Occurrence, Distribution and Transport of Pesticides, Trace Elements and Selected Inorganic Constituents into the Salton Sea Basin, California, 2001–2002

By Lawrence A. LeBlanc, Roy A. Schroeder, James L. Orlando, and Kathryn M. Kuivila

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Conversion Factors, Datum, and Abbreviations

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Area	
square meter (m^2)	0.0002471	acre
square kilometer (km^2)	247.1	acre
	Volume	
cubic kilometer (km^3)	0.2399	cubic mile (mi^3)
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	61.02	cubic inch (in^3)
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
	Mass	
pound, avoirdupois (lb)	0.4536	kilogram

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

$$°C=(°F-32)/1.8$$

DATUM

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD27)

Abbreviations

CDPR	California Department of Pesticide Regulation
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
GIS	Geographic Information System
GPC/HPLC	gel permeation/high pressure liquid chromatography
MASE	microwave-assisted solvent extraction
m/z	mass/charge ratio
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
psi	pounds per square inch
rpm	revolutions per minute
RWQCB	Regional Water Quality Control Board
SIM	selected ion monitoring
SIS	selected ion storage
SPE	solid phase extraction
TMDL	total maximum daily load
UC	University of California
USGS	U.S. Geological Survey

BHC	benzenehexachloride
C	carbon
CO_2	carbon dioxide
DDE	dichlorodiphenyldichloroethylene
DDD	dichlorodiphenyldichloroethane
DDT	dichlorodiphenyltrichloroethane
DOC	dissolved organic carbon
EPTC	eptam
N	nitrogen
N_2	nitrogen gas
NPOC	non-purgeable organic carbon
OC	organic carbon
PAH	polyclic aromatic hydrocarbon
TOC	total organic carbon
UV/Vis	ultraviolet/visible
cc	cubic centimeter
dpm	degrees per minute

ev	electronvolts
L	liter
L/min	liter per minute
mL	milliliter
mL/min	milliliter per minute
mg	milligram
mg/kg	milligram per kilogram
mg/L	milligram per liter
mm	millimeter
ng	nanogram
ng/g	nanogram per gram
ng/L	nanogram per liter
ng/µL	nanogram per microliter
nm	nanometer
µamps	microamperes
µL	microliter
µm	micrometer
µS/cm (µS cm^{-1})	microsiemens per centimeter

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Abstract

A study of pesticide distribution and transport within the Salton Sea Basin, California, was conducted from September 2001 to October 2002. Sampling for the study was done along transects for the three major rivers that flow into the Salton Sea Basin: the New and Alamo Rivers at the southern end of the basin and the Whitewater River at the northern end. Three stations were established on each river: an outlet station approximately 1 mile upstream of the river discharge, a near-shore station in the river delta, and off-shore station in the Salton Sea. Water and suspended and bed sediments were collected at each station in October 2001, March–April 2002, and September 2002, coinciding with peak pesticide applications in the fall and spring.

Fourteen current-use pesticides were detected in the water column. Concentrations of dissolved pesticides typically decreased from the outlets to the sea in all three rivers, consistent with the off-shore transport of pesticides from the rivers to the sea. Dissolved concentrations ranged from the limits of detection to 151 nanograms per liter (ng/L); however, diazinon, eptam (EPTC), and malathion were detected at much higher concentrations (940–3,830 ng/L) at the New and Alamo River outlet and near-shore stations. Concentrations of carbaryl, dacthal, diazinon, and eptam were higher during the two fall sampling periods, whereas concentrations of atrazine, carbofuran, and trifluralin were higher during the spring. Current-use pesticides also were detected on suspended and bed sediments in concentrations ranging from method detection limits to 106 ng/g (nanograms per gram). Chlorpyrifos, dacthal, eptam, trifluralin, and DDE were the most frequently detected pesticides on sediments from all three rivers. The number and concentrations of pesticides associated with suspended sediments frequently were similar for the river outlet and near-shore sites, consistent with the downstream transport of sediment-associated pesticides out of the rivers. Seasonal trends in pesticide concentration were similar to those for dissolved concentrations in fall 2001 and spring 2002, but not in fall 2002. Generally, the pesticides detected in the suspended sediments were the same pesticides detected in the bed sediments, and concentrations were similar, especially at the Alamo River outlet site in spring 2002 and fall 2002. Pesticides generally were not detected in sediments from the off-shore sites; however, the samples from these sites also had greater incidences of matrix interference during analysis. Sediment-associated pesticide concentrations were above equilibrium in water, suggesting a bound fraction of sediment-associated pesticides that are resistant to desorption. Concentrations of trace elements and other inorganic constituents in suspended sediments collected during the fall 2001 followed expected trends with dilution of river-derived minerals owing to highly organic autochthonous production within the Salton Sea Basin. However, calculation of enrichment ratios provided evidence for the bioconcentration of several trace elements, notably selenium in the off-shore biota.

Introduction

Several studies by the U.S. Geological Survey (USGS) and others since the late 1960s identified elevated concentrations of agriculture-related chemicals and their metabolites in waters adjacent to the Salton Sea area (Irwin, 1971; Eccles, 1979; Setmire, 1984; Spencer and others, 1985; Setmire and others, 1993, Crepeau and others, 2002). Elevated levels (parts per billion) of organochlorine and organophosphorous pesticides also were reported in these waters. Organochlorine pesticides were reported in bottom material collected from irrigation drainage canals (Setmire and others, 1993). More recently, Crepeau and others (2002) reported elevated concentrations of a number of current-use pesticides in water collected in 1996 and 1997 from the Alamo River and from the Salton Sea. The elevated pesticide concentrations in the Alamo River correspond with acute toxicity measured during standardized 96-hour aquatic toxicity tests done by deVlaming and others (2000).

Recent requirements for the Regional Water Quality Control Board (RWQCB), Colorado River Region, to develop total maximum daily loads (TMDLs) for contaminants, including pesticides, pointed to a need for a more complete understanding of the occurrence and transport of pesticides within the Salton Sea Basin. In addition, proposed remedial actions, such as the Salton Sea Restoration Project (a federal-state-local endeavor), and proposed water transfers to the San Diego County Water Authority, which may influence pesticide concentrations in rivers and drains that discharge into the Salton Sea and potentially within the sea itself, also indicate a need for a better understanding of the occurrence and transport of pesticides within the basin. Water transfers may lead to a shrinking of the sea, exposing more of the shoreline which consists of potentially contaminated sediment. The RWQCB requested the USGS to conduct a study to examine the distribution of pesticides in water and on suspended sediments and bed sediments in the rivers that drain into the Salton Sea, as well as within the sea itself. As a part of the study, the USGS analyzed trace elements and other selected inorganic constituents in suspended sediments.

Purpose and Scope

The primary objective of this study was to determine the occurrence and transport of historical and current-use pesticides in the Salton Sea Basin. A major focus of the study was to examine the distribution of pesticides in water, on suspended sediments and bed sediments in the three rivers that drain into the Salton Sea, and in the sea itself. Three sampling sites were established on each river in a transect beginning at the river outlet and extending into the sea (*fig. 1*). Water, suspended sediments, and bed sediments were collected at each site.

