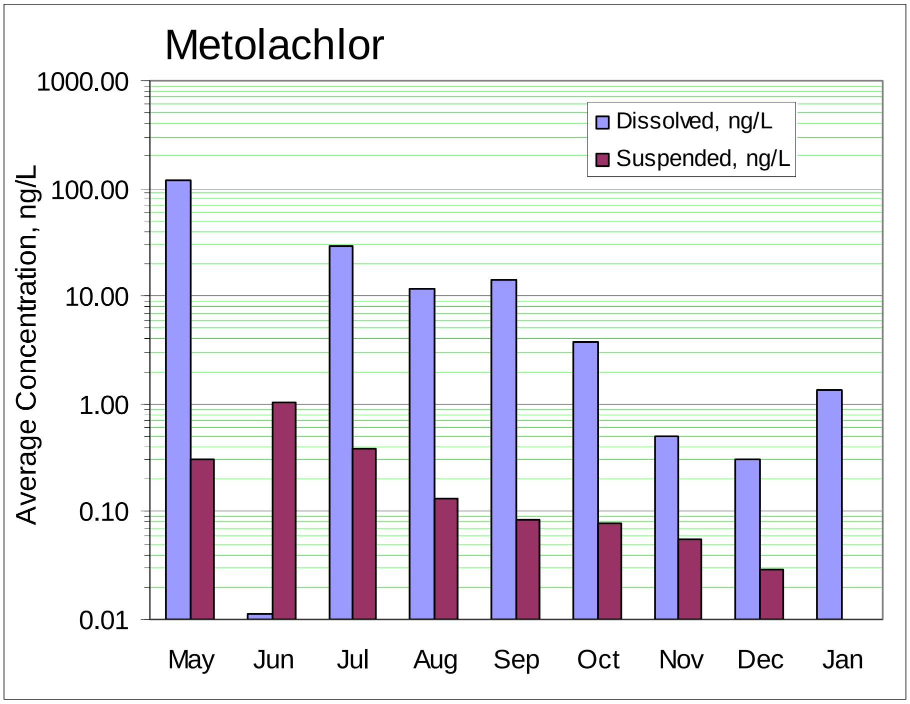


Figure 7d.—Average dissolved and suspended concentrations of the organophosphate insecticide Fonofos for the 1999–2000 study period (top graph). Values of 0.011 indicate non-detected (refer to Appendix 3, Tables A3-1 and A3-2 for estimated detection limits for each sample) Concentrations are plotted on a logarithmic scale. Bottom, 1997 Fonofos formulation applications near the Tracy Fish Collection Facility (TFCF). Large nearby applications of Fonofos also occurred in March (2,075 lb [941 kg]) and April (1,850 lb [839 kg]) 1997. English units are used in the lower graph of agricultural chemical applications because of common usage by the agricultural community, local governments, and water districts (1 lb = 0.453 kg).



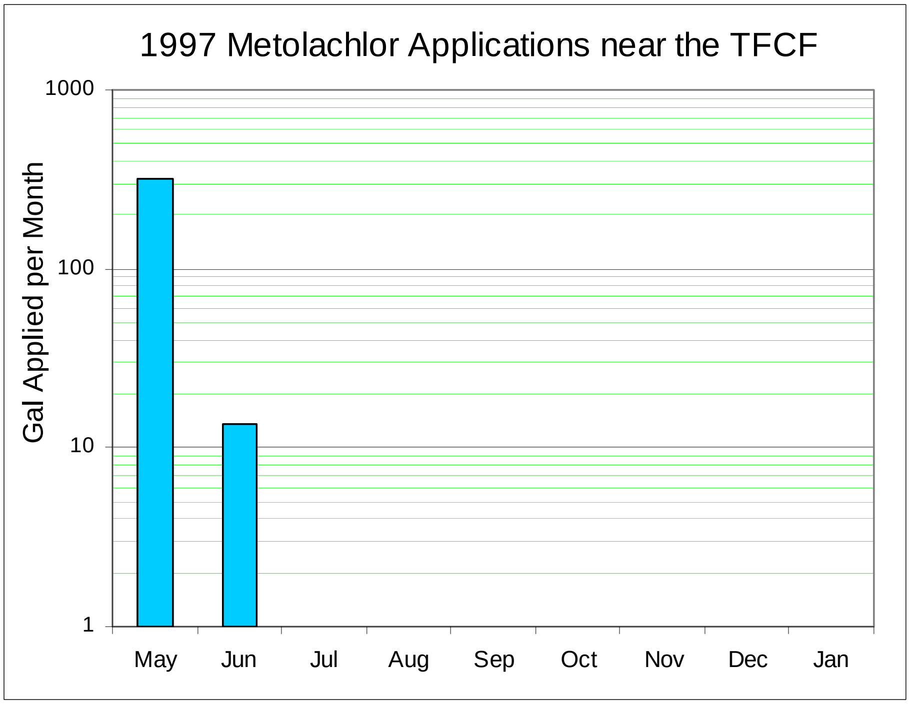


FIGURE 7e.—Average dissolved and suspended concentrations of the chloracetanilide herbicide Metolachlor for the 1999-2000 study period (top graph). Values of 0.011 indicate non-detected (refer to Appendix 3, Tables A3-1 and A3-2 for estimated detection limits for each sample). Concentrations are plotted on a logarithmic scale. Bottom, 1997 Metolachlor formulation applications near the Tracy Fish Collection Facility (TFCF). Metolachlor was also applied locally during February (18.8 gal [71.2 L]), March (312 gal [1,181 L]) and April (226 gal [856 L]), 1997. English units are used in the lower graph of agricultural chemical applications because of common usage by the agricultural community, local governments, and water districts (1 gal = 3.84 L).

1997 application schedule and detection of Trifluralin seen in Figure 7f. Trifluralin was detected in both dissolved and suspended fractions of all composites, with dissolved values ranging from 0.260 to 24.5 ng/L. Suspended concentrations ranged from 0.013 to 0.254 ng/L, around 50 times less than dissolved. These data were not corroborated by the USGS (DL = 60 ng/L, n = 410) which reported no detections from 1991–1994. Similarly, the CDPR data (DL = 8 ng/L, n = 672) only reported 6 detections (0.9 percent of samples) at concentrations similar to our average dissolved data. Our data suggest that Trifluralin was a ubiquitous contaminant in the south Delta.

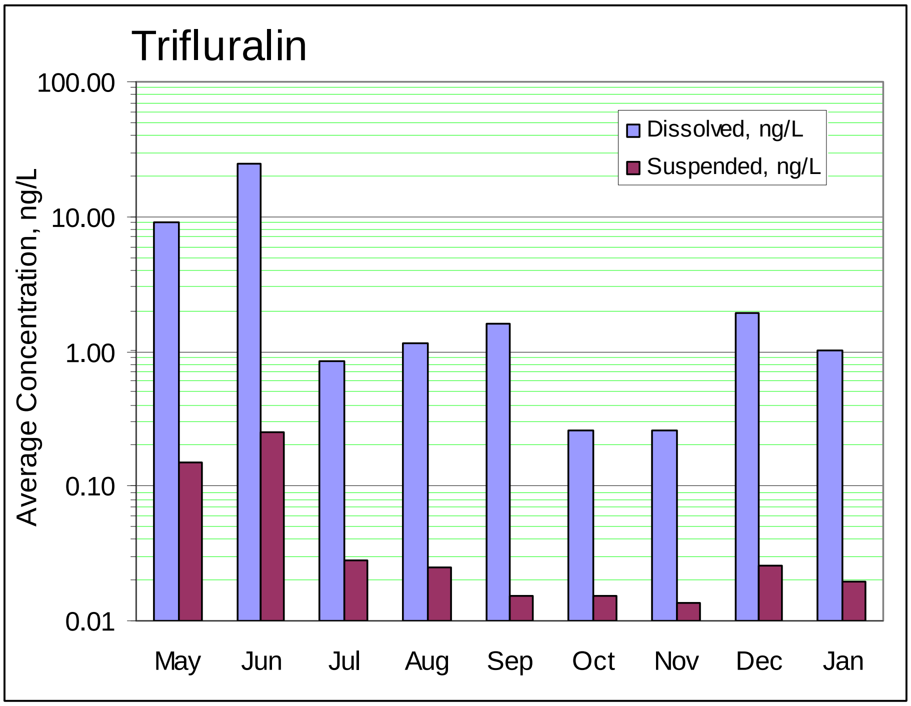
Permethrin, a pyrethroid insecticide COC, was only observed in the suspended May composite at a low concentration of 0.033 ng/L. Phosmet, another organophosphorus insecticide COC, was only observed in May and January at average concentrations below 1 ng/L. The USGS did not analyze for Permethrin or Phosmet, and the CDPR only reported non-detections for Permethrin (n = 55) and Phosmet (n = 155).

Other Locally Applied Agricultural Compounds Not on the Compounds of Concern List

Table 5a lists other organic compounds detected in the composite samples that were also applied near the TFCF in 1997. Highest concentrations were found for the organophosphorus pesticide Methamidophos, exclusively in the dissolved fractions ranging from 0.259 to 21.9 ng/L. As with the other COC list results, the dissolved concentrations dominated. Only Alachlor and Linuron were detected more than once (5 of 9) in the suspended composites. Notable dissolved detections included Alachlor, Dacthal, Linuron, Malathion (7 of 9, 0.046–14.4 ng/L), Methamidophos, Methyl Parathion (7 of 9, 0.055–9.15 ng/L), and Pendimethalin.

Table 5b summarizes USGS data (MacCoy *et al*., 1995) and Table 5c data reported by the CDPR (CDPR, 2008) for non-COC chemicals they routinely detected in the SJR at Vernalis, several of which were not analyzed in this study (Cyanazine, Methidathion, Simazine, Thiobencarb, and all compounds in Table 5c). Cyanazine, Dachthal, Methidathion, and Thiobencarb were not applied near the TFCF; however, they were routinely reported by the USGS and CDPR in the SJR at Vernalis.

Of the non-COCs in Table 5a, several were applied in significant quantities near the TFCF in 1997, including Carbaryl (13,800 lb [6,260 kg]), Diuron (7,280 lb [3,302 kg]), Eptam (7,790 lb [3,533 kg]), Hexazinone (2,000 lb [907 kg]), Linuron (2,020 lb [916 kg]), Methomyl (3,380 lb [1,533 kg]), and Napropamide (5,640 lb [2,558 kg]). We detected the carbamate insecticide Carbaryl in 6 of 9 dissolved composites with concentrations from 0.095 to 6.80 ng/L (Table 5a), but no suspended Carbaryl was detected. The USGS (Table 5b) reported dissolved Carbaryl (DL = 44 ng/L, n = 515) only 5 percent of the time with a maximum over 190 ng/L. The CDPR (Table 5c) reported values for Diuron ranging from 33–5,160 ng/L (n = 128), Eptam from 3–674 ng/L, Hexazinone from 55–160 ng/L (n = 5), and Napropramide from 8–17 ng/L (n = 2).



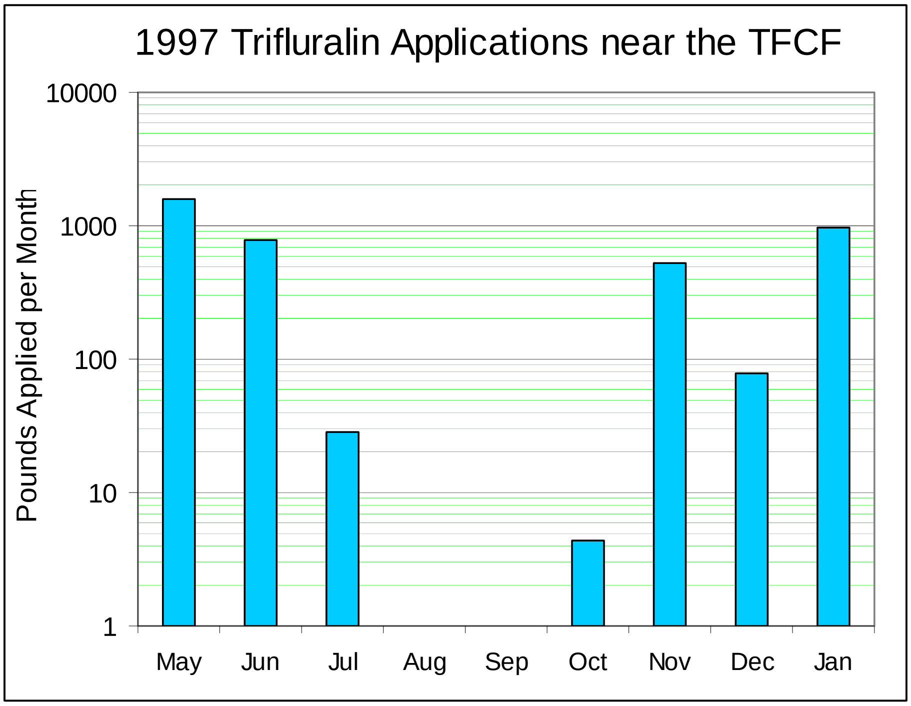


FIGURE 7f.—Average dissolved and suspended concentrations of the dinitroaniline herbicide Trifluralin for the 1999–2000 study period (top graph). Concentrations are plotted on a logarithmic scale. Bottom, 1997 Trifluralin applications near the Tracy Fish Collection Facility (TFCF). English units are used in the lower graph of agricultural chemical applications because of common usage by the agricultural community, local governments, and water districts (1 lb = 0.453 kg).

TABLE 5a.—Summary of high-resolution mass spectrometry data from this study for agricultural chemicals not included on the Tracy compounds of concerns (COC) list but applied near the Tracy Fish Collection Facility (TFCF). Dacthal and Carbaryl have been observed in the south Delta by others (MacCoy *et al*., 1995; CDPR, 2008).

Compound	**Chemical Class**	**1997 Application**	**Dissolved, ng/L**	**Suspended, ng/L**
Alachlor	acetanilide	114 gal (432 L)	0.018–3.98 (8 out of 9)	0.018–0.033 (5 out of 9)
Carbaryl	carbamate	13,800 lb (6,260 kg)	0.095–6.80 (6 out of 9)	< 0.012–0.023 (0 out of 9)
Dacthal	chlorinated phthalate	16.0 lb (7.3 kg)	0.064–1.86 (9 out of 9)	0.004–0.020 (3 out of 9)
Disulfoton	organophosphorus	771 gal (2,919 L)	1.37 (1 out of 9)	< 0.012–0.138 (0 out of 9)
Ethalfluralin	dinitroaniline	277 gal (1,049 L)	0.005–0.262 (7 out of 9)	< 0.003–0.030 (0 out of 9)
Linuron	substituted urea	2,020 lb (916 kg)	0.056–2.26 (9 out of 9)	0.036–0.257 (5 out of 9)
Malathion	thiophosphorythio/mercaptan	198 gal (750 L)	0.046–14.4 (7 out of 9)	< 0.020–1.08 (0 out of 9)
Methamidophos	organophosphorus	139 gal (526 L)	0.259–21.9 (9 out of 9)	< 0.070–0.749 (0 out of 9)
Methomyl	carbamate	3,380 lb (1,533 kg)	0.052–0.556 (3 out of 9)	< 0.011–0.113 (0 out of 9)
Methyl Parathion	organophosphorus	729 gal (2,760 L)	0.044–9.15 (7 out of 9)	0.027 (1 out of 9)
Pendimethalin	dinitroaniline	143 gal (541 L)	0.210–5.48 (8 out of 9)	0.076 (1 out of 9)

TABLE 5b.—Summary of MacCoy *et al.,* (1995) data for the San Joaquin River at Vernalis, California, for other agricultural chemicals not on the Tracy chemicals of concern (COC) list. Data are rounded to 2 significant figures.