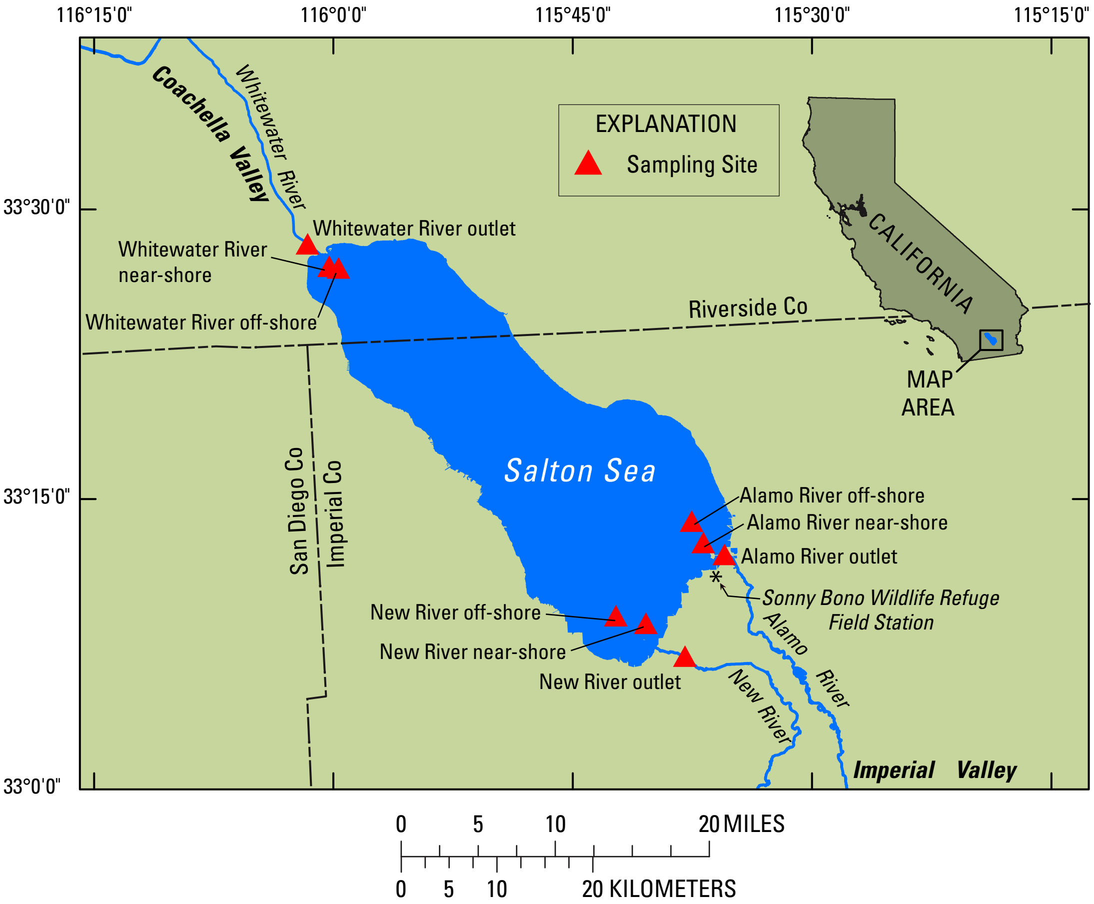

Figure 1. Location of study area and of sampling sites in the Salton Sea Basin, California.

This report presents the results for three sampling periods: October 2001, March and April 2002, and September 2002. Included are descriptions of sample collection and laboratory analytical methods for pesticide analysis, along with concentrations of current-use and organochloride pesticides in water, suspended sediment, and bed sediment. Pesticide-use data for 2001 for the State of California (California Department of Pesticide Regulation, 2001) are also presented. Suspended sediment concentration and the percentage of suspended sediment in the fine-grained fraction (less than 62 μm in diameter) were measured in all water samples. Dissolved organic carbon (DOC) was measured in water samples collected in October 2001. In September 2002, water from two sites on the New River were passed through an ultrafilter and both retentate (colloid) and filtrate fractions were analyzed for current-use pesticides. Organic carbon (OC) was measured in all suspended and bed sediments for all sampling periods. Trace elements and selected inorganic compounds were analyzed in suspended sediments collected during fall 2001.

Hydrogeologic Setting

The study area is in southeastern California; it includes the Salton Sea and the Coachella and Imperial Valleys adjacent to the north and south sides of the sea (*fig. 1*). This is an area of intensive agriculture; various crops are grown, including alfalfa, grapes, dates, cotton, and a variety of vegetables. The Salton Sea is a large (1,000 km^2) shallow (mean depth = 8 m) saline lake; its shoreline is at an elevation of about 70 m below sea level. The sea was formed as a freshwater lake between 1905 and 1907 as the result of uncontrolled flooding from the Colorado River. The water level in the Salton Sea has been maintained largely by agricultural irrigation drainage, which presently is about 1.7 km^3 per year (Schroeder and others, 2002). The largest rivers that flow into the sea, in order of their annual discharge, are the Alamo, New, and Whitewater Rivers. Forty-two year median daily flows ranged from 451 to 1,140 cubic feet per second (ft^3/s) for the Alamo River, 456 to 758 ft^3/s for the New River, and 81 to 120 ft^3/s for the Whitewater River (*fig. 2*) (U.S. Geological Survey, 2001). The Alamo and New Rivers flow into the southern end of the basin and the Whitewater River flows into the northern end (*fig. 1*). The Salton Sea has no outlet and minimal groundwater interaction (Schroeder and others, 2002). Because it is located in an arid region (precipitation is about 7 cm per year) with high evapotranspiration (approximately 1.8 m per year) and because freshwater flows consist of a high percentage of agricultural return water (water high in dissolved salts), salinity has been steadily increasing over time. The present salinity in the Salton Sea measured as conductivity is approximately 55,000 μS/cm; this is roughly equivalent to 45 parts per thousand (Setmire and Schroeder, 1998; Schroeder and others, 2002), which is about 1–3 times that of ocean water.

The Alamo and New Rivers receive small amounts of treated sewage from towns in the Imperial Valley. The New River also receives a large amount of wastewater and potentially untreated sewage from the relatively large municipality of Mexicali before the river crosses over into the United States. In addition to the issues of bacteria and pesticides in water from treated and untreated sewage, other issues of concern in the Salton Sea Basin include elevated concentrations of metals and nutrients (Setmire and others, 1993, Schroeder and others, 2002).

At their outlets to the Salton Sea, the Alamo and New Rivers are approximately 1 m deep and suspended sediment concentrations are a few hundred milligrams per liter. Suspended-sediment data in the USGS National Water Information System (NWIS) consist of four measurements from 1988–89 and ranged from 389 to 849 mg/L for the Alamo River and 351 to 613 mg/L for the New River (U.S. Geological Survey, 2001). Deposition of high loads of suspended sediment delivered by the rivers has resulted in the formation of broad shallow deltas, especially at the mouths of the New and Alamo Rivers. These shallow areas harbor large numbers of fish and birds and are adjacent to federal and state wildlife refuges.