	Carbaryl	**Cyanazine**	**Dacthal**	**Methidathion**	**Simazine**	**Thiobencarb**
Samples	515	192	293	515	640	601
Percentiles	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
0.5th Percentile	-44	-50	-63	-63	-82	-60
1st Percentile	-44	-50	-63	-63	-82	-60
2.5th Percentile	-44	-50	-63	-63	-82	-60
5th Percentile	-44	-50	-63	-63	-82	-60
16th Percentile	-44	-50	-63	-63	-82	-60
Median	-44	-50	-63	-28	53	-60
84th Percentile	-44	150	11	-28	220	-60
95th Percentile	29	300	35	74	440	-60
97.5th Percentile	50	520	44	170	730	15
99th Percentile	99	600	89	430	1,000	35
99.5th Percentile	190	800	140	650	1,100	110

TABLE 5c.—Summary of data from California Department of Pesticide Regulation for agricultural chemicals applied near the Tracy Fish Collection Facility (TFCF), and reported in the San Joaquin River near Vernalis, California, but not analyzed in this study.

Compound	Chemical Class	1997 Application	Number of Samples	Minimum, ng/L	Maximum, ng/L
Diuron	substituted urea	7,280 lb (3,302 kg)	128	33	5,160
Eptam/EPTC	carbamate	7,790 lb (3,533 kg)	42	3	674
Hexazinone	triazine-dione	2,000 lb (907 kg)	5	55	160
Napropamide	naphthyl ether	5,640 lb (2,558 kg)	2	8	17
Pebulate	carbamate	714 gal (2,703 L)	7	17	1,046
Simazine	triazine	207 gal (784 L)	343	12	1,747

Small amounts of the carbamate insecticide Pebulate (714 gal [2,703 L]) and the triazine herbicide Simazine (207 gal [784 L]) were applied near the TFCF in 1997, but the USGS and CDPR reported fairly frequent detection of these compounds with maximum concentrations above 1 µg/L (1,000 ng/L) for both Simazine, and Pebulate. These data from the SJR well upstream of the TFCF reiterate the influence of basin-wide agricultural chemical applications on the water quality at the TFCF.

Other Persistent, Regulated, and Agricultural Compounds Detected

Table 6a lists the other organic compounds detected in the dissolved and suspended composite samples, representing several banned and regulated agricultural compounds and their metabolites and isomers (Aldrin, Chlordanes, Dieldrin, Endrin, Lindane, and Mirex), along with other agricultural compounds not applied near the TFCF. Table 6b lists the organic compounds of concern monitored by the RMP and concentrations in µg/L corresponding to California and EPA water quality guidelines. Table 6c lists the regulated concentrations for persistent and bioaccumulating organic compounds (State of California, 2005).

Notably, all the regulated and persistent compounds we analyzed were detected in both dissolved and suspended composite samples. All dissolved concentrations were very low relative to the Table 6c regulated concentrations; however, we observed several compounds at concentrations higher than those recently reported by the RMP (SFEI, 2006), and exceeding some of the lower concentration Table 6b water quality guidelines.

The banned pesticide Chlordane is a persistent chemical that produces a variety of metabolites including cis- and trans- isomers of Chlordane (c-Chlordane and t-Chlordane), heptachlor, heptachlor epoxide, oxychlordane, and c-nonachlor and t-nonachlor. Almost all of these compounds were detected in both dissolved and suspended composite samples. Total dissolved Chlordanes ranged from 0.147 to 2.66 ng/L, and suspended Chlordanes from 0.143 to 1.257 ng/L, suggesting that suspended fractions account for around 30–50 percent of total. The RMP reported maximum dissolved sum of Chlordanes at 0.052 ng/L from their river samples near Suisiun Bay (SFEI, 2006). These concentrations were well below the values we observed, suggesting significantly higher inland concentrations of Chlordane compounds. Some of both dissolved and suspended c-Chlordane concentrations we observed were also higher than the Table 6b Fresh Water Human Health criteria of 0.57 ng/L.

TABLE 6a.—Summary of high-resolution mass spectrometry data from this study for organic chemicals found in composite samples, but not applied in the immediate vicinity of the Tracy Fish Collection Facility (TFCF). A** indicates compounds regulated by the State of California (2005).

	Dissolved			**Suspended**		
Compound	**Minimum, ng/L**	**Maximum, ng/L**	**Detected, n of 9**	**Minimum, ng/L**	**Maximum, ng/L**	**Detected, n of 9**
Aldrin**	0.002	0.012	9	0.001	0.010	9
Butylate	0.002	0.047	8	ND	ND	0
Chlordane Isomers and Metabolites**						
c-Chlordane**	0.096	1.89	9	0.123	0.997	9
t-Chlordane**	0.016	0.282	9	0.004	0.065	9
Heptachlor**	0.004	0.033	9	0.003	0.055	9
Heptachlor-Epoxide**	0.006	0.158	9	0.001	0.013	8
Oxychlordane**	0.008	0.097	6	0.005	0.013	7
c-Nonachlor**	0.005	0.107	9	0.003	0.046	9
t-Nonachlor**	0.012	0.088	9	0.004	0.068	9
Chlorothalonil		0.054	1	ND	ND	0
Dieldrin**	0.078	2.24	9	0.008	0.107	9
Dimethoate	0.064	26.7	7	ND	ND	0
Dioxacarb	0.017	0.083	5		0.050	1
Disulfoton-Sulfone	0.589	18.5	8	0.005	0.056	6
Endosulphan-Sulphate	0.056	1.32	9	0.004	0.034	7
alpha-Endosulphan	0.013	0.206	9	0.012	0.125	9
beta-Endosulphan	0.015	0.178	8	0.010	0.085	9
Endrin**	0.003	0.117	9	0.001	0.016	8
Ethion	0.008	0.418	5	ND	ND	0
Hexachlorobenzene	0.002	0.029	9	0.003	0.030	9
HCH – Hexachlorocyclohexane Isomers**						
alpha-HCH**	0.026	0.864	9	0.001	0.009	9
beta-HCH**	0.008	0.420	9	0.001	0.007	6
delta-HCH**	0.003	0.462	9	0.001	0.002	4
gamma-HCH/Lindane**	0.127	3.17	9	0.001	0.016	9
Imidcloprid	0.064	0.404	6	ND	ND	0
Mirex**	0.002	0.019	9	0.003	0.027	9
Phorate	0.006	0.043	4	ND	ND	0
Propoxur	0.049	0.162	6	ND	ND	0
Quintozene	0.005	0.194	8		0.004	1
Tebuconazol	0.099	2.92	8	0.027	0.125	3
Terbufos		0.018	1	ND	ND	0
Total-Cypermethrins	ND	ND	0		0.054	1

TABLE 6b.—Water quality guidelines and California Toxics Rule (CTR) water quality criteria for organic compounds used by the Regional Monitoring Program (RMP) in their water quality assessments (SFEI, 1997; SFEI, 2006; EPA, 2000). Criteria for organic compounds are listed on a total basis (dissolved + particulate).

	Aquatic Life, µg/L				**Human Health, µg/L (10^{-4} Risk for Carcinogens)**	
	Fresh Water		**Salt Water**		**Fresh Water**	**Salt and Fresh**
Analyte	**1-hour**	**4-day**	**1-hour**	**4-day**	**Water and Organisms**	**Organisms Only**
Alpha-HCH	-	-	-	-	0.0039	0.013
Acenaphthene	-	-	-	-	1200	2700
Anthracene	-	-	-	-	9600	110000
Benzo(a)anthracene	-	-	-	-	0.0044	0.049
Benzo(a)pyrene	-	-	-	-	0.0044	0.049
Benzo(b)fluoranthene	-	-	-	-	0.0044	0.049
Benzo(k)fluoranthene	-	-	-	-	0.0044	0.049
Beta-HCH	-	-	-	-	0.014	0.046
Chlordane	2.4	0.0043	0.09	0.004	0.00057	0.00059
Chlorpyrifos (4)	0.083	0.041	0.011	0.0056	-	-
Chrysene	-	-	-	-	0.0044	0.049
Diazinon (5)	-	-	-	-	.	0.04
Dibenz(a,h)anthracene	-	-	-	-	0.0044	0.049
Dieldrin	0.24	0.056	0.71	0.0019	0.00014	0.00014
Endrin	0.086	0.036	0.037	0.0023	0.76	0.81
Fluoranthene	-	-	-	-	300	370
Fluorene	-	-	-	-	1300	14000
Gamma-HCH	0.095	0.08	0.16	.	0.019	0.063
Heptachlor	0.52	0.0038	0.053	0.0036	0.00021	0.00021
Heptachlor Epoxide	0.52	0.0038	0.053	0.0036	0.0001	0.00011
Hexachlorobenzene	-	-	-	-	0.00075	0.00077
Indeno(1,2,3-cd)pyrene	-	-	-	-	0.0044	0.049
p,p'-DDD	-	-	-	-	0.00083	0.00084
p,p'-DDE	-	-	-	-	0.00059	0.00059
p,p'-DDT	1.1	0.001	0.13	0.001	0.00059	0.00059
Pyrene	-	-	-	-	960	11000
Mirex (5)	-	0.001	-	0.001	-	-
Total PAHs (6)	-	.	-	-	0.031	0.031
Total PCBs	-	0.014	-	0.03	0.00017	0.00017

(4) Chlorpyrifos and Mirex criteria from USEPA (1999). (5) Diazinon guideline is from California Department of Fish and Game (Menconi and Fox, 1994). (6) Total PAH guideline is from the footnote in the Basin Plan, 2004 (SFBRWQB, 2004). However, the current objective is 15 µg/L.

TABLE 6c.—List of persistent and bioconcentrating toxic organic compounds and their Soluble Threshold Limit Concentrations (STLC, in water) and Total Threshold Limit Concentrations (TTLC, in tissue) (State of California, 2005)

Substance	STLC mg/L	TTLC Wet Weight mg/kg
Aldrin	0.14	1.4
Chlordane	0.25	2.5
DDT-DDE-DDD	0.1	1
2,4-Dichlorophenoxyacetic acid (2,4-D)	10	100
Dieldrin	0.8	8
Dioxin (2,3,7,8-TCDD)	0.001	0.01
Endrin	0.02	0.2
Heptachlor	0.47	4.7
Kepone	2.1	21
Lead compounds, organic	na	13
Lindane	0.4	4
Methoxychlor	10	100
Mirex	2.1	21
Pentachlorophenol	1.7	17
Polychlorinated biphenyls (PCBs)	5	50
Toxaphene	0.5	5
Trichloroethylene	204	2,040
2,4,5-trichlorophenoxypropionic acid	1	10

HCH (hexachlorocyclohexane) isomers were also consistently observed in both dissolved and suspended composite samples with dissolved forms dominant. Dissolved Lindane, or gamma-HCH ranged from 0.127 to 3.17 ng/L, the highest concentrations we observed for the HCH isomers. Sum of HCH isomers ranged from 0.164 to 4.92 ng/L for dissolved and 0.004 to 0.034 ng/L for suspended. Maximum dissolved sum of HCHs in 2004–2005 were reported in the Central San Francisco Bay by the RMP at 0.402 ng/L (SFEI, 2006). Again, this suggests higher inland concentrations in the south Delta for persistent HCH compounds. While higher compared to the RMP data, all the HCH isomer concentrations we observed were well below the Table 6b water quality criteria.

Aldrin, Deildrin, Endrin, and Mirex were consistently detected in both dissolved and suspended samples for almost all samples (Endrin was found in 8 of 9 suspended composites). Only Dieldrin exceeded Table 6b water quality criteria. We observed that Dieldrin was mostly dissolved and ranged from 0.078 to 2.24 ng/L. The maximum concentration was greater than both the 0.14 ng/L Human Health Fresh Water criterium, and the 1.9 ng/L salt water 4-day Aquatic Life criterium. The RMP also reported maximum dissolved Dieldrin in their river samples at 0.082 ng/L, well below our maximum, and very near our minimum concentrations.

A final observation is that two other currently used agricultural chemicals were found in significant quantities: Dimethoate, and Disulfoton-Sulfone. Dimethoate was mostly dissolved (0 of 9 suspended detections) and detected 7 of 9 months from 0.064 to 26.7 ng/L. Disulfoton-sulfone was mostly dissolved, although 6 of 9 suspended samples were detected, and dissolved concentrations ranged from 0.589 to 18.5 ng/L.

Trace Elements Composite Data

Trace element data for unfiltered composite samples are summarized in Appendix 3, Table A3-3. Note that many of the Table A3-3 trace elements are reported below detection limits (BDL). This is mostly the result of the analytical method having detection limits appropriate for regulatory purposes (EPA method 6020 for ICP–MS) in the low µg/L range, rather than the ng/L range as seen for the organic compounds data. There might be a tendency by non-specialists to conclude that the BDL data in Table A3-3 suggest that there were no trace elements in TFCF waters, however, this would be erroneous. Each trace element composite sample experienced dilution factors up to 30 times, so concentrations could have been much higher than reported detection limits for short (< 1 month) periods of time.

We include data in Appendix 3, Table A3-4 (Craft *et al*., 2000a) that applied ultra-clean sampling procedures and optimized ICP–MS analysis that allowed much lower detection limits in the ng/L range. These data were from clean-room-filtered and -unfiltered discrete grab samples collected in October 1997. Fall represents the “off” season for agricultural chemical applications in the Central Valley when irrigation return flows and snowmelt runoff are at minima, temporary barriers are removed, and before winter rain events occur that tend to mobilize trace elements in storm runoff. Therefore, these data likely represent lower ranges for trace elements in TFCF waters, and are useful for Table A3-3 composite data comparisons. Table 7a summarizes recent maximum observed trace elements data from the RMP (SFEI, 2006), and Table 7b summarizes the water quality guidelines for dissolved trace elements (except Hg and Se, which are based on total recoverable concentrations) adopted by the RMP (SFEI, 2006). Note that the water quality criteria for Ag, Cd, Cu, Ni, Pb, and Zn are dependent on hardness in water (calcium plus magnesium expressed as mg/L as $CaCO_3$), and assume a hardness concentration of 100 mg/L.

Silver, Ag

Table A3-3 shows that Ag was below detection (< .0 µg/L, or 1,000 ng/L) in all composite samples; however, the 1997 data show that dissolved Ag ranged from 22.1 to 67.9 ng/L and suspended Ag from BDL to 32.1 ng/L. Table A3-4 data (Craft *et al*., 2000a) suggest that water near the TFCF and downstream of temporary barriers had around 40–50 percent suspended Ag. The RMP (SFEI, 2006) reported maximum total Ag in San Pablo Bay at 53.7 ng/L with only 12.9 percent in the dissolved phase. During 1996, the RMP reported a July maximum for Ag with a February river minimum below 1 ng/L (SFEI, 1997). While the RMP Fresh Water Aquatic Life 1-hour guideline is 3.4 µg/L (SFEI, 2006), the U.S. Department of Energy's Savannah River Nuclear Facility uses an Aquatic Toxicity Reference Value (TRV) for Ag of 12 ng/L (Jones *et al*., 1997; Savannah River Site, 2008). If the October 1997 data represent the lower range of Ag concentrations for the TFCF, then Ag may pose a chronic toxicity issue.