Previous Studies

The earliest study of pesticides in the Salton Sea Basin include analysis of DDT in the Alamo and New Rivers in samples collected monthly between August 1969 and June 1970 (Irwin, 1971). High concentrations were found in the river water because DDT was still being used in the United States and Mexico. DDT has not been detected in the water since 1986 (Setmire and others, 1990), 14 years after its use was banned in the United States and 3 years after its use was banned in Mexico. However, the metabolite DDE was still present in sediments from both rivers, and concentration gradients (decreasing concentration downstream) were similar to that of the aqueous DDT concentrations from 20 years prior (Schroeder, 1996). This was taken as strong evidence that DDT and (or) its metabolites persist in surrounding agricultural soils and continue to be transported to the agricultural drains and rivers through agricultural tailwater. Concentrations of DDE have been reported in sediments from rivers and drains in the Salton Sea Basin (Schroeder and others, 1988). Residues of DDE have also been reported recently in biota from this area (Schroeder and others, 1993; Setmire and others, 1993).

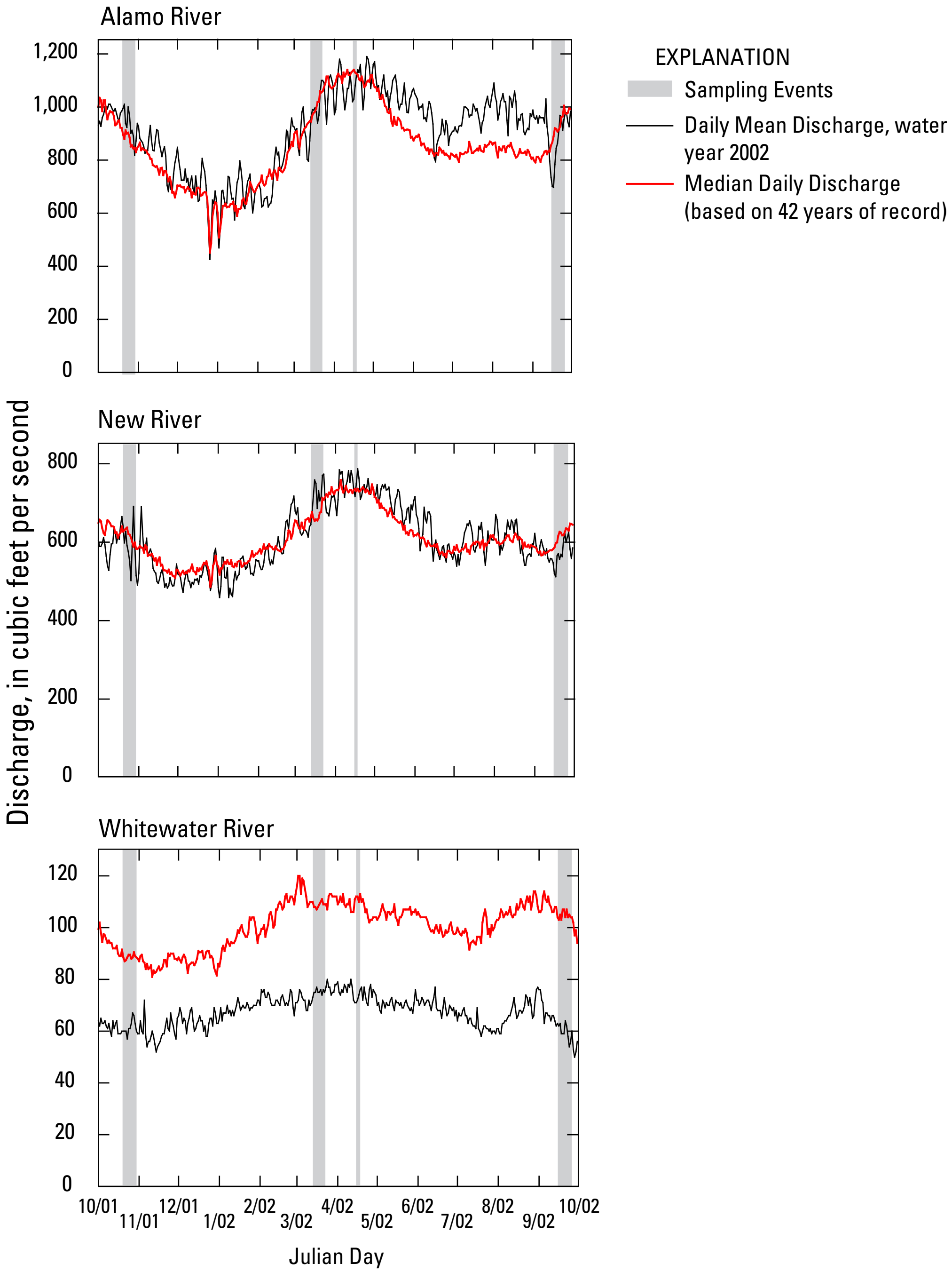

Figure 2. Daily mean discharge during three sampling periods and 42-year daily mean discharge for the Alamo, New, and Whitewater rivers in the Salton Sea Basin, California.

Numerous studies by the USGS during the last 30 years have documented the presence of organochlorine and current-use pesticides in water. Bimonthly monitoring for a period of 1 year in 1977–78 by the USGS showed that the temporal pattern of concentrations for many pesticides in drains and rivers in the Imperial Valley matched the seasonal pattern of pesticide application in the valley, with the maximum concentrations occurring in the late winter and early spring and again in the early fall (Eccles, 1979). The concentrations of pesticides in samples collected by the USGS in March through April 1992 and again in 1995–96 exhibited the same temporal pattern (Roy Schroeder, U.S. Geological Survey, [retired] written commun., 2002). Monthly monitoring on the Alamo River in 1994–95 by the University of California (UC) at Davis confirmed the same temporal pattern and identified five commonly used pesticides (carbaryl, carbofuran, chlorpyrifos, diazinon, and malathion) as the cause of high mortality of Ceriodaphnia dubia during standardized aquatic toxicity tests (de Vlaming and others, 2000). A 1996–98 study by the USGS, in collaboration with the UC Davis Toxicology Laboratory, identified elevated levels (greater than 100 ng/L) of nine pesticides in water from the Alamo River 1 mi upstream from the discharge point at Garst Road, as well in water from

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Pesticide-Use Database and GIS Methods

For the purpose of defining pesticide use in the Salton Sea watershed, data from the California Department of Pesticide Regulation's (CDPR) Pesticide Use database (California Department of Pesticide Regulation, 2001) were compiled in a Geographic Information System (GIS). The Salton Sea watershed, derived from the 12-digit hydrologic unit boundaries for California, comprises all areas that drain naturally into the Salton Sea. Records of registered pesticide use for 2001 were extracted from the CDPR Pesticide-Use database (California Department of Pesticide Regulation, 2001) using the limits of the watershed boundary, which includes portions of Imperial and Riverside Counties. The data was reported as total pesticide use for 2001 (*table 1*).

Table 1. Pesticides applied within the Salton Sea Basin, California, April 2000–October 2001, that were included in the water and sediment analyses.

[All values are in pounds (lbs.). Source: California Department of Pesticide Regulation (2001). Samples were also analyzed for the following pesticides, which had not been applied in the Salton Sea Basin during the study period: azinphos-methyl, butylate, diethylatyl-ethyl, fonofos, hexazinone, methidathion, monlinate, pebulate, sulfotep, and thiobencarb]

Pesticide	Pesticide application periods		
	November 2000–October 2001	November 2000–March 2001	April 2000–October 2001
Alachlor	91	91	0
Atrazine	19,208	14,108	5,100
Bifenthrin	423	23	400
Carbaryl	3,337	432	2,905
Carbofuran	8,909	8,828	81
Chlorpyrifos	101,368	27,320	74,048
Cycloate	6,011	2,074	3,937
Cyfluthrin	4,690	2,352	2,338
Cypermethrin	1,734	1,091	643
Dacthal	42,799	5,361	37,438
Diazinon	39,280	8,392	30,888
EPTC (eptam)	106,569	41,560	65,009
Esfenvalerate	3,286	552	2,734
Ethafluralin	126	126	0
lambda Cyhalothrin	2,550	1,097	1,453
Malathion	122,730	91,950	30,780
Methyl parathion	15	0	15
Metolachlor	228	0	228
Napropamide	1,362	346	1,016
Oxyfluorfen	5,312	3,526	1,786
Pendimethalin	28,770	17,960	10,810
Permethrin	10,961	4,461	6,500
Phosmet	138	63	75
Prometryn	953	640	313
Simazine	126	124	2
Trifluralin	277,604	211,600	66,004

Sample Collection Methods

Transects consisting of three sampling sites each for the three major rivers in the Salton Sea Basin were established to examine the transport of pesticides (*fig. 1*). The outlet sites were established approximately 1.6 km upstream of the mouths of the New and Alamo Rivers and 6 km upstream of the mouth of the Whitewater River. The near-shore sites were established close to the river, and the off-shore sites were established in water 15-ft deep. Samples collected during fall 2002 at the New River near-shore site were taken from above and below the halocline. The halocline, which was easily visible, is the sharp transition zone between the fresh, less dense river water flowing above the more dense, saltier Salton Sea water. The coordinates for each site are listed in *table 2*. Water temperature and conductivity were measured using a handheld digital thermometer (VWR Scientific, Westchester, Pa.) and an Orion conductivity meter (Orion Instruments, San Jose, Calif.), respectively. Fifty mL water samples were collected during the pumping of the large volume water samples (described in the section entitled "Large Volume Water Samples") and sent to the organic chemistry laboratory at the USGS California District office in Sacramento for more accurate measurements of pH and conductivity.

Large-Volume Water Samples

Large-volume water samples (for isolating suspended sediments) and bed sediment samples were collected at the nine sampling sites in the Salton Sea and adjacent rivers (*fig. 1*). Samples were collected using a large peristaltic pump powered by a portable generator and equipped with a stainless steel and Teflon inlet hose. Sample water was pumped directly into pre-cleaned 20 L stainless-steel containers for transport. The volume of the water samples varied for each sampling site but generally were greater than 300 L. One-liter aliquots were taken from the large-volume water samples for analysis of dissolved pesticides. The collection of samples from the off-shore sites required multiple boat trips, but sampling always was completed within a 24-hour period.

Samples from the three outlet sites were collected by pumping water samples into the stainless-steel containers from bridges and a culvert. The samples were collected from a single point at the center of the river channel using a pump inlet hose suspended at a depth of 0.5 m. The six near-shore and off-shore sites were accessed by boat and located using a handheld global positioning system device (Garmin GPS 12, Garmin International Inc., Olathe, Kans.). Samples from the three near-shore delta sites were collected at a depth representing the mixing zone between fresh river water and more saline sea water, which was determined at the time of collection using a handheld specific conductance meter. Samples from the deeper water off-shore sites were collected from a depth of approximately 0.5 m below the surface.

Additional samples were collected to measure suspended-sediment concentrations and percent fine-grained sediments. For these samples, water was pumped into pre-cleaned 500-mL clear glass bottles during the large-volume sample collection.

Isolation of Suspended Sediments

Suspended sediments were isolated by pumping the water through a flow-through centrifuge (Westphalia model KA-2, Westfalia Corporation, Odele, Federal Republic of Germany). Water (300–900 L) was pumped at a flow rate of 2 L/min through the centrifuge, which spun at 9,800 revolutions per minute (rpm) and operated at a centrifugal force of 9,500 times the gravitational constant, g. A 2-L/min flow-rate has been shown to be an optimal flow rate for efficient capture of a wide variety of grain sizes (2 µm and larger) at a wide range of suspended sediment concentrations (Horowitz and others, 1989). Sediment was carefully removed from each of the concentric centrifuge bowls. Water remaining in the bowls was used to rinse the sediment off the surfaces of all the bowls. The resulting sediment slurry was stored refrigerated at 4°C in pre-cleaned glass bottles and transported to the organic chemistry laboratory at the USGS California District Office Sacramento for further dewatering. In the laboratory, the suspended material was futher dewatered by centrifuging in 200-mL stainless-steel centrifuge bottles for 20 minutes at 10,000 rpm in a high-speed refrigerated centrifuge (Sorvall RC-5B centrifuge, Du Pont Company, Wilmington, Del.). The water was decanted and the remaining solid material scraped out of the centrifuge bottles and stored frozen in pre-cleaned glass screw-cap bottles until analysis.

Collection of Samples for Dissolved Pesticide Analysis

Samples for analysis of dissolved pesticides were collected in 1 L amber glass bottles from the outlet of the Westfalia flow-through centrifuge. The Westphalia centrifuge has been found to retain particles of 0.5 µm and greater (Horowitz and others, 1989). A similar centrifuge described by Rees and others (1991) retained particles of 0.3 µm and greater. Because of the large amount of water filtered for suspended sediments (300–900 L), the samples were collected during the beginning, middle, and end of the centrifuging process. There appeared to be no difference between these replicate samples in terms of the pesticides detected, or their relative concentrations (see discussion of replicate variability in the section entitled "Solid-Phase Extraction of Water Samples" in the "Methods" section).

Table 2. Pesticide sampling sites in the Salton Sea Basin, California.

[See *figure 1* for location of sampling sites. Horizontal datum is North American Datum of 1927 (NAD27). USGS, U.S. Geological Survey. m, meter; km, kilometer]

Station name	Latitude	Longitude	USGS station identifier	USGS site name	Description
Alamo River outlet	33°11′56″	115°35′46″	10254730	Alamo River near Niland	Bridge at Garst Road
Alamo River near-shore	33°12′42″	115°37′14″	331242115371401	Salton Sea near mouth of Alamo River	Within Salton Sea, approximately 0.25 km from river mouth
Alamo River off-shore	33°14′00″	115°38′00″	331400115380001	Salton Sea in Alamo River Delta	Within Salton Sea approximately, 2.9 km from river mouth
New River outlet	33°05′59″	115°38′56″	33055911585601	New River at Lack Road near Calipatria	Bridge at Lack Road
New River near-shore	33°08′03″	115°41’40″	330803115414001	Salton Sea near mouth of New River	Within Salton Sea, approximately 100 m from river mouth
New River off-shore	33°08′35″	115°43′45″	330835115434501	Salton Sea in New River Delta	Within Salton Sea, approximately 3.5 km from river mouth
Whitewater River outlet	33°31′29″	116°04′36″	10259540	Whitewater River near Mecca	Culvert at Lincoln Road
Whitewater River near-shore	33°30′06″	116°03′15″	333006116031501	Salton Sea near mouth of Whitewater River	Within Salton Sea, approximately 500 m from river mouth
Whitewater River off-shore	33°29′58″	116°02′35″	332958116023501	Salton Sea in Whitewater River Delta	Within Salton Sea, approximately 1.5 km from river mouth

Over the course of the study, a few samples were collected in a manner different from that described above. Samples were collected at the New River near-shore site in fall 2002; the samples were collected from above and below the halocline to compare pesticide abundances from river-transported water (above the halocline) with those in Salton Sea water (below the halocline). Normally, the near-shore water samples were collected at the freshwater/saltwater interface, where the pump hose continuously moved up and down through the halocline with the motion of the boat.