Arsenic, As

As was not detected in composites with a DL = 2 µg/L (2,000 ng/L); however, the 1997 Table A3-4 data suggest that As was indeed present around and below this DL. Table A3-4 dissolved As ranged from 1.80 to 2.14 µg/L (1,800 to 2,140 ng/L) with dissolved forms dominating total As. Given these lower ranges, it seems likely that As was above the 1999 DL of 2 µg/L but was diluted during composite sample collection. The RMP (SFEI, 2006) reported maximum As in the lower south San Francisco Bay stations with dissolved As of 3.94 µg/L and total As of 4.12 µg/L. As suggested by the Table 7b Fresh Water Aquatic Life guidelines, it appears that As at the TFCF was well below chronic and acute exposure levels for As.

Cadmium, Cd

Cd was not detected in the composite samples with DL = 1 µg/L, and Table A3-4 data from 1997 suggest that dissolved Cd was present in the range of 9.8 to 13.4 ng/L and suspended Cd ranged from 0.0 to 5.8 ng/L during the fall. These values were well below the maxima reported in the central San Francisco Bay samples by the RMP (SFEI, 2006), with total Cd of 153 ng/L and dissolved Cd of 94 ng/L. The 1997 RMP data (SFEI, 1997) for river samples reported dissolved Cd around 5–10 ng/L and total Cd around 20 ng/L. Considering dilution from composite sampling and higher reported Cd concentrations in the San Francisco Bay and Estuary it is likely that Cd was higher during the irrigation season near the TFCF, but probably not above the 660 ng/L TRV (EPA, 1992; Savannah River Site, 2008).

Chromium, Cr

Cr was detected in all composite samples with total concentrations ranging from 3.7 to 8.5 µg/L. The ultramafic rock in the Central Valley watershed is thought to account for naturally enriched concentrations of Cr (Hornberger *et al*., 1999). Maximum total Cr was observed for the August composite sample. These data compare closely to the 1996 RMP total Cr data (SFEI, 1997) where river samples ranged from 2 to 9 µg/L. In the October 1997 discrete samples, total Cr ranged from 1.93 to 2.23 µg/L with the dissolved form dominant. Old River suspended Cr was not detected, and suspended concentrations ranged from 16.2 to 23.4 percent elsewhere near the TFCF.

Copper, Cu

Cu was observed in all composite samples ranging from a low of 3.9 µg/L in November to a high of 7.0 µg/L in July. The October 1997 discrete samples showed total Cu ranging from 1.43 to 2.08 µg/L, with around 30 percent suspended for samples not in the Old River. The RMP reported maximum 2004 total Cu in San Pablo Bay of 7.0 µg/L (SFEI, 2006) and unfiltered Cu in river samples ranged from around 2.0 to 3.5 µg/L (SFEI, 1997). Maximum RMP 1996 river Cu concentrations were reported for February samples with lowest concentrations in April. If the higher composite sample concentrations reported here are valid, Cu may have exceeded the Table 7b 4-day Fresh Water Aquatic Life standard of 9.0 µg/L. Any future investigations in the south Delta should consider discrete sampling at daily or weekly frequency to establish when Cu concentrations exceed water quality guidelines.

Mercury, Hg, and Methylmercury, Me-Hg

Total Hg was slightly above the DL of 10 ng/L for the July, August, and September composite samples, with detections ranging from 12.5 to 15 ng/L. Maximum total Hg was reported by the RMP in San Pablo Bay at 45 ng/L, and the Table 7b 4-day Fresh Water Aquatic Life guideline is 25 ng/L. Short-term concentrations higher than 25 ng/L may have been possible given the summer composite sample detections. Table A3-4 October 1997 dissolved Hg ranged from 0.71 to 1.07 ng/L with suspended Hg from 1.26 ng/L to 3.12 ng/L. The 1997 data suggest that suspended Hg ranged from 50–80 percent of total near the TFCF. Me-Hg concentrations were well below 0.1 ng/L and ranged from 9 to 27 pg/L for dissolved, and from 6 to 54 pg/L for suspended. Suspended Me-Hg ranged from 18 to 79 percent of total. The October 1997 samples were all below, but in the range of the maximum RMP reported dissolved total Hg in Suisun Bay of 5 ng/L. The Hg data from this study, ongoing fish consumption advisories and reported Hg elevated in south Delta fish (Bennett *et al*., 2001; Gassel *et al*., 2007) suggest that bioaccumulative concentrations of Hg are likely present in TFCF waters during the summer months, and perhaps other times of the year.

Nickel, Ni

Ni was detected in all composite samples ranging from 3.50 µg/L in November, up to 29.0 µg/L in August. Ni, like Cr and V, is naturally enriched in Central Valley waters (Hornberger *et al*., 1999). The October 1997 discrete samples showed that Ni is almost all suspended, at least in the fall, and showed the highest concentrations ranging from 281 to 431 ng/L near the TFCF. The composite sample for October suggested a much higher average concentration around 4.4 µg/L. The RMP (SFEI, 2006) reported maximum total Ni in San Pablo Bay at 14.7 µg/L, and maximum dissolved Ni at 3.01 µg/L in the lower south San Francisco Bay, suggesting greater dissolved Ni in salt water. The 1996 RMP data for river samples (SFEI, 1997) reported total Ni from 1 to 10 µg/L and dissolved Ni from 1 to 2 µg/L.

Lead, Pb

Pb was detected in all composite samples except November and ranged from 1.0 –1.5 µg/L; however, these data were very close to the 1.0 µg/L DL, and should be considered semi-quantitative. The 1997 Table A3-4 discrete samples showed total Pb ranging from 17.3 ng/L (in the Old River) up to 343 ng/L (at the Grant Line-Old River confluence) with almost all Pb in the suspended phase. The discrete sample data were similar to 1996 river samples RMP data (SFEI, 1997) with dissolved Pb ranging from 50 to 100 ng/L and unfiltered Pb from 500 to 1,000 ng/L. While the composite data here may suggest Pb exceeded the TRV of 1.32 µg/L (EPA, 1992), other reported data are not corroborative and do not suggest a chronic toxicity issue with Pb near the TFCF.

Selenium, Se

Se was not detected in composite samples with a DL = 2 µg/L; however, the October 1997 data suggested that Se was present almost completely in the dissolved phase ranging from 486 to 746 ng/L. Concentrations were likely higher in the TFCF region of the south Delta during the irrigation season when salinized marine sedimentary soils in the SJR basin were flooded. The RMP reported 1997 river samples with dissolved Se in the range of 100 ng/L (SFEI, 1997) and maximum dissolved Se in rivers in 2004 reported at 446 ng/L (SFEI, 2006). The lack of detection of Se in composite samples was likely caused by dilution and relative insensitivity of the ICP–MS method for this element.

Uranium, U

U is not monitored by the RMP and was mostly undetected (DL = 5 µg/L) in the composite samples. However, the October 1997 discrete samples showed fairly high concentrations of mostly dissolved U ranging from 7.34–10.2 µg/L. Perhaps observed elevated U in TFCF waters was a byproduct of the natural geochemistry of the marine shale Monterey Formation in the southern SJR basin where U is enriched (6 times average) along with Se relative to average shale deposit concentrations (Piper and Isaacs, 1995). The 1997 data also exceeded the TRV of 2.3 µg/L recommended for U (Suter and Tsao, 1996; EPA, 1996d; Savannah River Site, 2008), suggesting that U may represent a chronic stressor to aquatic life near the TFCF.

Zinc, Zn

Zn was observed in all unfiltered composite samples ranging from 9.00–24.0 µg/L. The October 1997 discrete samples suggested that unfiltered Zn ranged from 0.680 to 1.81 µg/L, with suspended Zn near the TFCF around 65–70 percent of total. The October 1999 composite sample Zn of 9.00 µg/L seemed high relative to the discrete sample October 1997 measurements. The composite data were also somewhat higher compared to 1996 RMP rivers unfiltered Zn that ranged from 2 to 8 µg/L, with minimum concentrations reported in April (SFEI, 1997). The 1996 RMP data suggested a snowmelt associated runoff dilution cycle with Zn concentrations. Regardless of data corroboration, a Fresh Water Aquatic Life guideline of 120 µg/L does not suggest that Zn represented a toxicity issue for the TFCF.

Other Elements

Though not included on the list of COC elements, there were data worth noting for several other elements from the composite samples and the October 1997 discrete samples. Total Al, Fe, and Mn observed in the composite samples were fairly high and likely associated with suspended inorganic aluminosilicates. Fe and Mn oxyhydrates are known to adsorb onto these suspended materials (Stumm and Morgan, 1996). Composite sample Al ranged from 1,500 to 2,800 µg/L, Fe from 1,600 to 2,900 µg/L, and Mn from 72.0 to 120 µg/L. The 1997 discrete samples showed much lower concentrations of these elements with total Al ranging from 141 to 329 µg/L, total Fe ranging from 116 to 389 µg/L, and total Mn ranging from 55.7 to 66.9 µg/L. These 1997 discrete data compare to October 1999 composite Al of 1,600 µg/L and Fe of 1,900 µg/L. While the composite Mn data do compare with other sources, the composite Al and Fe appeared to be an order of magnitude higher compared to the discrete samples. This discrepancy suggests that contamination may have biased the composite trace element samples (fugitive dust typically contains Fe and Al), or that perhaps suspended sediments were higher during 1999.

Vanadium (V) was only detected in the August composite sample, but was observed in the 1997 discrete samples with dissolved concentrations ranging from 3.26 to 4.62 µg/L and suspended V from 0 to 1.06 µg/L. These data, along with higher levels of Cr and Ni, corroborate observations by Hornberger *et al*., (1999) regarding the higher crustal levels of these metals in the ultramafic rock of the Central Valley watershed.

CONCLUSIONS AND RECOMMENDATIONS

Organic Compounds Data

The filtration and SPE using an automated sampling pump successfully collected composite samples that provided data on a broad range of organic compounds at the TFCF.

The HRGC–LRMS open scan data showed that petroleum derived contaminants, including alkanes, PAHs, surfactants, and plasticizers, were common background contaminants in TFCF waters. These contaminants ranged in the ng/L to low µg/L concentration range and were more frequently observed during winter months.

The use of SPE, preconcentration associated with composite sampling, and the application of sensitive HRGC–HRMS and LC–MS/MS analyses allowed for very low quantitative detection limits, often in the tens of pg/L. These data showed that both locally and regionally applied agricultural chemicals and persistent chemicals were present in TFCF waters most of the time during the sampling period, and almost all detected COCs and other current use pesticides were found in the dissolved phase. Of the COC agricultural chemicals analyzed, only one (Aldicarb) was not detected, and many were detected in all, or almost all, months of sampling. Detected average concentrations for the COC list analytes ranged from tens of pg/L to over 100 ng/L, and Metolachlor was observed with the highest overall concentrations. Some agricultural compounds may have been present in

TFCF waters at concentrations as high as 1,000 ng/L for short periods of time. Other non-COC agricultural chemicals were also detected in similar concentration ranges to the COC analytes. Some of these compounds were applied near the TFCF, and others elsewhere in the SJR watershed.

There were no clear correlations between localized chemical applications from the 1997 data summary and the 1999 composite sample data. The lack of correlation is thought be caused by the influence of basin-wide chemical applications, and perhaps changes in local applications during 1999. These results suggest a re-evaluation of the COC analytes list using chemical application data from a much larger area in the south Delta, and including evaluation of more recent monitoring data.

Persistent chemicals such as Aldrin, Chlordane isomers and metabolites, Endrin, Lindane and other HCH isomers, and Mirex were consistently detected in the composite samples in the < 10 ng/L to pg/L range of concentration. These data, along with recent reports of wildlife tissue concentrations of persistent chemicals (Greenfield *et al*., 2003; Davis *et al*., 2006; Fairey *et al*., 1997; Ohlendorf and Miller, 1984), show that banned and restricted organic compounds remain a concern for water quality and fishery health in the Delta and San Francisco Bay.

Trace Element Data

The unfiltered composite trace element samples showed that Cr, Ni, and V were elevated above background averages as reported elsewhere, but not at concentrations that would affect water quality. Elevated composite Cr, Ni, and V were also corroborated by data from the October 1997 discrete samples. The concentrations of Cu and Zn in the composite samples were in the same concentration range, but higher than those reported by the RMP (SFEI, 1997; SFEI, 2006), and almost all composite detections were higher than the discrete samples collected in October 1997. Elevated Al, Fe, and Zn in unfiltered composites suggest either very elevated suspended particulates in 1999 TFCF waters, or possible contamination artifacts.

Based on an assessment of both the 1999 composite samples and the October 1997 discrete sample results, the only elements suggesting water quality concern and further investigation in the TFCF or south Delta are Ag, Hg, Cu, and U. Ag was not detected in composites, but was elevated in the October 1997 discrete samples relative to the TRV of 12 ng/L. Hg is a known problem Delta-wide based on elevated tissue concentrations, and while the October 1997 discrete sample data were not indicative of regulatory exceedance, the composite data observed during summer months suggest further study. Cu seemed to be borderline, but dissolved concentrations may exceed the California 4-day Fresh Water Aquatic Life guideline of 9.0 µg/L. U was only detected in one composite sample above a 5 µg/L DL, but we noted fairly elevated concentrations in all October 1997 discrete samples in the 7–10 µg/L range. This finding suggests that future trace element sampling should confirm and establish seasonal concentration of U in south Delta waters.

Recommendations for Future Studies

General Composite Sampling

Given the power interruption issues that affected collection of samples, we recommend that any future composite sampling effort, for either organic compounds or trace elements, use an uninterruptable power supply as a backup, or that solar powered pumps be utilized. We also suggest that a depth-integrating sample inlet be installed near mid-channel to improve sample representativeness of the entire channel.

Organic Sampling and Analyses

If future composite sampling for organic analyses is performed at the TFCF, we recommend that a full year of samples be collected to fully cover the dormant application and rainy season from February through May. Organic analytes should continue to utilize the highly sensitive HRGC–HRMS and LC–MS/MS for current use pesticides and carbamates, chlorinated compounds, and additional target analytes such as common PBDEs. Consideration should also be given to pumping larger volumes for composites to enhance preconcentration and detection of compounds that were below detection in this study, but were likely present in TFCF waters.

Trace Element Sampling and Analyses

Comparison of the unfiltered composite sample data with the discrete samples collected in October 1997 suggested that future sampling for trace elements at the TFCF should use more sensitive methods for ICP–MS analysis with detection limits for Ag, As, Cd, Cu, Hg, Ni, Pb, Se, U, and Zn in the low ng/L range. EPA Method 1638 (EPA, 1996b) or a method that exceeds 1638 performance should be used for higher sensitivity and lower detection ICP–MS analysis. EPA Method 6020 (EPA, 2008), used for composite samples in this study, should *not* be used. Hg should be analyzed using EPA Method 1631 (Bloom, 1996; EPA, 1996c) and Me-Hg using the method of Bloom (1989) employing aqueous phase ethylation.