Ultrafiltration and Colloid Isolation

During the fall 2002 sampling period, water from the New River near-shore and off-shore sites was passed through an ultrafiltration apparatus consisting of an Amicon spiral-wound cartridge filter (regenerated cellulose fiber with an area of 3.05 m^2 and an effective molecular weight cutoff of 1,000 daltons) and an Amicon DC-10 centrifugal pump (Amicon Corporation, Beverly, Mass.). The water, which was passed through the flow-through centrifuge to remove suspended sediment, was separated into retentate and filtrate portions to determine colloidally bound (retentate) and 'truly dissolved' (filtrate) pesticide pools. Approximately 40 L of effluent from the flow-through centrifuge was pumped through the ultrafilter to yield approximately 2 to 4 L of retentate (the colloid fraction). The retentate (2–4 L) and a subsample of the filtrate (approximately 4 L) were preserved using 150 to 250 mL of methylene chloride and transported to the USGS California District organic chemistry laboratory in Sacramento. There, each sample was extracted three times with methylene chloride and the extracts were reduced and analyzed using gas chromatography/mass spectrometry (GC/MS) for current-use pesticides, as described below and in Crepeau and others (2000).

Three samples were processed through the ultrafilter for analysis of pesticides in filtrate and retentate fractions. One sample was from the New River outlet site (basically fresh water) and one sample was from the considerably more saline New River off-shore site. To aid in the comparison of the outlet and the off-shore samples, sea salts (Instant Ocean, Aquarium Systems, Inc., Mentor, Ohio) were added to a second outlet sample so that the resulting conductivity matched the conductivity measured in the off-shore sample prior to ultrafiltration. This was done to examine how differences in salinity would effect the partitioning of pesticides between the colloidal and retentate fractions at the same site and with identical pesticide concentrations. Differences observed in partitioning between the river outlet and the off-shore samples greater than those observed between the salted and the unsalted outlet samples may be attributed to factors other than salinity.

Ultrafilter Calibration

The Amicon filter was calibrated by determining the retention efficiency of a marker compound of a known size and shape. Vitamin B12, with a molecular size of 1,355 daltons, was added to 20 L of water and passed through the ultrafilter. Because the nominal cutoff given by the manufacturer is 1,000 daltons, it was expected that a large percentage of vitamin B12 would be retained by the filter if it was working properly. The retention efficiency of the filter was determined for deionized water with vitamin B12 and for deionized water with vitamin B12 and sea salts added. Concentrations of vitamin B12 were determined in the retentate and filtrate using ultraviolet/visible (UV/Vis) spectroscopy (Cary UV/Vis spectrophotometer, Varian Corporation, Walnut Creek, Calif.) at a wavelength of 360 nm. Samples of filtrate and retentate were monitored during the ultrafiltration. A mass balance was calculated by summing filtrate and retentate concentrations at the end of the filtration and comparing the mass balance value with the initial concentration.

Similar measurements and calculations were made for the three samples (New River outlet sample, New River off-shore sample, and the salt enhanced New River outlet sample) using dissolved organic carbon as a marker. DOC contains a spectrum of compounds, with a variety of molecular weights and sizes (some smaller than 1,000 daltons), and so would not be expected to be retained to the same degree as the vitamin B12. However, measuring DOC allowed us to confirm that a DOC-rich (colloidal) fraction was successfully isolated, and mass-balance calculations verified that no unexplained losses of DOC occurred as a result of the ultrafiltration. DOC concentrations were measured in the retentate and filtrate fractions of each sample as described in the next section. Ultrafiltrate and retentate DOC concentrations were summed and compared with DOC concentrations in whole water for mass balance calculations. Retention efficiciency was calculated by dividing the total mass of DOC in the retentate by the sum of DOC in retentate plus filtrate.

Calibration of the Amicon filter resulted in 75 percent or better retention of vitamin B12, using both deionized water as well as deionized water with sea salts added (*table 3*). The mass balance between the filtrate and retentate was excellent, giving us further confidence that we could efficiently isolate dissolved organic material in the molecular weight range of 1,000 daltons or larger.

Table 3. Retention and mass balance estimates of vitamin B12 in deionized water and dissolved organic carbon in samples from the New River in the Salton Sea Basin, California, September 2002.

[DI, deionized. mg/L, milligram per liter]

Sample	Retention (percent)	Mass balance (percent)	Concentration factor
Vitamin B12			
Amicon filter, DI water	76	105	4.8
Amicon filter, DI water[1]	84	111	7.9
Amicon filter, DI water + sea salts	84	93	3.2
Amicon filter, DI water + sea salts[1]	75	87	6.4
Dissolved organic carbon (mg/L)			
New River outlet	52	75	8.2
New River outlet + sea salts	22	120	15.2
New River off-shore	37	82	17.4

[1] Duplicate sample.

Retention efficiency and mass balance estimates for DOC in the two water samples from the New River outlet and the one sample from the off-shore site are also shown in *table 3*. There was a difference in percent retention of organic carbon between the highly saline samples (New River outlet sample with salts added and the New River off-shore sample) and the outlet sample, which may be due to a salinity effect not replicated by the use of sea salts. Also, higher concentration factors used for the salt-enhanced outlet sample and the off-shore sample may have resulted in a decrease in retention efficiency of the dissolved organic material. The retention efficiency of low molecular weight DOC can be affected by higher concentrations factors (Guo and Santschi, 1996; Guo and others, 2000).

Adding salt to a second New River outlet sample, to approximate the salinity of the New River off-shore sample, did not provide useful information for interpreting the difference in partitioning between the two types of samples (highly saline off-shore sample and less saline river sample). Upon addition of the salt, a great deal of flocculation began to occur, which quite possibly removed both dissolved organic material and pesticides from the water. This was most likely due to the fact that several divalent ions were at near saturation concentrations in river water, a fact discussed by Schroeder and others (2002).

Bed Sediment

Bed sediment samples were collected concurrently with the water samples at each of the nine sampling sites. Samples taken at the outlet sites were collected using either a 9-inch Ekman grab sampler or a 2-inch diameter, Teflon-barreled hand corer. Multiple grabs were required to obtain approximately 0.5 L for each site. Samples were collected only from the top 2 cm of undisturbed sediment collected during each grab. At the river sites, multiple core samples (5–7) were composited to make a sample. At the near-shore and off-shore sites, composites of 2 to 3 grabs were taken using the Eckman dredge. Sediment was scooped into cleaned, 0.5-L glass jars using a stainless-steel spoon.

Laboratory Methods

Solid-Phase Extraction of Water Samples

Pesticides were extracted from water samples using solid-phase extraction (SPE) cartridges. This method is described in detail in Crepeau and others (2000). Prior to sample extraction, the volume of water to be extracted was determined and 100 µL of a 2 ng/µL surrogate (terbuthylazine) was spiked into the sample. The water then was pumped through a pre-cleaned and conditioned C8 SPE cartridge (Varian Bond-Elut, 500 mg, 300 cubic centimeter size barrel, Varian Analytical Corporation, Walnut Creek, Calif.) using 12-volt ceramic-piston metering pumps at a rate of 20 to 25 mL/min. To condition the SPE cartridge, 3 mL of methanol followed by 3 mL of organic-free water was passed through the cartridge. The cartridge was then kept wet using water until the extraction step. After the extraction, excess water was removed from the cartridge by passing air through it using a luer-lock syringe. Cartridges were labeled and kept refrigerated; within 3 days of collection they were sent to the USGS California District organic chemistry laboratory in Sacramento for storage. Upon receipt of the samples in Sacramento, the cartridges were further dried using carbon dioxide (CO_2) for at least 1 hour. Cartridges were stored frozen until analysis, which did not exceed the established holding time of 2 months (Crepeau and others, 2000).

Samples were eluted from the SPE cartridges using 9 mL of ethyl acetate, reduced in volume to 500 µL by evaporation using a stream of nitrogen gas (N-evap, Organomation Associates, Kansas City, Mo.) and appropriate concentrations of internal standards added. Deuterated polyclic aromatic hydrocarbon (PAH) compounds were used as internal standards and included d_{10}-acenaphthene, d_{10}-phenanthrene and d_{10}-pyrene. The d subscript designation (for example, d_{10}) refers to the number of labeled deuterium atoms incorporated into the compound. Extracts were brought to a final volume of 200 µL and analyzed using GC/MS as described in the “Instrumental Analysis” section. Full details of the extraction method are provided in Crepeau and others (2000).

Several quality-control procedures were implemented during this study. Samples processed for quality-control purposes included field and laboratory blanks, national laboratory sample replicates, and matrix spikes.

Field equipment blanks consisted of 1-L samples of organic-free deionized water (as determined by the method of Bird and others [2003]) from the water-purification system at the California District organic chemistry laboratory in Sacramento. This water was passed through the centrifuge and collected in 1-L amber bottles and extracted using C8 SPE cartridges. In addition, a 1-L bottle of deionized water was left uncapped for several days to assess background pesticide concentrations in the field. For laboratory water blanks, 1 L of deionized water was extracted using a C-8 SPE cartridge. The sample was subsequently eluted and then analyzed using GC/MS.

For a select number of sites (three per sampling trip), replicate water samples were collected, extracted using C18-SPE cartridges and the same procedures as those used for the C8-SPE cartridges, and mailed to the USGS National Water Quality Laboratory (NWQL) in Denver, Colo., for analysis. This served as an independent check of our water analysis procedures. Sample handling and holding-time requirements of the NWQL were strictly adhered to.

For matrix spikes, a solution containing 400 ng of each of the analytes listed in *table 4* was spiked to 1-L bottles of deionized water and processed using the SPE water extraction method. Three matrix spike samples were processed for each sampling period, for a total of nine matrix spike samples.

Detection limits for dissolved pesticides were in the low nanogram per liter range (*table 5*). The average recoveries for pesticides spiked to the water matrix spike samples were 85 ± 20 percent but generally were greater than 80 percent. Results of the analysis of replicate samples for fall 2001 showed excellent agreement, within 10 percent (coefficient of variation). A comparison of pesticide concentrations in the nine replicate samples analyzed in Sacramento, Calif., and Denver, Colo., laboratories also showed excellent agreement, with concentrations often agreeing within 10 percent, and never exceeding 25 percent. Field or equipment blanks generally showed low detections of pesticides or no detection. However, low concentrations (1–2 ng/L) of diazinon and dacthal were discovered in two field blanks. The presence of background concentrations of a few pesticides was demonstrated during the fall 2002 sampling period by leaving a bottle of deionized water uncovered for several days during sample processing. Background concentrations of chlorpyrifos and dacthal (4 ng/L) and somewhat higher concentrations of EPTC, also known as eptam (30 ng/L), were detected in this sample. No pesticides were detected in the laboratory blanks processed at the USGS California District laboratory.

Table 4. Current-use pesticide analytes and quantification and confirmation ions monitored during gas chromatography/mass spectrometry analysis of water samples from sampling sites in the Salton Sea Basin, California.

[See *table 8* for internal and surrogate standards]

Pesticides	Quantification ions	Confirmation ions
Alachlor	160	188, 146
Atrazine	200	202, 215
Azinphos-methyl	132	181, 160
Bifenthrin	181	166, 165
Butylate	146	156, 90
Carbaryl	144	115, 116
Carbofuran	164	149, 131
Chlorpyrifos	314	314, 197
Cyanazine	212	198, 172
Cycloate	154	155, 186
Dacthal	301	299, 303
Diazinon	179	137, 199
Diethylatyl-ethyl	188	160, 262
EPTC (eptam)	128	132, 127
Esfenvalerate	225	125, 167
Ethafluralin	276	316, 292
Fonofos	109	137, 110
Hexazinone	171	128, 172
lambda-Cyhalothrin	181	197, 141
Malathion	173	125, 173
Methidathion	145	93, 125
Methyl parathion	263	247, 246
Metolachlor	162	238, 240
Molinate	126	98, 127
Napropamide	100	125, 257
Oxyflurofen	300	300, 302
Pebulate	128	132, 127
Pendimethalin	252	191, 162
Permethrin	183	127, 163
Phosmet	160	133, 206
Piperonyl Butoxide	176	177, 149
Prometryn	184	241, 226
Simazine	201	186, 173
Sulfotep	322	238, 210
Thiobencarb	100	125, 257
Trifluralin	264	306, 248

Liquid-Liquid Extraction of Ultrafiltered Water: Retentate and Filtrate Fractions

Pesticides were isolated and concentrated from retentate and filtrate fractions of the ultrafiltered water by liquid-liquid extraction, using methylene chloride. The samples, which contained 200 to 250 mL methylene chloride, were poured into separatory funnels, and the terbuthylazine surrogate standard was added. Additional methylene chloride was added to the separatory funnels to bring the methylene chloride volume to 10 percent of the sample water volume; the samples were shaken for approximately 3 minutes. The methylene chloride was drawn out of the bottom of the separatory funnel and the process repeated twice more. The extracts were combined and dried over sodium sulfate. The volumes of the extracts then were reduced by rotary evaporation (Yamato Rotory Evaporator, Yamato Scientific Co, Japan) to approximately 10-mL, transferred to 10 mL condensor tubes and further reduced in volume to 500 µL by nitrogen evaporation. Deuterated PAH internal standards were added, and the samples were reduced to a final volume of 200 µL prior to injection into the GC/MS.

Dissolved Organic Carbon Analysis

Water samples were filtered using 2.7 µm (Whatman GF/A, Whatman Scientific, Maidstone, England) and 0.7 µm (Whatman GF/F) glass fiber filters and a 0.45 µm polypropylene filter (Pall Gelman GH Polypro Membrane, Gelman Sciences, Inc., Ann Arbor, Mich.). After filtration, the samples were stored in amber glass bottles at 4°C until analyzed.