Because of the inherent dilution from compositing and lack of preconcentration, we recommend that composite sampling be replaced with discrete sampling using ultra-clean field sampling procedures (EPA, 1996a) and contamination reduction protocols. Lab selection should be a careful process and significant experience with ultra-trace analytical methods and adequate facilities are essential. A minimum schedule should include monthly collection at mid-month during mid-tide, but biweekly sampling would establish a better baseline data set of reliable ultra-trace data. Discrete samples should be collected from a single station in the channel behind the trash rack at the TFCF using a depth integrating inlet. Samples should only be filtered and preserved under clean room or semi-clean room conditions by the analysis lab, and field blanks, random duplicates, and spikes should included as QA blind samples.

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APPENDICES

APPENDIX 1

Instrumental Conditions and Standards Used for HRGC–HRMS and LC–MS/MS Organic Quantitative Analyses

TABLE A1-1.—High-resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS) conditions for multiresidue pesticides (organophospohrus, chlorinated compounds, triazines, and pyrethroids) analysis.

GC Temperature (T) Program	
Initial T (°C)	50
Hold time (min)	1.0
Rate (°C/min)	10
T 2 (°C)	180
Hold time (min)	0
Rate (°C/min)	1.5
T 3 (°C)	200
Hold time (min)	2
Rate (°C/min)	6.0
T 4 (°C)	295
Hold time (min)	1

General GC Conditions	
Injector Temp (°C)	220
Injector	Split/Splitless, 2 min
Carrier Gas	Helium, 200 kpa (new column) Variable (dependent on column length)

MS Conditions	
Source Temp (°C)	280
Electron Energy (eV)	~ 35
Trap Current (µA)	500–900
Mass Resolution	8000
Detector Voltage (V)	340–400

TABLE A1-2.—Analytes and quantification criteria for the high-resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS) multiresidue quantitative analyses for chlorinated, organophosphorus, triazine, and pyrethroid pesticides.

Analyte Name	Quantified Against Labeled Standard	Typical Retention Time	Mass1	Mass2	m1/m2 Ratio	Ion Ratio Tolerance Percentage
Methamidophos	^{13}C-PCB-52	8:55	93.9642	94.9721	N/A	35
Tecnazene	^{13}C-HCB	14:38	258.8761	260.8732	0.78	35
Phorate	^{13}C-PCB-52	16:05	260.0128	262.0086	6.92	35
HCB	^{13}C-HCB	15:49	283.8102	285.8072	1.25	25
alpha-HCH	^{13}C-gamma-HCH	16:29	218.9116	220.9086	2.08	25
Desethylatrazine	^{13}C-Atrazine	16:47	172.0390	174.0360	3.11	35
Terbufos	^{13}C-PCB-52	17:04	232.9696		N/A	N/A
Quintozene	^{13}C-HCB	17:32	236.8413	238.8384	1.56	35
Diazinon-Oxon	d$_{10}$-Diazinon	17:46	273.1004	288.1239	N/A	35
Diazinon	d$_{10}$-Diazinon	17:36	276.0698	304.1011	N/A	35
Simazine	^{13}C-Atrazine	18:15	201.0781	203.0752	3.1	35
Atrazine	^{13}C-Atrazine	17:54	215.0938	217.0908	3.08	35
gamma-HCH	^{13}C-gamma-HCH	18:09	218.9116	220.9086	2.08	25
Disulfoton	^{13}C-PCB-52	18:26	274.0285	275.0318	N/A	35
Fonofos	^{13}C-Fonofos	18:18	246.0302	247.0336	N/A	35
Dimethoate	^{13}C-PCB-52	19:24	228.9996		N/A	N/A
Heptachlor	^{13}C-Heptachlor	19:30	271.8102	273.8072	1.25	25
beta-HCH	^{13}C-beta-HCH	19:22	218.9116	220.9086	2.08	25
delta-HCH	^{13}C-delta-HCH	20:55	218.9116	220.9086	2.08	25
Chlorothalonil.	^{13}C-PCB-52	21:00	263.8816	265.8786	0.78	35
Chlorpyriphos-Methyl	^{13}C-PCB-52	21:17	285.9261	287.9232	1.44	35
Aldrin	^{13}C-Aldrin	21:08	262.8569	264.854	1.56	25
Parathion-Methyl	^{13}C-PCB-52	22:19	263.0017	264.0051	N/A	35
Ametryn	^{13}C-PCB-52	22:31	227.1205	228.1238	N/A	35
Pirimiphos-Methyl	^{13}C-PCB-52	22:32	276.0572	290.0728	N/A	35
Metribuzin	^{13}C-PCB-52	22:56	198.0701	199.0735	N/A	35
Dacthal	^{13}C-PCB-52	23:08	298.8836	300.8807	0.780	35
Octachlorostyrene	^{13}C-Aldrin	23:07	270.8443	272.8413	0.630	25
Chlorpyriphos	^{13}C-PCB-52	23:23	313.9574	315.9545	1.44	35
Fenitrothion	^{13}C-PCB-52	23:57	260.0146	277.0174	N/A	35
Malathion	^{13}C-PCB-52	24:01	283.9942	285.0020	N/A	35
Oxychlordane	^{13}C-Oxychlordane	24:01	262.8569	264.8540	1.56	25
Parathion-Ethyl	^{13}C-PCB-52	24:16	291.0330	292.0364	N/A	35
Chlorpyriphos-Oxon	^{13}C-PCB-52	24:18	269.9490	271.9462	1.54	35
Heptachlor-Epoxide	^{13}C$_{12}$-Heptachlor-Epoxide	25:04	262.8569	264.8540	1.56	25
t-Chlordane	^{13}C-t-Chlordane	26:31	262.8569	264.8540	1.56	25
t-Nonachlor	^{13}C-t-Nonachlor	26:40	262.8569	264.8540	1.56	25
c-Chlordane	^{13}C-t-Chlordane	27:32	262.8569	264.8540	1.56	25
Alpha-Endosulphan	^{13}C$_9$-alpha-Endosulphan	27:41	262.8569	264.8540	1.56	25
Dieldrin	^{13}C-Dieldrin	30:22	262.8569	264.8540	1.56	25
Cyanazine	^{13}C-PCB-52	28:04	240.0890	242.0861	3.06	35
o,p-DDE	^{13}C-p,p-DDE	27:55	246.0003	247.9974	1.56	25
p,p-DDE	^{13}C-p,p-DDE	30:27	246.0003	247.9974	1.56	25
Captan	^{13}C-PCB-52	31:15	263.9653	265.9623	1.44	35
Disulfoton-Sulfone.	^{13}C-PCB-52	32:40	213.0173	214.0251	N/A	35
o,p-DDD	^{13}C-o,p-DDT	32:12	235.0081	237.0052	1.56	25

TABLE A1-2 (continued)

Analyte Name	**Quantified Against Labeled Standard**	**Typical Retention Time**	**Mass1**	**Mass2**	**m1/m2 Ratio**	**Ion Ratio Tolerance Percentage**
Perthane	^{13}C-PCB-52	32:52	223.1487	224.1520	N/A	35
Endrin	^{13}C$_{12}$-Endrin	32:46	262.8569	264.8540	1.56	25
c-Nonachlor	^{13}C-c-Nonachlor	33:11	262.8569	264.8540	1.56	25
Ethion	^{13}C-PCB-52	34:39	232.9695		N/A	N/A
beta-Endosulphan	^{13}C$_9$-beta-Endosulphan	34:25	264.8540	262.8569	0.64	25
Endosulphan-Sulphate	^{13}C$_9$-beta-Endosulphan	36:48	264.8540	262.8569	0.64	25
o,p-DDT	^{13}C-o,p-DDT	33:51	235.0081	237.0052	1.56	25
p,p-DDD	^{13}C-p,p-DDT	34:24	235.0081	237.0052	1.56	25
p,p-DDT	^{13}C-p,p-DDT	35:46	235.0081	237.0052	1.56	25
Mirex	^{13}C-Mirex	39:23	236.8413	238.8384	1.56	25
Hexazinone	^{13}C-PCB-52	39:31	171.0882	172.0916	N/A	35
Methoxychlor	^{13}C$_{12}$-Methoxychlor	39:38	227.1072	228.1106	N/A	35
Endrin-Ketone	^{13}C$_{12}$-Endrin	39:40	247.8521	249.8491	0.63	25
Phosmet	^{13}C-PCB-52	40:49	160.0399	161.0432	N/A	35
Azinphos-Methyl	d$_6$-Azinphos-Methyl	42:32	160.0511	161.0544	N/A	35
Permethrins-Peak_1	^{13}C-Permethrins-Peak_1	41:58	183.0810	184.0843	N/A	35
Permethrins-Peak_2	^{13}C-Permethrins-Peak_2	42:16	183.0810	184.0843	N/A	35
Cypermethrins-Peak_1	^{13}C-Permethrins-Peak_1+2	43:46	163.0081	165.0052	1.56	35
Cypermethrins-Peak_2	^{13}C-Permethrins-Peak_1+2	43:59	163.0081	165.0052	1.56	35
Cypermethrins-Peak_3	^{13}C-Permethrins-Peak_1+2	44:06	163.0081	165.0052	1.56	35
^{13}C-HCB	^{13}C-PCB-52	15:48	289.8303	291.8273	1.25	25
d$_{10}$-Diazinon	^{13}C-PCB-52	17:25	282.1074	314.1638	N/A	35
^{13}C-Atrazine	^{13}C-PCB-52	17:54	218.1038	220.1009	3.08	35
^{13}C-gamma-HCH	^{13}C-PCB-52	18:08	222.9346	224.9317	0.77	25
^{13}C-Fonofos	^{13}C-PCB-52	18:17	252.0503	253.0537	N/A	35
^{13}C-Heptachlor	^{13}C-PCB-52	19:28	276.8269	278.8240	1.24	25
^{13}C-beta-HCH	^{13}C-PCB-52	19:21	222.9346	224.9317	0.77	25
^{13}C-delta-HCH	^{13}C-PCB-52	20:53	222.9346	224.9317	0.77	25
^{13}C-Aldrin	^{13}C-PCB-52	21:05	269.8804	271.8775	1.56	25
^{13}C-Oxychlordane	^{13}C-PCB-52	23:59	269.8804	271.8775	1.56	25
^{13}C$_{12}$-Heptachlor-Epoxide	^{13}C-PCB-52	25:01	269.8804	271.8775	1.56	25
^{13}C-t-Chlordane	^{13}C-PCB-52	26:29	269.8804	271.8775	1.56	25
^{13}C-t-Nonachlor	^{13}C-PCB-52	26:38	269.8804	271.8775	1.56	25
^{13}C$_9$-alpha-Endosulphan	^{13}C-PCB-52	27:39	269.8804	271.8775	1.56	25
^{13}C-Dieldrin	^{13}C-PCB-52	30:19	269.8804	271.8775	1.56	25
^{13}C-p,p-DDE	^{13}C-PCB-52	30:25	258.0406	260.0376	1.56	25
^{13}C$_{12}$-Endrin	^{13}C-PCB-52	32:43	269.8804	271.8775	1.56	25
^{13}C-c-Nonachlor	^{13}C-PCB-52	33:09	269.8804	271.8775	1.56	25
^{13}C$_9$-beta-Endosulphan	^{13}C-PCB-52	34:23	269.8804	271.8775	1.56	25
^{13}C-o,p-DDT	^{13}C-PCB-52	33:49	247.0484	249.0454	1.56	25
^{13}C-p,p-DDT	^{13}C-PCB-52	35:46	247.0484	249.0454	1.56	25
^{13}C-Mirex	^{13}C-PCB-52	39:22	241.8581	243.8551	1.56	25
^{13}C$_{12}$-Methoxychlor	^{13}C-PCB-52	39:37	239.1475	240.1508	N/A	35
d$_6$-Azinphos-Methyl	^{13}C-PCB-52	42:27	160.0511	161.0544	N/A	35
^{13}C-Permethrins-Peak_1	^{13}C-PCB-52	41:58	189.1011	190.1045	N/A	35
^{13}C-Permethrins-Peak_2	^{13}C-PCB-52	42:16	189.1011	190.1045	N/A	35
^{13}C-PCB-52			301.9626	303.9597	0.78	25

TABLE A1-3.—Calibration standards in ng/mL used for the high-resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS) multiresidue quantitative analyses for chlorinated, organophosphorus, triazine, and pyrethroid pesticides.

Compound	**Level AA**[1]	**Level A**	**Level B**	**Level C**	**Level D**	**Level E**
Methamidophos	4	10	30	80	200	400
Tecnazene	2	5	15	40	100	200
Phorate	4	10	30	80	200	400
Hexachlorobenzene	1.6	4	12	32	80	160
HCH, alpha	3.2	8	24	64	160	320
Desethylatrazine	2	5	15	40	100	200
Terbufos	1	2.5	7.5	20	50	100
Quintozene	4	10	30	80	200	400
Diazinon-Oxon	4	10	30	80	200	400
Diazinon	4	10	30	80	200	400
Simazine	4	10	30	80	200	400
Atrazine	4	10	30	80	200	400
HCH, gamma	3.2	8	24	64	160	320
Disulfoton	20	50	150	400	1000	2000
Fonofos (Dyfonate)	4	10	30	80	200	400
Dimethoate	20	50	150	400	1000	2000
Heptachlor	1.6	4	12	32	80	160
HCH, beta	3.2	8	24	64	160	320
HCH, delta	3.2	8	24	64	160	320
Chlorothalonil	2	5	15	40	100	200
Chlorpyriphos-Methyl	5	12.5	37.5	100	250	500
Aldrin	3.2	8	24	64	160	320
Parathion-Methyl	12	30	90	240	600	1200
Ametryn	4	10	30	80	200	400
Pirimphos-Methyl	4	10	30	80	200	400
Metribuzin	1	2.5	7.5	20	50	100
Dacthal	1	2.5	7.5	20	50	100
Octachlorostyrene	1.6	4	12	32	80	160
Chlorpyriphos (Dursban)	4	10	30	80	200	400
Fenitrothion	4	10	30	80	200	400
Malathion	52	130	390	1040	2600	5200
Oxychlordane	3.2	8	24	64	160	320
Parathion-Ethyl (Parathion)	4	10	30	80	200	400
Chlorpyriphos-Oxon	4	10	30	80	200	400
Heptachlor Epoxide	1.6	4	12	32	80	160
Chlordane, gamma (trans)	1.6	4	12	32	80	160
Nonachlor, trans-	1.6	4	12	32	80	160
Chlordane, alpha (cis)	1.6	4	12	32	80	160
alpha-Endosulphan	1.6	4	12	32	80	160
Dieldrin	1.6	4	12	32	80	160
Cyanazine	4	10	30	80	200	400

TABLE A1-3 (continued)

Compound	**Level AA**[1]	**Level A**	**Level B**	**Level C**	**Level D**	**Level E**
2,4'-DDE	1.6	4	12	32	80	160
4,4'-DDE	1.6	4	12	32	80	160
Captan	10	25	75	200	500	1000
Disulfoton Sulfone	0.32	0.8	2.4	6.4	16	32
2,4'-DDD	1.6	4	12	32	80	160
Perthane	1.6	4	12	32	80	160
Endrin	1.6	4	12	32	80	160
Nonachlor, cis-	1.6	4	12	32	80	160
Ethion	0.8	2	6	16	40	80
beta-Endosulphan	1.6	4	12	32	80	160
Endosulphan Sulphate	1.6	4	12	32	80	160
2,4'-DDT	1.6	4	12	32	80	160
4,4'-DDD	1.6	4	12	32	80	160
4,4'-DDT	1.6	4	12	32	80	160
Mirex	1.6	4	12	32	80	160
Hexazinone	5	12.5	37.5	100	250	500
Methoxychlor	1.6	4	12	32	80	160
Endrin Ketone	1.6	4	12	32	80	160
Phosmet (Imidan)	10	25	75	200	500	1000
Azinphos-Methyl	5	12.5	37.5	100	250	500
Permethrins	2	5	15	40	100	200
Cypermethrins	10	25	75	200	500	1000
^{13}C-HCB	86	86	86	86	86	86
D_{10}-Diazinon	77	77	77	77	77	77
^{13}C-Atrazine	77	77	77	77	77	77
^{13}C-gamma-HCH	130	130	130	130	130	130
^{13}C-Fonofos	77	77	77	77	77	77
^{13}C-Heptachlor	73	73	73	73	73	73
^{13}C-beta-HCH	77	77	77	77	77	77
^{13}C-delta-HCH	77	77	77	77	77	77
^{13}C-Aldrin	77	77	77	77	77	77
^{13}C-Oxychlordane	77	77	77	77	77	77
^{13}C-Heptachlor-Epoxide	79	79	79	79	79	79
^{13}C-t-Chlordane	77	77	77	77	77	77
^{13}C-t-Nonachlor	77	77	77	77	77	77
$^{13}C_9$-alpha-Endosulphan	77	77	77	77	77	77
^{13}C-Dieldrin	77	77	77	77	77	77
^{13}C-p,p-DDE	77	77	77	77	77	77
$^{13}C_{12}$-Endrin	77	77	77	77	77	77
^{13}C-c-Nonachlor	77	77	77	77	77	77

TABLE A1-3 (continued)

Compound	**Level AA**[1]	**Level A**	**Level B**	**Level C**	**Level D**	**Level E**
^{13}C-o,p-DDT	77	77	77	77	77	77
^{13}C-p,p-DDT	77	77	77	77	77	77
^{13}C-Mirex	84	84	84	84	84	84
$^{13}C_{12}$-Methoxychlor	77	77	77	77	77	77
D_6-Azinphos-Methyl	77	77	77	77	77	77
^{13}C-Permethrins	78	78	78	78	78	78
Recovery Standard						
$^{13}C_{12}$-PCB 52	80	80	80	80	80	80

[1] The level AA calibration standard solution is only used with “Clean Water” and “Clean Solids” samples.

TABLE A1-4.—High-resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS) chromatographic conditions for organonitrogen pesticides analysis.

GC Temperature (T) Program		**General GC Conditions**	
Initial T (°C)	50	Injector Temp (°C)	260
Hold time (min)	0	Injector	Split/Splitless, 2 min
Rate (°C/min)	20	Carrier Gas	Helium, 200 kpa (new column) Variable (dependent on column length)
T 2 (°C)	140		
Hold time (min)	0		
Rate (°C/min)	2	**MS Conditions**	
T 3 (°C)	150	Source Temp (°C)	280
Hold time (min)	2	Electron Energy (eV)	~ 35
Rate (°C/min)	12	Trap Current (µA)	500–900
T 4 (°C)	300	Mass Resolution	8000
Hold time (min)	1.0	Detector Voltage (V)	340–400

TABLE A1-5.—Analytes and quantification criteria for the high-resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS) quantitative analyses for organonitrogen pesticides.

Analyte Name	Quantified Against Labeled Standard	Typical Retention Time	Mass1	Mass2	m1/m2 ratio	Ion Ratio Tolerance Percentage
Butylate	^{13}C-PCB-52	6:57	156.1388	174.0953	N/A	35
Ethalfluralin	^{13}C-PCB-52	11:43	316.0909	276.0596	N/A	35
Trifluralin	^{13}C-PCB-52	11:51	264.0232	306.0702	N/A	35
Triallate	^{13}C-PCB-52	16:06	268.0330	270.0300	1.44	35
Dimethenamid	^{13}C-PCB-52	17:23	230.0406	232.0377	2.68	35
Alachlor	^{13}C-Alachlor	17:34	160.1126	188.1074	N/A	35
Methoprene	^{13}C-PCB-52	17:56	191.1800	192.1833	N/A	35
Butralin	^{13}C-PCB-52	18:08	266.1141	267.1174	N/A	35
Metolachlor	^{13}C-Metolachlor	18:16	162.1283	163.1316	N/A	35
Flufenacet	^{13}C-PCB-52	18:18	151.0797	210.9789	N/A	35
Linuron	d_6-Linuron	18:28	159.9721	161.9692	1.56	35
Pendimethalin	^{13}C-PCB-52	19:02	252.0984	253.1018	N/A	35
Flutrialfol	^{13}C-PCB-52	20:42	219.0621	220.0655	N/A	35
Tebuconazol	^{13}C-PCB-52	22:09	250.0747	252.0718	3.02	35
^{13}C-Alachlor	^{13}C-PCB-52	17:34	166.1328	194.1277	N/A	35
^{13}C-Metolachlor	^{13}C-PCB-52	18:16	168.1484	169.1518	N/A	35
d_6-Linuron	^{13}C-PCB-52	18:24	159.9721	161.9692	1.56	35
^{13}C-PCB-52		17:57	232.0249	234.0220	1.56	25

TABLE A1-6.—Nominal concentration of calibration standard solutions in ng/mL for high-resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS) analyses for organonitrogen pesticides.

Compound	**A-Cal** **ng/ml**	**B-Cal** **ng/ml**	**C-Cal** **ng/ml**	**D-Cal** **ng/ml**	**E-Cal** **ng/ml**
Butylate	5	12	32	80	200
Ethalfluralin	55	132	352	880	2200
Trifluralin	5	12	32	80	200
Triallate	5	12	32	80	200
Dimethenamid	5	12	32	80	200
Alachlor	12	28.8	76.8	192	480
Methoprene	25	60	160	400	1000
Butralin	10	24	64	160	400
Flufenacet	8	19.2	51.2	128	320
Metolachlor	2.5	6	16	40	100
Linuron	20	48	128	320	800
Pendimethalin	40	96	256	640	1600
Flutriafol	50	120	320	800	2000
Tebuconazol	25	60	160	400	1000
Quantification standards					
^{13}C-Alachlor	82	82	82	82	82
^{13}C-Metolachlor	80	80	80	80	80
D_6-Linuron	320	320	320	320	320
Recovery standard					
$^{13}C_{12}$ PCB 52	80	80	80	80	80

TABLE A1-7.—Chromatographic and mass spectrometry (MS) conditions for carbamates analysis by liquid chromatograph–tandem mass spectrometry (LC–MS/MS).

LC Gradient Program		**LC Flow Rate Program**		**General LC Conditions**	
Time (min)	**Flow mixture**[1]	**Flow, mL/min**	**Gradient Curve**		
0	80A 20B	0.15	1	Column Temp (°C)	Ambiant
1.5	50A 50B	0.15	6	Flow Rate (mL/min)	0.15 –0.25
9	100B	0.20	10	Max Pressure (bar)	300
15	100B	0.25	6	**MS Conditions**	
16	80A 20B	0.15	6	Source Temp (°C)	120
20	80A 20B	0.15	1	Desolvation Temp (°C)	325

[1] Eluent A = 0.1 Formic acid buffer in high-performance liquid chromatography (HPLC) water, Eluent B = Acetonitrile

Table A1-8.— Positive electrospray ionization–tandem mass spectrometry ([+]ESI-MS/MS) Parameters for target analytes and labeled standards used in liquid chromatography–tandem mass spectrometry (LC–MS/MS) analysis for carbamates.

Analytes	**RT, min**	**Parent ion (m/z)**	**Daughter ion (m/z)**	**Cone voltage (V)**	**Collision energy (eV)**	**[M-H]+/ [M-NH4]+**	**Quantification Standard**
Aldicarb	8.51	116	89	50	7	[Frag]>[Frag]	$^{13}C_3$-Atrazine
Aldicarb Sulfone	5.08	223	86	21	12	$[M-H]^+$	$^{13}C_3$-Atrazine
Aldicarb Sulfoxide	3.91	207	132	21	5	$[M-H]^+$	$^{13}C_3$-Atrazine
Aminocarb	4.75	209	152	21	12	$[M-H]^+$	$^{13}C_3$-Atrazine
Bendiocarb	9.60	224	109	21	19	$[M-H]^+$	$^{13}C_3$-Atrazine
Carbaryl	10.10	202	145	21	12	$[M-H]^+$	$^{13}C_3$-Atrazine
Carbofuran	9.60	222	165	21	12	$[M-H]^+$	$^{13}C_6$-Carbofuran
3(OH)-Carbofuran	7.05	238 (255)	163	21	12	[M-H]+	$^{13}C_3$-Atrazine
Dioxacarb	7.57	224	167	21	8	$[M-H]^+$	$^{13}C_3$-Atrazine
Methiocarb	11.83	226	169	21	12	$[M-H]^+$	$^{13}C_3$-Atrazine
Methomyl	5.91	163	88 (106)	13	5	$[M-H]^+$	D_3-Methomyl
Mexacarbamate	11.03	223	166	29	12	$[M-H]^+$	$^{13}C_3$-Atrazine
Oxamyl	5.89	237	72	13	13	$[M-NH4]^+$	D_3-Oxamyl
Primicarb	9.39	239	182	46	16	$[M-H]^+$	$^{13}C_3$-Atrazine
Promecarb	12.08	208	151	21	12	$[M-H]^+$	$^{13}C_3$-Atrazine
Proxpoxur	9.60	210	111	21	12	$[M-H]^+$	$^{13}C_3$-Atrazine
Diazinon	13.40	305	169	18	24	$[M-H]^+$	D_{10}-Diazinon
Clorpyrifos	14.15	349.8	197.5	20	18	$[M-H]^+$	D_6-Methyl chlorpyrifos
Imidacloprid	7.26	256	209	42	16	$[M-H]^+$	$^{13}C_3$-Atrazine
Piperonyl Butoxide	13.77	357	177	35	11	$[M-NH4]^+$	D_{10}-Diazinon
Quantification Standards							
$^{13}C_6$-Carbofuran	9.60	228	171	21	12	$[M-H]^+$	$^{13}C_3$-Atrazine
D_{10}-Diazinon	13.40	315	170	20	20	$[M-H]^+$	$^{13}C_3$-Atrazine
D_3-Methomyl	5.91	166	88 (106)	13	5	$[M-H]^+$	$^{13}C_3$-Atrazine
D_3-Oxamyl	5.89	240	72	13	13	$[M-NH4]^+$	$^{13}C_3$-Atrazine
D_6-Methyl chlorpyrifos	11.8	329.8	278.8	26	16	$[M-H]^+$	$^{13}C_3$-Atrazine
Recovery Injection							
$^{13}C_3$-Atrazine	10.44	220	134 (177)	27	19	$[M-H]^+$	External Std

TABLE A1-9.—Compounds and amounts used to spike samples during liquid chromatography–tandem mass spectrometry (LC–MS/MS) analysis for carbamates.

Compound Spiked	**Amount added to each SPM sample (ng)**	**Amount added to each test sample (ng)**
Piperonyl butoxide	0.5	–
Diazinon	0.5	–
Chlorpyrifos	20	–
Aldicarb	5	–
Aldicarb sulphoxide	5	–
Primicarb	5	–
Carbofuran	5	–
Dioxacarb	5	–
3-Hydroxycarbofuran	5	–
Mexacarbate	5	–
Oxamyl	5	–
Propoxur	5	–
Methomyl	5	–
Aminocarb	5	–
Carbaryl	5	–
Aldicarb sulphone	10	–
Promecarb	10	–
Bendiocarb	10	–
Methiocarb	10	–
Imidacloprid	10	–
Surrogate Standards		
$^{13}C_6$-Carbofuran	200	200
D_3-Methomyl	100	100
D_3-Oxamyl	100	100
D_{10}-Diazinon	10	10
D_6-Methyl chlorpyrifos	100	100
Recovery Standards		
$^{13}C_3$-Atrazine	100	100

TABLE A1-10.—Nominal concentrations of calibration standards used for liquid chromatography–tandem mass spectrometry (LC–MS/MS) carbamate analysis.

Compound	**Cal-A ng/mL**	**CAL-B ng/mL**	**CAL-C ng/mL**	**CAL-D ng/mL**	**CAL-E ng/mL**	**CAL-F ng/mL**	**CAL-G ng/mL**
Piperonyl butoxide	0.05	0.10	0.51	2.53	12.64	63.2	126
Diazinon	0.05	0.10	0.50	2.51	12.55	62.8	126
Chlorpyrifos	1.00	2.00	4.00	20.0	100	500	1000
Aldicarb	0.50	1.00	5.00	25.0	125	624	1249
Aldicarb sulfoxide	0.50	1.00	5.00	25.0	125	625	1250
Primicarb	0.50	1.00	5.00	25.0	125	625	1250
Carbofuran	0.50	1.01	5.03	25.2	126	629	1258
Dioxacarb	0.50	1.00	5.00	25.0	125	625	1250
3-Hydroxycarbofuran	0.50	0.99	4.97	24.9	124	621	1243
Mexacarbate	0.49	0.99	4.93	24.7	123	616	1233
Oxyamyl	0.50	1.01	5.05	25.2	126	631	1261
Propoxur	0.50	1.01	5.03	25.1	126	628	1256
Methomyl	0.50	1.00	5.02	25.1	125	627	1254
Aminocarb	0.51	1.01	5.07	25.4	127	634	1268
Carbaryl	0.50	1.00	5.00	25.0	125	625	1250
Malathion	0.24	0.49	2.45	12.2	61	306	612
Aldicarb sulfone	1.00	2.00	10.02	50.1	251	1253	2505
Promecarb	1.00	2.00	9.98	49.9	250	1248	2495
Bendiocarb	1.01	2.01	10.06	50.3	252	1258	2515
Methiocarb	1.01	2.01	10.05	50.3	251	1256	2513
Imidacloprid	1.00	2.00	10.00	50.0	250	1250	2500
Surrogate Standards							
$^{13}\mathrm{C}_6$-Carbofuran	200	200	200	200	200	200	200
D_3-Methomyl	100	100	100	100	100	100	100
D_3-Oxamyl	100	100	100	100	100	100	100
D_{10}-Diazinon	10	10	10	10	10	10	10
D_6-Methyl chlorpyrifos	100	100	100	100	100	100	100
Field Standard							
$^{13}\mathrm{C}_6$-Carbaryl	0.5	1	5	25	120	620	1250
Recovery Standard							
$^{13}\mathrm{C}_3$-Atrazine	102	102	102	102	102	102	102

APPENDIX 2

Guide to CD-ROM Files and Total Ion Chromatograms for Composite Sample Organic Qualitative Analyses by Open Scan HRGC–LRMS

TABLE A2-1.—Guide to file names on enclosed CD-ROM for total ion chromatograms from open scan high-resolution gas chromatography–low-resolution mass spectrometry (HRGC–LRMS) analysis of composite sample filter and XAD-2 extracts and fractions. Note that the AMOIS program is required to read these files and is available from http://chemdata.nist.giv/mass-spc/amdis/. Filter extracts represent suspended constituents and XAD-2 extracts represent dissolved constituents. F1 fractions are less polar and F2 fractions are moderately polar.