DOC measurements were made using a Shimadzu TOC-5000A total organic carbon analyzer (Shimadzu Scientific Instruments, Columbia, Md.). The instrument was calibrated using potassium hydrogen phthalate standards prepared in organic-free water, with standard concentrations bracketing the concentration of the samples. Aliquots of a sample (4.5 mL) were acidified using 30 µL of 2-normal hydrochloric acid and sparged using N_2 for 3 minutes to remove inorganic carbon as CO_2. The non-purgeable organic carbon (NPOC) was analyzed by direct injection of a liquid sample into a high-temperature (680ºC) combustion tube packed with platinum catalyst. The CO_2 produced by oxidation of the NPOC was detected using a non-dispersive infrared photometric cell. Each sample was injected three times and the resultant mean concentration for the three injections was calculated. Additional details about the instrumental method can be found in Bird and others (2003).

Table 5. Method detection limits for pesticides in water samples from sampling sites in the Salton Sea Basin, California, 2001.

Pesticides	Method detection limit, in nanograms per liter
Alachlor[1]	2.1
Atrazine	4.2
Azinphos-methyl[1]	11.1
Butylate[1]	1.8
Carbaryl	4.2
Carbofuran	3.3
Chlorpyrifos	4.2
Cyanazine[1]	3.0
Cycloate	1.5
Dacthal	1.2
Diazinon	3.6
Diethatyl-ethyl[1]	3.6
EPTC (eptam)	4.5
Ethalfluralin[1]	2.4
Fonfos[1]	2.4
Hexazinone[1]	5.7
Malathion	2.1
Methidathion[1]	5.4
Methyl parathion[1]	4.2
Metolachlor[1]	3.3
Molinate[1]	2.7
Napropamide	7.2
Oxyfluorfen	4.2
Pebulate[1]	.6
Pendimethalin	2.4
Phosmet[1]	4.2
Piperonyl butoxide[1]	3.3
Simazine	6.9
Sulfotep[1]	1.2
Thiobencarb[1]	3.9
Trifluralin	3.0

[1] Pesticide not detected in any sediment samples during any of the sampling periods.

Sediment Analysis

Extractions from suspended sediment and bottom sediment samples were performed using either soxhlet or microwave-assisted solvent extraction (MASE). The MASE system was an MSP 1000 (CEM Corporation, Matthews, N.C.). Soxhlet extraction was used on the samples collected from the deep-water areas because pressure buildup inside the teflon extraction vessels during the MASE extraction process occurred quite rapidly, sometimes leading to a containment failure and a loss of the sample. For both types of extraction methods, wet sediments were extracted to avoid any artifacts associated with the drying of sediment, and because water is needed in the sample for efficient extraction when using MASE (Jayaraman and others, 2001). Approximately 5 grams (dry weight) of sediment was extracted for each sample. Percent water in each sample was determined gravimetrically by weighing the wet sediments and then drying and reweighing to a constant dry weight. A wet weight equivalent to 5 grams dry weight was calculated for each sample after determining the percent water.

After the wet sediments were weighed into the extraction vessels (teflon MASE vessels or pre-cleaned cellulose soxhlet extraction thimbles), a surrogate solution containing 400 ng each of ${}^{13}C_6$-α–benzenehexachloride (α-BHC), ${}^{13}C_6$-permethrin (*cis/trans* mixture), ${}^{13}C_3$-simazine, and d_{10}-chlorpyrifos (Cambridge Isotope Laboratories, Inc, Andover, Mass.) was spiked into each sample. The sediments were extracted using a mixture of methylene chloride and acetone (50:50 volume/volume). The soxhlet extraction took 16 hours and used 150 mL of solvent whereas the MASE extraction, which was done twice, took only 20 minutes and used only 30 mL of solvent. The samples in the MASE extractor reached temperatures of 120°C and pressures of 150 pounds per square inch (psi). Comparisons of MASE and soxhlet extraction techniques for the extraction of a wide variety of hydrocarbons, including current-use pesticides on soils and sediments, have yielded similar results (Pastor and others, 1997; Blanco and others, 2000 and Camel, 2000).

Extracts were decanted into separatory funnels containing 100 mL (for MASE) or 250 mL (for soxhlet) of deionized, organic-free water. The mixture was shaken for approximately 1 minute and the methylene chloride removed. The aqueous phase was extracted twice more using two volumes of methylene chloride (2 × 30 mL for MASE and 2 × 100 mL for soxhlet). The combined extracts were then dried over sodium sulfate and reduced to approximately 1 mL by rotary evaporation. These extracts, many of which were darkly colored, were cleaned by passing them through an SPE column consisting of 500 mg of activated carbon (6-cubic centimeter size barrel, Restek Corporation, Bellefonte, Pa.) followed by elution using 10 mL of methylene chloride.

Samples were then solvent-exchanged to ethyl acetate, reduced in volume to 0.5 mL by nitrogen evaporation and further purified using a gel permeation/high pressure liquid chromatography system (GPC/HPLC). The sample was injected into a Perkin Elmer HPLC consisting of a PE 410 4-stage pump and a LC-95 UV fixed wavelength detector (Perkin Elmer Corporation, Norwalk, Conn.). The analytical column was a gel permeation column from Polymer Laboratories (Amherst, Mass.). Column dimensions were 300 × 7.5 mm and the packing was polydivylbenzene (10 mm, 50-angstrom pore size). Ethyl acetate (which was used as the mobile phase in the procedure) was pumped through the column at a rate of 1 mL/min. The size of the collection window was verified daily using pesticide standards and monitoring at a wavelength of 254 nm. GPC/HPLC provided additional matrix cleanup, especially with the elimination of elemental sulfur, which is a major co-extractant that interferes with GC/MS instrumental analysis (Goerlitz and Law, 1971; Jensen and others, 1977).

After the GPC/HPLC cleanup step, the sample extract, at a volume of 9 mL, was reduced to approximately 500 µL. For GC/MS analysis, internal standards (the same as for the water samples) were added to the sample and the sample was brought to a final volume of 500 µL by N_2 evaporation. In the case of extremely colored extracts, the sample was brought to a volume of 1 mL prior to the GC/MS analysis.

Method Validation

Significant modifications to the multi-residue pesticide method for sediments (Bergamaschi and others, 1999) were made during this investigation. The resulting method included several additional analytes and improved method detection limits. Method detection limit concentrations ranged from 0.6 to 7.6 ng/g (*table 6*). Pesticides having detection limits greater than 2 ng/g generally showed greater variability in calibration standards and in spiked sediment extracts, and were the first compounds to begin tailing as the GC column began to age. The sediment matrix spikes for bottom sediment from an agricultural drain along the Sacramento River in northern California showed reasonable recoveries for most of the analytes (*table 7*). Some analytes, however, such as disulfoton, cyanazine, butylate, eptam, pebulate, and phorate had recoveries of 60 percent or less. Of these compounds, only eptam was detected in significant quantities. Eptam most likely was lost during extract concentration (rotary evaporation and N_2 evaporation steps) due to its low vapor pressure and high volatility (Mackay and others, 1997).

Table 6. Method detection limits for pesticides and DDTs in sediments from sampling sites in the Salton Sea Basin, California.