ChemStation File Name	**Axys Lab Number**	**Sample Month**	**Dissolved/Suspended**	**Fraction**
OS992431.D	TFF-034	May 1999	Dissolved (XAD)	F1
CL090130.D	TFF-035	Jun 1999	Dissolved (XAD)	F1
CL090132.D	TFF-036	Jul 1999	Dissolved (XAD)	F1
CL090133.D	TFF-037	Aug 1999	Dissolved (XAD)	F1
OS071236.D	TFF-038	Sep 1999	Dissolved (XAD)	F1
OS071237.D	TFF-039	Oct 1999	Dissolved (XAD)	F1
OS071238.D	TFF-040	Nov 1999	Dissolved (XAD)	F1
OS071250.D	TFF-041	Dec 1999	Dissolved (XAD)	F1
OS071252.D	TFF-042	Jan 2000	Dissolved (XAD)	F1
OS992434.D	TFF-034	May 1999	Dissolved (XAD)	F2
CL090137.D	TFF-035	Jun 1999	Dissolved (XAD)	F2
CL090139.D	TFF-036	Jul 1999	Dissolved (XAD)	F2
CL090140.D	TFF-037	Aug 1999	Dissolved (XAD)	F2
OS071244.D	TFF-038	Sep 1999	Dissolved (XAD)	F2
OS071245.D	TFF-039	Oct 1999	Dissolved (XAD)	F2
OS071246.D	TFF-040	Nov 1999	Dissolved (XAD)	F2
OS071256.D	TFF-041	Dec 1999	Dissolved (XAD)	F2
OS071258.D	TFF-042	Jan 2000	Dissolved (XAD)	F2
OS992432.D	TFF-034	May 1999	Suspended (Filter)	F1
CL090131.D	TFF-035	Jun 1999	Suspended (Filter)	F1
CL090134.D	TFF-036	Jul 1999	Suspended (Filter)	F1
CL090135.D	TFF-037	Aug 1999	Suspended (Filter)	F1
OS071233.D	TFF-038	Sep 1999	Suspended (Filter)	F1
OS071234.D	TFF-039	Oct 1999	Suspended (Filter)	F1
OS071235.D	TFF-040	Nov 1999	Suspended (Filter)	F1
OS071251.D	TFF-041	Dec 1999	Suspended (Filter)	F1
OS071253.D	TFF-042	Jan 2000	Suspended (Filter)	F1
OS992435.D	TFF-034	May 1999	Suspended (Filter)	F2
CL090138.D	TFF-035	Jun 1999	Suspended (Filter)	F2
CL090141.D	TFF-036	Jul 1999	Suspended (Filter)	F2
CL090142.D	TFF-037	Aug 1999	Suspended (Filter)	F2
OS071241.D	TFF-038	Sep 1999	Suspended (Filter)	F2
OS071242.D	TFF-039	Oct 1999	Suspended (Filter)	F2
OS071243.D	TFF-040	Nov 1999	Suspended (Filter)	F2
OS071257.D	TFF-041	Dec 1999	Suspended (Filter)	F2
OS071259.D	TFF-042	Jan 2000	Suspended (Filter)	F2

TABLE A2-2.—Guide to file names on enclosed CD-ROM for total ion chromatograms for calibration and blanks associated with analysis of Tracy Fish Collection Facility composite samples.

ChemStation File Name	Purpose	Compounds	Fraction
OS071228.D	Calibration	Alkanes	F1
OS071229.D	Calibration	PAHs	F2
OS071230.D	Calibration	Herbicides+Pesticides	F1or F2
OS992436.D	Calibration	Chlorinated+PCB #1	F1or F2
CL090127.D	Calibration	Chlorinated+PCB #2	F1or F2
OS071227.D	Calibration	Chlorinated+PCB #3	F1or F2
OS071247.D	Calibration	Chlorinated+PCB #4	F1or F2
OS071260.D	Calibration	Chlorinated+PCB #5	F1or F2
CL090136.D	Filter Blank	Background	F1
CL090143.D	Filter Blank	Background	F2
OS992430.D	Method Blank	Background	F1
CL090129.D	Method Blank	Background	F1
OS992433.D	Method Blank	Background	F2
CL090129.D	Method Blank	Background	F2

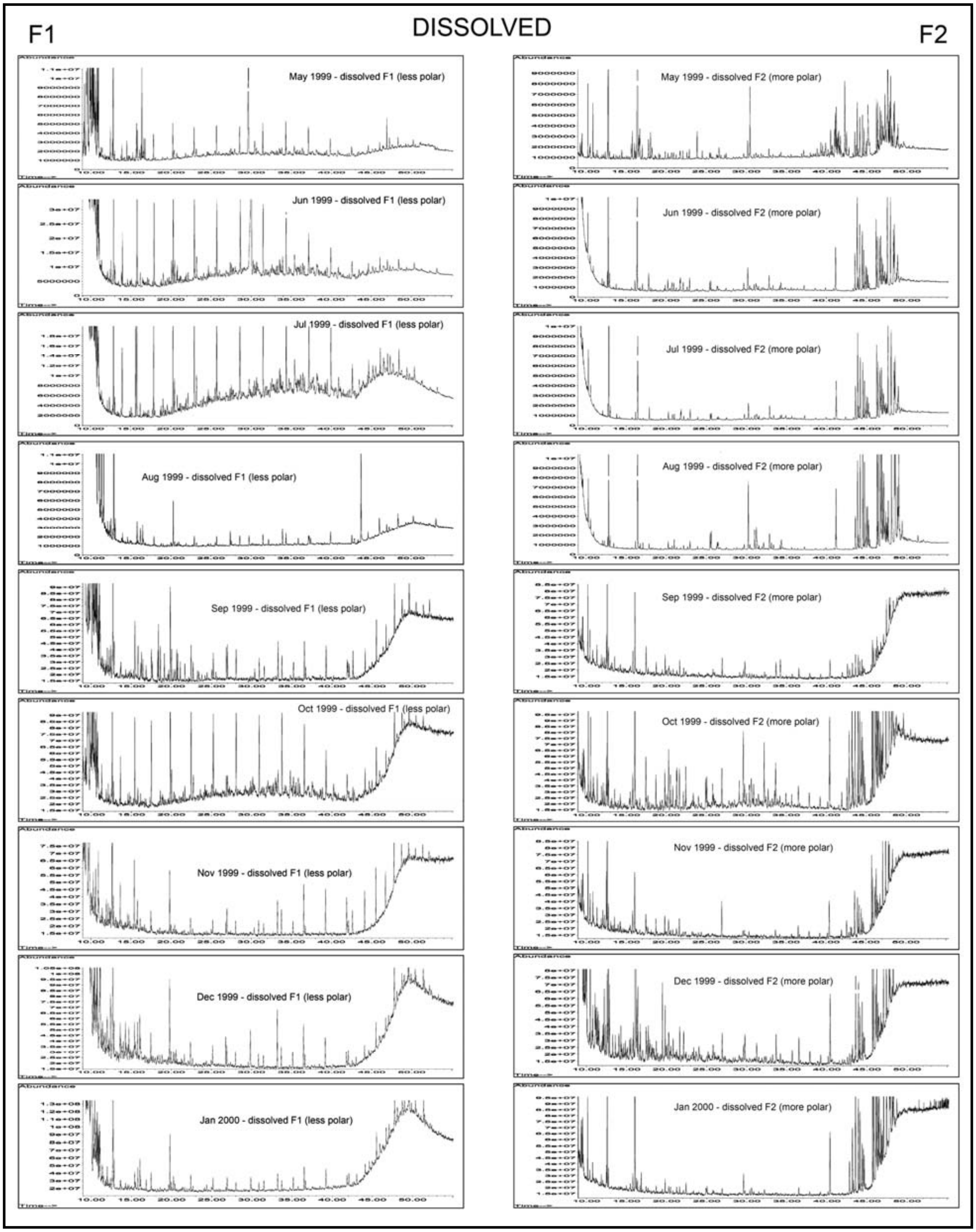

FIGURE A2-1.—Total ion chromatograms for dissolved F1 and F2 fractions from XAD-2 extractions for composite samples arranged top to bottom from May 1999 to January 2000.

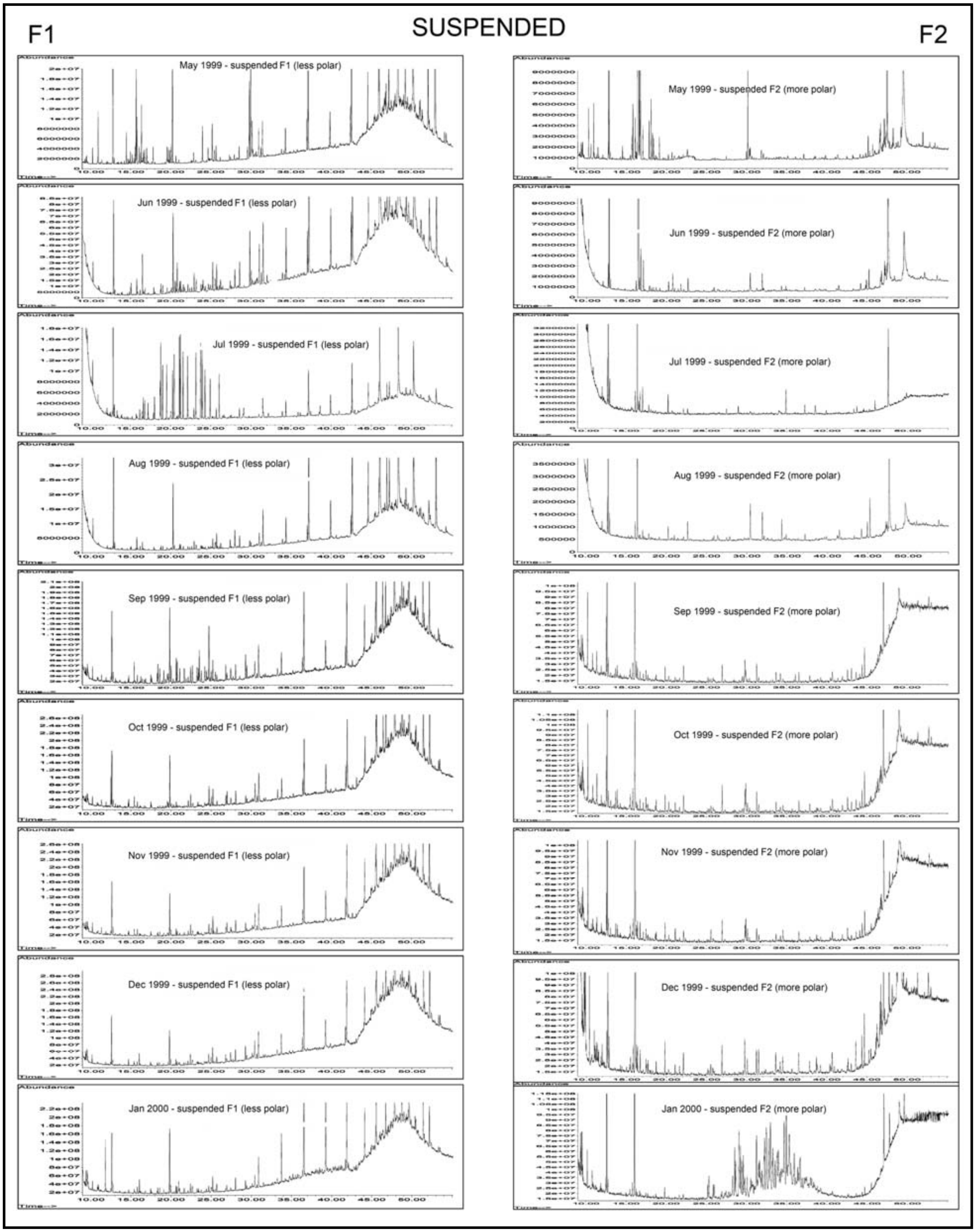

FIGURE A2-2.—Total ion chromatograms for suspended F1 and F2 fractions from filter extractions for composite samples arranged top to bottom from May 1999 to January 2000.

APPENDIX 3

Summary Tables for Quantitative Organic Analyses by HRGC–HRMS and LC–MS/MS, and Trace Elements by ICP–MS for Tracy Fish Collection Facility Composite Samples

TABLE A3-1.—Quantitative data for dissolved pesticides and persistent compounds for composite samples collected at the Tracy Fish Collection Facility from May 1999 through Jan 2000. ** Denotes compound detected in blank.

Italicized Compound Detected	***Compound on COC List***	***Applied Near TFCF***	***Semi-Quantitative***	***ND, Inverse of Detection Limit***

Date Range	**5/24/99 – 6/01/99**	**6/01/99 – 7/01/99**	**7/01/99 – 8/04/99**	**8/04/99 – 9/03/99**		**9/03/99 – 10/04/99**	**10/04/9 – 11/01/99**	**11/01/99 – 11/29/99**	**11/29/99 – 1/10/00**	**1/10/00 – 2/07/00**
General Period	**Late May**	**June**	**July**	**August**		**September**	**October**	**November**	**December**	**January**
Total Volume, L	**175**	**269**	**59**	**315**		**286**	**338**	**308**	**634**	**258**
Sample Material	**Column**	**Column**	**Column**	**Column**	**Column**	**Column**	**Column**	**Column**	**Column**	**Column**
Fraction	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**
Units	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**
Tecnazene	-0.008	-0.017	-0.023	-0.004	-0.004	-0.005	-0.004	-0.004	0.003	-0.005
HCB	0.025	0.002	0.015	0.011	0.015	0.029	0.015	**0.008	0.009	0.009
Quintozene	0.045	0.194	-0.023	0.005	0.010	0.043	0.006	0.019	0.043	0.020
Heptachlor	0.021	0.018	0.033	0.008	0.010	0.023	0.006	0.005	0.004	0.006
alpha-HCH	0.397	0.864	0.030	0.066	0.104	0.336	0.297	0.088	0.026	0.041
gamma-HCH	1.272	3.167	0.127	0.251	0.423	1.175	0.813	0.278	0.161	0.165
beta-HCH	0.296	0.420	0.020	0.022	0.047	0.273	0.215	0.056	0.008	0.019
delta-HCH	0.282	0.462	0.009	0.008	0.018	0.228	0.207	0.054	0.003	0.018
Chlorothalonil	-0.008	-0.017	-0.023	-0.004	-0.004	0.054	-0.004	-0.004	-0.002	-0.005
Aldrin	0.009	0.005	0.007	0.006	0.008	0.012	0.006	**0.002	0.002	0.003
Dacthal	0.670	1.855	0.064	0.378	0.783	0.909	0.199	0.102	0.072	0.265
Octachlorostyrene	-0.001	-0.003	-0.004	-0.001	-0.001	-0.001	-0.001	-0.000	-0.000	-0.001
Oxychlordane	0.045	0.045	-0.021	-0.019	-0.008	0.097	0.045	-0.009	0.008	0.013
Heptachlor-Epoxide	0.057	0.158	0.014	0.014	0.031	0.029	0.015	**0.007	0.006	0.009
t-Chlordane	0.142	0.282	0.032	0.044	0.057	0.117	0.062	0.019	0.019	0.016
c-Chlordane	0.482	1.890	0.965	0.248	0.444	0.601	0.303	**0.154	0.096	0.292

TABLE A3-1.—DISSOLVED ORGANICS (continued)

General Period	**Late May**	**June**	**July**	**August**		**September**	**October**	**November**	**December**	**January**
Total Volume, L	**175**	**269**	**59**	**315**		**286**	**338**	**308**	**634**	**258**
Fraction	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**
Units	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**
t-Nonachlor	0.088	0.082	0.016	0.025	0.047	0.061	0.042	0.018	0.012	0.013
c-Nonachlor	0.041	0.107	0.016	0.013	0.027	0.034	0.018	0.008	0.005	0.005
alpha-Endosulphan	0.105	0.206	0.118	0.036	0.056	0.081	0.035	0.023	0.013	0.043
beta-Endosulphan	0.178	0.157	0.067	0.019	0.032	-0.060	0.031	0.021	0.015	0.038
Dieldrin	0.450	2.240	0.173	0.324	0.804	0.611	0.257	0.096	0.078	0.101
Perthane	-0.171	-0.236	-0.218	-0.080	-0.037	-0.349	-0.120	-0.045	-0.017	-0.062
Endrin	0.030	0.117	0.016	0.014	0.034	0.028	0.011	**0.006	0.003	0.005
Endosulphan-Sulphate	0.823	1.321	0.119	0.176	0.406	0.751	0.373	0.120	0.056	0.070
Mirex	0.007	0.015	0.019	0.004	0.003	0.008	0.004	0.004	0.002	0.004
Methamidophos	3.726	21.875	0.838	0.698	3.471	5.455	0.947	0.259	0.301	0.527
Phorate	0.027	-0.029	-0.028	-0.004	-0.004	0.043	-0.004	-0.014	0.006	0.014
Terbufos	0.018	-0.035	-0.033	-0.016	-0.009	-0.081	-0.010	-0.010	-0.004	-0.008
Diazinon-Oxon	0.229	-0.027	0.032	0.083	-0.005	0.149	0.118	0.014	0.017	0.075
Diazinon	7.695	-0.068	0.809	2.954	-0.011	5.967	2.158	0.835	0.646	2.796
Disulfoton	-0.093	-0.198	-0.212	-0.032	-0.026	1.371	-0.025	-0.027	-0.013	-0.032
Fonofos	1.912	4.427	0.170	0.153	0.317	0.118	0.034	0.013	0.191	1.307
Dimethoate	26.743	-0.637	6.757	5.291	-0.051	20.559	0.600	-0.260	0.064	0.153
Chlorpyriphos-Methyl	-0.008	-0.017	-0.023	-0.004	-0.004	-0.005	-0.004	-0.004	-0.002	-0.005
Parathion-Methyl	1.478	9.152	0.558	1.033	1.837	1.450	0.195	-0.105	0.044	-0.045
Pirimiphos-Methyl	-0.008	-0.017	-0.023	-0.004	-0.004	-0.008	-0.004	-0.004	-0.002	-0.005
Chlorpyriphos	24.152	37.975	0.617	4.152	10.921	18.508	3.266	1.017	0.574	2.233
Fenitrothion	-0.020	-0.034	-0.049	-0.006	-0.005	-0.033	-0.006	-0.011	-0.002	-0.005

TABLE A3-1.—DISSOLVED ORGANICS (continued)

General Period	**Late May**	**June**	**July**	**August**		**September**	**October**	**November**	**December**	**January**
Total Volume, L	**175**	**269**	**59**	**315**		**286**	**338**	**308**	**634**	**258**
Fraction	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**
Units	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**
Malathion	1.455	-0.574	-0.721	0.669	-0.075	14.359	2.817	0.159	0.046	0.094
Parathion-Ethyl	-0.027	-0.108	-0.106	-0.007	-0.010	-0.030	-0.007	-0.017	-0.002	-0.007
Chlorpyriphos-Oxon	0.139	-0.035	-0.023	0.012	0.005	0.077	0.015	-0.004	-0.002	0.012
Disulfoton-Sulfone	3.162	-0.021	1.360	5.376	-0.004	18.508	3.069	0.589	3.113	6.770
Ethion	0.135	0.418	-0.057	-0.048	0.041	-0.106	0.043	-0.020	0.008	-0.022
Phosmet	0.308	-0.198	-0.264	-0.035	-0.015	-0.245	-0.065	-0.059	-0.012	0.103
Azinphos-Methyl	-1.448	-0.187	-0.626	-0.298	-0.055	-1.021	-0.406	0.092	-0.070	-0.089
Total-Permethrins	-0.296	-0.065	-0.119	-0.076	-0.013	-0.256	-0.099	-0.045	-0.019	-0.032
Total-Cypermethrins	-0.021	-0.050	-0.042	-0.006	-0.004	-0.012	-0.010	-0.020	-0.004	-0.007
Butylate	0.047	0.030	0.030	0.012	-0.004	0.044	0.012	0.007	0.002	-0.005
Ethalfluralin	0.179	0.262	0.053	0.036	0.108	0.052	0.005	0.008	-0.002	-0.005
Trifluralin	9.143	24.500	0.834	0.597	1.731	1.594	0.260	0.261	1.907	1.008
Triallate	-0.008	-0.017	-0.023	-0.004	-0.004	-0.005	-0.004	-0.004	-0.002	-0.005
Dimethenamid	-0.008	-0.017	-0.023	-0.004	-0.004	-0.018	-0.004	-0.004	-0.002	-0.005
Alachlor	3.977	0.075	0.685	0.201	-0.011	-0.207	0.099	0.023	0.018	0.070
Methoprene	-2.354	-2.695	-3.751	-0.762	-0.207	-1.273	-0.473	-0.628	-0.269	-0.693
Butralin	-0.146	-0.306	-0.414	-0.065	-0.020	-0.214	-0.103	-0.036	-0.022	-0.069
Flufenacet	-1.234	-0.107	-0.502	-0.182	-0.007	-0.797	-0.258	-0.108	-0.056	-0.078
Metolachlor	120.381	-0.034	29.605	23.238	-0.004	14.172	3.799	0.498	0.307	1.339
Linuron	2.263	0.324	0.420	0.474	0.056	0.499	0.166	0.085	0.540	1.876
Pendimethalin	1.707	5.477	-0.569	0.250	0.412	2.685	0.354	0.210	0.318	2.171

TABLE A3-1.—DISSOLVED ORGANICS (continued)

General Period	**Late May**	**June**	**July**	**August**		**September**	**October**	**November**	**December**	**January**
Total Volume, L	**175**	**269**	**59**	**315**		**286**	**338**	**308**	**634**	**258**
Fraction	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**	**Dissolved**
Units	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**
Flutriafol	-0.211	-0.409	-0.273	-0.201	-0.008	-1.002	-0.037	-0.052	-0.037	-0.084
Tebuconazol	0.574	-0.338	0.599	0.166	-0.005	2.923	0.769	0.099	0.215	0.338
Aldicarb	-0.038	-0.087	-0.113	-0.021	-0.021	-0.023	-0.020	-0.022	-0.011	-0.026
AldicarSulfone	-0.076	-0.175	-0.226	-0.042	-0.042	-0.047	-0.039	-0.043	-0.021	-0.052
AldicarSulfoxide	-0.054	-0.087	-0.113	-0.048	-0.021	-0.072	-0.077	-0.042	-0.019	-0.028
Aminocarb	-0.038	-0.087	-0.113	-0.021	-0.021	-0.023	-0.020	-0.022	-0.011	-0.026
Bendiocarb	-0.114	-0.175	-0.226	-0.211	-0.042	-0.226	-0.314	-0.184	-0.046	-0.112
Carbaryl	6.804	-0.087	-0.113	0.095	-0.021	-0.191	0.292	0.378	0.223	0.263
Carbofuran	8.457	-0.087	0.470	0.491	-0.021	0.918	0.277	0.120	0.128	0.127
Diazinon	3.817	-0.009	0.434	1.490	-0.002	2.270	1.270	0.978	0.372	1.514
Dioxacarb	-0.038	-0.087	-0.113	-0.021	-0.021	0.083	0.074	0.051	0.017	-0.026
3[OH] Carbofuran	0.201	-0.087	-0.113	-0.021	-0.021	-0.023	-0.020	-0.022	-0.011	-0.026
Imidcloprid	0.363	-0.175	-0.226	-0.042	-0.042	0.360	0.351	0.404	0.064	0.116
Malathion	-0.525	-0.437	-1.216	-0.601	-0.106	-0.662	-0.907	-0.723	-0.124	-0.505
Methiocarb	-0.661	-0.175	-0.416	-0.155	-0.042	-0.376	-0.213	-0.119	-0.073	-0.110
Methomyl	-0.038	-0.087	0.556	-0.021	-0.021	0.054	-0.020	0.052	-0.011	-0.026
Mexacarbate	-0.038	-0.087	-0.113	-0.021	-0.021	-0.023	-0.020	-0.022	-0.011	-0.026
Oxamyl	-0.038	-0.087	-0.113	-0.021	-0.021	-0.023	-0.020	-0.022	-0.011	-0.026
Pirimicarb	-0.038	-0.087	-0.113	-0.021	-0.021	-0.023	-0.020	-0.022	-0.011	-0.026
Promecarb	-0.426	-0.087	-0.113	-0.096	-0.021	-0.165	-0.185	-0.074	-0.057	-0.082
Propoxur	0.082	-0.087	-0.113	0.049	-0.021	-0.023	0.162	0.141	0.052	0.071
Piperonyl butoxide	0.360	-0.009	0.067	0.201	-0.002	0.970	1.132	1.134	0.446	0.340

TABLE A3-2.—Quantitative data for suspended pesticides and persistent compounds for composite samples collected at the Tracy Fish Collection Facility from May 1999 through Jan 2000. ** Denotes compound detected in blank.

Italicized = Detected	***Compound on COC List***	***Applied Near TFCF***	***Semi-Quantitative***	***ND - Inverse of Detection Limit***

Date Range	**5/24/99 – 6/01/99**	**6/01/99 – 7/01/99**	**7/01/99 – 8/04/99**	**8/04/99 – 9/03/99**	**9/03/99 – 10/04/99**	**10/04/99 – 11/01/99**	**11/01/99 – 11/29/99**	**11/29/99 – 1/10/00**	**1/10/00 – 2/07/00**
General Period	**Late May**	**June**	**July**	**August**	**September**	**October**	**November**	**December**	**January**
Total Volume, L	**175**	**269**	**59**	**315**	**286**	**338**	**308**	**634**	**258**
Sample Material	**Filter**	**Filter**	**Filter**	**Filter**	**Filter**	**Filter**	**Filter**	**Filter**	**Filter**
Fraction	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**
Units	***ng/L***	***ng/L***	***ng/L***	***ng/L***	***ng/L***	***ng/L***	***ng/L***	***ng/L***	***ng/L***
Tecnazene	-0.008	-0.017	-0.023	-0.004	-0.005	-0.004	-0.004	0.0021	-0.005
HCB	0.015	0.030	0.010	0.006	0.006	0.006	0.006	0.0026	0.004
Quintozene	-0.008	-0.017	-0.023	0.004	-0.005	-0.004	-0.004	-0.0021	-0.005
Heptachlor	0.012	0.032	0.055	0.009	0.010	0.009	0.009	0.0029	0.006
alpha-HCH	0.003	0.009	0.002	0.002	0.002	0.002	0.002	0.0008	0.001
gamma-HCH	0.006	0.016	0.005	0.002	0.003	0.003	0.002	0.0010	0.002
beta-HCH	0.003	0.007	-0.002	0.001	0.002	0.003	0.001	-0.0003	-0.001
delta-HCH	0.002	-0.003	-0.002	0.001	0.001	0.001	-0.001	-0.0003	-0.001
Chlorothalonil	-0.008	-0.017	-0.023	-0.004	-0.005	-0.004	-0.004	-0.0021	-0.005
Aldrin	0.005	0.010	0.007	0.002	0.003	0.001	0.002	0.0010	0.002
Dacthal	0.008	0.020	-0.023	0.004	-0.005	-0.004	-0.004	-0.0021	-0.005
Octachlorostyrene	-0.001	-0.002	-0.003	-0.000	-0.001	-0.001	-0.001	-0.0002	-0.001
Oxychlordane	0.011	-0.021	-0.009	0.007	0.013	0.009	0.005	0.0057	0.005
Heptachlor-Epoxide	0.007	0.013	-0.004	0.002	0.002	0.002	0.002	0.0014	0.003
t-Chlordane	0.038	0.065	0.010	0.009	0.010	0.010	0.009	0.0041	0.007
c-Chlordane	0.488	0.681	0.997	0.244	0.153	0.211	0.177	0.1230	0.282
t-Nonachlor	0.046	0.068	0.007	0.009	0.012	0.010	0.008	0.0041	0.005
c-Nonachlor	0.020	0.046	0.007	0.006	0.007	0.006	0.005	0.0029	0.003

TABLE A3-2.—SUSPENDED ORGANICS (continued)

General Period	**Late May**	**June**	**July**	**August**	**September**	**October**	**November**	**December**	**January**
Total Volume, L	**175**	**269**	**59**	**315**	**286**	**338**	**308**	**634**	**258**
Fraction	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**
Units	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**
alpha-Endosulphan	0.044	0.082	0.125	0.022	0.029	0.021	0.023	0.0121	0.032
beta-Endosulphan	0.045	0.075	0.085	0.012	0.020	0.013	0.019	0.0103	0.026
Dieldrin	0.048	0.107	0.019	0.022	0.020	0.017	0.013	0.0081	0.008
Perthane	-0.077	-0.325	-0.139	-0.030	-0.033	-0.033	-0.025	-0.0129	-0.166
Endrin	0.006	0.016	0.012	0.003	0.004	0.003	0.004	0.0013	-0.002
Endosulphan-Sulphate	0.031	0.034	-0.016	0.008	0.009	0.007	0.006	0.0040	-0.012
Mirex	0.013	0.027	0.018	0.004	0.006	0.007	0.006	0.0031	0.005
Methamidophos	-0.210	-0.749	-0.669	-0.247	-0.140	-0.203	-0.143	-0.0696	-0.196
Phorate	-0.008	-0.017	-0.024	-0.004	-0.005	-0.004	-0.004	-0.0021	-0.005
Terbufos	-0.008	-0.017	-0.023	-0.004	-0.006	-0.005	-0.005	-0.0021	-0.005
Diazinon-Oxon	-0.008	-0.027	-0.023	-0.004	-0.005	-0.004	-0.005	-0.0021	-0.005
Diazinon	0.033	0.117	-0.078	0.012	-0.014	-0.012	0.044	0.0059	0.020
Disulfoton	-0.038	-0.138	-0.110	-0.023	-0.023	-0.024	-0.029	-0.0122	-0.024
Fonofos	0.031	0.066	-0.023	0.015	0.011	0.015	0.010	0.0095	0.010
Dimethoate	-0.060	-0.163	-0.310	-0.043	-0.047	-0.037	-0.049	-0.0207	-0.040
Chlorpyriphos-Methyl	-0.008	-0.017	-0.023	-0.004	-0.005	-0.004	-0.004	-0.0021	-0.005
Parathion-Methyl	-0.048	-0.094	-0.094	0.027	-0.017	-0.016	-0.019	-0.0070	-0.023
Pirimiphos-Methyl	-0.008	-0.017	-0.023	-0.004	-0.005	-0.004	-0.004	-0.0021	-0.005
Chlorpyriphos	0.505	0.597	0.080	0.152	0.161	0.098	0.071	0.0273	0.076
Fenitrothion	-0.008	-0.020	-0.023	-0.004	-0.005	-0.004	-0.005	-0.0021	-0.005
Malathion	-0.081	-0.296	-0.373	-0.055	-0.083	-0.060	-0.071	-0.0196	-0.055
Parathion-Ethyl	-0.013	-0.047	-0.056	-0.007	-0.009	-0.008	-0.015	-0.0029	-0.006

TABLE A3-2.—SUSPENDED ORGANICS (continued)

General Period	**Late May**	**June**	**July**	**August**	**September**	**October**	**November**	**December**	**January**
Total Volume, L	**175**	**269**	**59**	**315**	**286**	**338**	**308**	**634**	**258**
Fraction	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**
Units	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**
Chlorpyriphos-Oxon	-0.008	-0.017	-0.023	-0.004	-0.005	-0.004	-0.004	-0.0021	-0.005
Disulfoton-Sulfone	0.056	0.041	-0.023	0.010	0.021	0.005	0.005	-0.0161	-0.019
Ethion	-0.023	-0.062	-0.026	-0.010	-0.015	-0.010	-0.014	-0.0041	-0.009
Phosmet	-0.062	-0.152	-0.119	-0.020	-0.029	-0.023	-0.029	-0.0113	-0.024
Azinphos-Methyl	-0.123	-0.159	-0.249	-0.044	-0.031	-0.044	-0.044	-0.0257	-0.083
Total-Permethrins	0.033	-0.064	-0.043	-0.012	-0.012	-0.012	-0.013	-0.0061	-0.010
Total-Cypermethrins	-0.009	0.054	-0.029	-0.004	-0.006	-0.006	-0.005	-0.0025	-0.006
Butylate	-0.010	-0.017	-0.023	-0.004	-0.005	-0.004	-0.004	-0.0023	-0.005
Ethalfluralin	-0.008	-0.026	-0.030	-0.005	-0.005	-0.004	-0.004	-0.0033	-0.008
Trifluralin	0.150	0.254	0.028	0.025	0.015	0.015	0.013	0.0259	0.019
Triallate	-0.008	-0.017	-0.023	-0.004	-0.005	-0.004	-0.004	-0.0021	-0.005
Dimethenamid	-0.008	-0.017	-0.023	-0.004	-0.005	-0.004	-0.004	-0.0021	-0.005
Alachlor	-0.076	-0.120	0.101	-0.021	0.033	0.029	-0.033	0.0181	0.034
Methoprene	-3.246	-7.210	-2.020	-0.919	-1.030	-0.970	-0.913	-0.6015	-0.848
Butralin	-0.131	-0.294	-0.282	-0.056	-0.036	-0.042	-0.052	-0.0318	-0.105
Flufenacet	-0.253	-0.423	-0.080	-0.078	-0.054	-0.059	-0.046	-0.0580	-0.097
Metolachlor	0.303	1.011	0.384	0.132	0.085	0.077	0.055	0.0292	0.051
Linuron	0.116	0.257	-0.271	-0.042	-0.062	0.043	-0.066	0.0355	0.086
Pendimethalin	-0.087	-0.241	-0.153	-0.042	-0.032	-0.036	-0.058	-0.0313	0.076
Flutriafol	-0.092	-0.191	-0.074	-0.021	-0.023	-0.022	-0.020	-0.0175	-0.034
Tebuconazol	-0.067	-0.264	-0.138	-0.037	0.027	0.092	0.125	-0.0197	-0.091

TABLE A3-2.—SUSPENDED ORGANICS (continued)

General Period	**Late May**	**June**	**July**	**August**	**September**	**October**	**November**	**December**	**January**
Total Volume, L	**175**	**269**	**59**	**315**	**286**	**338**	**308**	**634**	**258**
Fraction	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**	**Suspended**
Units	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**
Aldicarb	-0.038	-0.087	-0.113	-0.021	-0.023	-0.020	-0.022	-0.0105	-0.026
AldicarSulfone	-0.076	-0.175	-0.226	-0.042	-0.047	-0.039	-0.043	-0.0210	-0.052
AldicarSulfoxide	-0.038	-0.087	-0.113	-0.021	-0.023	-0.020	-0.022	-0.0105	-0.026
Aminocarb	-0.038	-0.087	-0.113	-0.021	-0.023	-0.020	-0.022	-0.0105	-0.026
Bendiocarb	-0.082	-0.175	-0.226	-0.042	-0.115	-0.159	-0.068	-0.0225	-0.052
Carbaryl	-0.038	-0.089	-0.113	-0.021	-0.031	-0.020	-0.029	-0.0123	-0.026
Carbofuran	-0.038	-0.087	-0.113	-0.021	-0.023	-0.020	-0.022	-0.0105	-0.026
Diazinon	0.016	0.051	-0.011	0.005	0.004	0.005	0.020	0.0023	0.008
Dioxacarb	-0.038	-0.465	-0.113	-0.101	0.050	-0.114	-0.047	-0.0431	-0.066
3[OH] Carbofuran	-0.038	-0.087	-0.113	-0.021	-0.023	-0.020	-0.022	-0.0105	-0.026
Imidcloprid	-0.076	-0.175	-0.226	-0.042	-0.047	-0.039	-0.043	-0.0210	-0.052
Malathion	-0.571	-1.080	-0.565	-0.149	-0.204	-0.108	-0.165	-0.0662	-0.129
Methiocarb	-0.517	-0.845	-0.226	-0.150	-0.159	-0.221	-0.148	-0.1689	-0.105
Methomyl	-0.038	-0.087	-0.113	-0.021	-0.023	-0.020	-0.022	-0.0105	-0.026
Mexacarbate	-0.038	-0.087	-0.113	-0.021	-0.023	-0.020	-0.022	-0.0105	-0.026
Oxamyl	-0.038	-0.087	-0.113	-0.021	-0.023	-0.020	-0.022	-0.0105	-0.026
Pirimicarb	-0.038	-0.087	-0.113	-0.021	-0.023	-0.020	-0.022	-0.0105	-0.026
Promecarb	-0.173	-0.217	-0.124	-0.021	-0.026	-0.020	-0.022	-0.0105	-0.065
Propoxur	-0.038	-0.087	-0.113	-0.021	-0.023	-0.020	-0.022	-0.0105	-0.026
Piperonyl butoxide	0.004	-0.009	-0.011	0.003	0.005	0.004	0.004	0.0021	-0.003

TABLE A3-3.—Quantitative data for trace elements by inductively coupled plasma–mass spectrometry (ICP–MS) for unfiltered composite samples collected at the Tracy Fish Collection Facility from May 1999 through Jan 2000. These data represent unfiltered samples and total concentrations.

Month	**Ag Silver, mg/L**	**Al Aluminum, mg/L**	**As Arsenic, mg/L**	**Cd Cadmium, mg/L**	**Co Cobalt, mg/L**	**Cr Chromium, mg/L**	**Cu Copper, mg/L**	**Fe Iron, mg/L**	**Hg Mercury, mg/L**	**Mn Manganese, mg/L**
May	-0.001	1.70	-0.002	-0.001	0.0010	0.0054	0.0046	2.20	-0.0100	0.100
June	-0.001	1.70	-0.002	-0.001	0.0012	0.0050	0.0047	2.40	-0.0100	0.110
July	-0.001	1.60	-0.002	-0.001	0.0011	0.0049	0.0070	2.10	0.0150	0.097
August	-0.001	2.80	0.002	-0.001	0.0015	0.0085	0.0061	2.90	0.0150	0.120
September	-0.001	1.80	-0.002	-0.001	0.0011	0.0053	0.0054	1.90	0.0125	0.088
October	-0.001	1.60	-0.002	-0.001	-0.0010	0.0045	0.0046	1.90	-0.0100	0.083
November	-0.001	1.50	-0.002	-0.001	-0.0010	0.0037	0.0039	1.60	-0.0100	0.072

	Mo Molybdenum, mg/L	**Ni Nickel, mg/L**	**Pb Lead, mg/L**	**Sb Antimony, mg/L**	**Se Selenium, mg/L**	**Tl Thallium, mg/L**	**V Vanadium, mg/L**	**U Uranium, mg/L**	**Zn Zinc, mg/L**
May	0.0017	0.0057	0.0010	-0.002	-0.002	-0.001	-0.010	-0.0050	0.0140
June	0.0016	0.0052	0.0014	-0.002	-0.002	-0.001	-0.010	-0.0050	0.0140
July	-0.0010	0.0053	0.0011	-0.002	-0.002	-0.001	-0.010	-0.0050	0.0240
August	0.0015	0.0290	0.0015	-0.002	-0.002	-0.001	0.011	-0.0050	0.0150
September	0.0016	0.0057	0.0011	-0.002	-0.002	-0.001	-0.010	-0.0050	0.0110
October	0.0019	0.0044	0.0010	-0.002	-0.002	-0.001	-0.010	-0.0050	0.0090
November	0.0021	0.0035	-0.0010	-0.002	-0.002	-0.001	-0.010	0.0051	0.0093

TABLE A3-4.—Trace element data from October 29, 1997 discrete grab sampling near the Tracy Fish Collection Facility (TFCF). Samples were collected with ultra-clean protocols and analyzed by Frontier Geosciences using high-resolution inductively coupled plasma–mass spectrometry (ICP–MS). ND for suspended indicates that filtered and unfiltered samples were very close in concentration.

Site #	**Location**	**Ag - Silver, µg/L**		**Al - Aluminum, µg/L**		**As - Arsenic, µg/L**		**Cd - Cadmium, µg/L**	
		Dissolved	**Suspended**	**Dissolved**	**Suspended**	**Dissolved**	**Suspended**	**Dissolved**	**Suspended**
Site 5	Old River at TFCF Intake outside debris boom	0.0221	0.0152	13.3	243	1.89	0.104	0.0119	0.0044
Site 4	Confluence of Grant Line Canal and Old River	0.0333	0.0321	15.9	327	1.80	0.297	0.0117	0.0020
Site 2	Old River 50 m downstream of temporary barrier	0.0679	0.0020	15.8	125	2.14	0.021	0.0134	ND
Site 1	Old River 50 m upstream of temporary barrier	0.0241	ND	16.0	125	2.11	ND	0.0102	ND
Site 3	Upstream of Grant Line Bridge at temporary barrier	0.0662	ND	8.14	202	1.81	0.260	0.0098	0.0058

		Co - Cobalt, µg/L		**Cr - Chromium, µg/L**		**Cu - Copper, µg/L**		**Fe Iron, µg/L**	
		Dissolved	**Suspended**	**Dissolved**	**Suspended**	**Dissolved**	**Suspended**	**Dissolved**	***Suspended***
Site 5	Old River at TFCF Intake outside debris boom	0.106	0.194	1.76	0.339	1.36	0.585	11.4	299
Site 4	Confluence of Grant Line Canal and Old River	0.0986	0.227	1.75	0.395	1.35	0.727	11.5	377
Site 2	Old River 50 m downstream of temporary barrier	0.171	0.048	1.93	ND	1.37	0.196	12.3	106
Site 1	Old River 50 m upstream of temporary barrier	0.184	0.006	1.57	ND	1.43	ND	15.8	100
Site 3	Upstream of Grant Line Bridge at temporary barrier	0.114	0.160	1.71	0.523	1.24	0.520	9.97	271

TABLE A3-4.—Continued.

		Hg Total Mercury, µg/L		**Me-Hg - Methylmercury, µg/L**		**Mn - Manganese, µg/L**		**Mo - Molybdenum, µg/L**	
		Dissolved	**Suspended**	**Dissolved**	**Suspended**	**Dissolved**	**Suspended**	**Dissolved**	**Suspended**
Site 5	Old River at TFCF Intake outside debris boom	0.00078	0.00296	0.000009	0.000016	2.33	53.4	2.800	ND
Site 4	Confluence of Grant Line Canal and Old River	0.00105	0.00288	0.000012	0.000035	2.77	53.4	2.540	ND
Site 2	Old River 50 m downstream of temporary barrier	0.00107	0.00126	0.000027	0.000006	58.6	8.34	3.000	ND
Site 1	Old River 50 m upstream of temporary barrier	0.00071	0.00127	0.000022	0.000018	59.5	ND	3.080	ND
Site 3	Upstream of Grant Line Bridge at temporary barrier	0.00092	0.00312	0.000014	0.000054	2.02	57.8	3.030	ND
		Ni - Nickel, µg/L		**Pb - Lead, µg/L**		**Sb - Antimony, µg/L**		**Se - Selenium, µg/L**	
		Dissolved	**Suspended**	**Dissolved**	**Suspended**	**Dissolved**	**Suspended**	**Dissolved**	**Suspended**
Site 5	Old River at TFCF Intake outside debris boom	<0.040	0.281	0.0124	0.316	0.0857	0.0002	0.651	0.092
Site 4	Confluence of Grant Line Canal and Old River	<0.040	0.431	0.0605	0.282	0.087	0.0078	0.486	0.0542
Site 2	Old River 50 m downstream of temporary barrier	<0.040	<0.040	0.0195	0.0939	0.107	ND	0.555	ND
Site 1	Old River 50 m upstream of temporary barrier	<0.040	0.068	0.0173	ND	0.104	ND	0.567	ND
Site 3	Upstream of Grant Line Bridge at temporary barrier	<0.040	0.037	0.0107	0.283	0.0805	0.0043	0.746	ND

TABLE A3-4.—Continued

		Thallium, µg/L		Uranium, µg/L		V - Vanadium, µg/L		Zn - Zinc, µg/L	
		Dissolved	Suspended	Dissolved	Suspended	Dissolved	Suspended	Dissolved	Suspended
Site 5	Old River at TFCF Intake outside debris boom	0.0012	0.0015	8.490	ND	3.530	0.7161	0.5404	1.010
Site 4	Confluence of Grant Line Canal and Old River	0.0006	0.0040	7.340	0.6394	3.470	1.060	0.5619	1.244
Site 2	Old River 50 m downstream of temporary barrier	0.0019	0.0003	9.440	0.0286	4.580	0.1684	0.6657	0.3227
Site 1	Old River 50 m upstream of temporary barrier	0.0020	ND	9.660	ND	4.620	ND	0.6797	ND
Site 3	Upstream of Grant Line Bridge at temporary barrier	0.0015	0.0011	10.19	0.0746	3.260	0.6921	0.5651	0.8682