[DDT refers to DDT and the metabolites DDD and DDE]

Pesticide	Method detection limit, in nanograms per liter
Alachlor	1.1
Atrazine[1]	.6
Azinphos-methyl[1]	7.6
Bifenthrin	.9
Butylate[1]	.5
Carbary[1]	1.2
Carbofuran	3.0
Chlorpyrifos	1.5
Cyanazine[1]	1.8
Cycloate[1]	1.8
Cyfluthrin[1]	7.9
Cypermethrin[1]	5.6
Dacthal	.6
Diazinon	1.5
Diethatyl-ethyl[1]	1.2
Endosulfan I[1]	5.5
EPTC (eptam)	.7
Esfenvalerate	1.4
Ethalfluralin[1]	1.9
Fenamiphos[1]	.8
Fonofos	2.5
Hexazinone[1]	3.2
lambda-Cyhalothrin	.5
Malathion[1]	1.5
Methidathion	3.4
Methyl parathion[1]	1.6
Metolachlor	1.0
Molinate[1]	2.0
Napropamide[1]	1.6
Oxyfluorfen	6.1
Pebulate[1]	.8
Pendimethalin	4.0
Permethrin	1.4
Phosmet[1]	.8
Piperonyl butoxide[1]	1.2
Prometryn	1.8
Simazine[1]	2.1
Sulfotep[1]	1.1
Thiobencarb[1]	4.4
Trifluralin	1.4
p,p′-DDD	2.9
p,p′-DDE	3.7
p,p′-DDT	3.9

[1] Pesticide not detected in any sediment samples during any of the sampling periods.

Quality Assurance/Quality Control

Sediment matrix spike and laboratory blank samples were processed for quality-control purposes. For matrix spikes, a mixture containing 400 ng each of the pesticides listed in tables *4* and 8, was spiked into suspended and bed sediments (five samples) obtained from the Whitewater River outlet and near-shore sites collected during fall 2001. The sediments were extracted and analyzed as described in the "Sediment Analysis" section. In addition to matrix spikes, percent recoveries were calculated for the four surrogate compounds described previously in the "Sediment Analysis" section.

Method detection limits were determined by spiking seven replicate sediment samples using a pesticide mix containing 50 ng each of the pesticides listed in *table 4*. Sediment from the agricultural drain in northern California also was used for matrix spike samples. Method detection limits were calculated by multiplying the standard deviation of the mean concentration of each analyte by 3.143, the corresponding value of Student's t for $p = 0.01$ and 6 degrees of freedom (from Sokal and Rohlf, 1983).

Matrix interference negatively affected both the surrogate and the matrix spike recoveries in the Salton Sea sediments. This effect was most prononounced in the off-shore suspended-solids samples, which consisted primarily of algal detritus. The mean recoveries of d_6-α-HCH, d_3-simazine, and d_{10}-chlorpyrifos for bed sediments and suspended sediments were 66 ± 16 percent, 91 ± 35 percent, 78 ± 19 percent, respectively. Recovery of the d_6-permethrin surrogate was extremely variable (92 ± 77 percent), which made the quantitation of permethrin, cypermethrin, and cyfluthrin in the sediments suspect. Therefore the qualifier "D" was used when permethrin or similar compounds (such as cyfluthrin and cypermethrin) were detected to signify that the compound was detected but that quantitation is highly uncertain.

Average recoveries for five sediment matrix spikes performed using suspended sediment and bed sediment from the Whitewater River off-shore sites were between 51and 109 percent for all compounds, with an overall mean average recovery of 72 ± 22 percent for the pesticides that were detected in suspended and bed sediments.

Instrumental Analysis

Water and sediment extracts were analyzed for pesticides using a Saturn 2000 GC/MS ion trap system (Varian, Inc., Walnut Creek, Calif.). Run conditions are listed in *table 9*. The instrument was operated in full scan mode during most of the run; however, later in the run, selected ion storage (SIS), which is equivalent to selected ion monitoring (SIM) in a quadrupole instrument, was used to optimize instrument sensitivity to select analytes.

Table 7. Average recovery of pesticides used in the Salton Sea Basin, California, spiked to bottom sediment from an agricultural drain along the Sacramento River in northern California.

Pesticides	Mean recovery ± standard deviation (n = 3) (percent)
Triazines/Triazones	
Atrazine	83 ± 14
Cyanazine	56 ± 11
Hexazinone	110 ± 12
Prometryn	70 ± 9.0
Simazine	83 ± 14
Terbuthylazine	73 ± 11
Anilines	
Ethafluralin	71 ± 7.3
Pendimethalin	79 ± 11
Trifluralin	74 ± 9.0
Chloracetanilides	
Alachlor	77 ± 9.3
Metolachlor	68 ± 9.8
Carbamates	
Carbaryl	100 ± 12
Carbofuran	78 ± 11
Thiocarbamates	
Butylate	55 ± 2.2
Cycloate	69 ± 3.7
EPTC (eptam)	54 ± 1.9
Molinate	79 ± 2.4
Pebulate	58 ± 3.0
Thiobencarb	160 ± 15
Organophosphates	
Azinphos-methyl	110 ± 11
Chlorpyrifos	69 ± 8.6
Diazinon	82 ± 12
Dimethoate	89 ± 13
Disulfoton	41 ± 4.7
Fenamiphos	91 ± 9.0
Fonofos	82 ± 8.2
Malathion	65 ± 9.0
Methidathion	78 ± 9.5
Methyl parathion	80 ± 11
Phorate	59 ± 3.2
Phosmet	89 ± 11
Profenfos	61 ± 8.8
Sulfotep	65 ± 5.6
Pyrethroids	
Bifenthrin	62 ± 8.5
Cyfluthrin	99 ± 8.8
Cypermethrin	97 ± 9.4
Esfenvalerate	92 ± 12
lambda-Cyhalothrin	74 ± 9.5
Permethrin	82 ± 12
Miscellaneous	
Dacthal	71 ± 9.6
Diethatyl-ethyl	70 ± 9.7
Endosulfan	74 ± 8.1
Napropamide	81 ± 9.9
Oxyflurofen	88 ± 12
Propargite	79 ± 12

Table 8. Organochlorine analytes, internal and surrogate standards, and corresponding ions monitored for quantification and confirmation purposes.

[BHC, benzenehexachloride; alpha, beta, delta, and gamma are positional isomers. Quantification ion is the ion from the mass spectra used to quantify the compound. Confirmation ions are ions that, with the quantification ion, are used to identify the compound. d is a notation used to signify the number of deuterium atoms in a deuterium-labeled compound. d_{10} signifies the presence of 10 deuterium atoms]

Compounds	Quantification ions	Confirmation ions
Organochlorine analytes		
Aldrin	263	293, 265
BHC, alpha	181	183, 219
BHC, beta	183	181, 219
BHC, delta	181	183, 219
BHC, gamma	181	183, 219
Heptachlor	272	274, 270
Endosulfan I	241	195, 243
DDD, 4,4′	235	237, 165
DDE, 4,4′	318	246, 316
DDT, 4,4′	235	237, 165
Dieldrin	277	279, 263
Endosulfan II	243	195, 207
Endrin	263	243, 245
Methoxychlor	227	228, 212
Internal standards		
d_{10}-Acenaphthene	162	164, 160
d_{12}-Chrysene	240	241, 236
d_{10}-Phenanthrene	188	187, 189
d_{10}-Pyrene	212	211, 213
Terbuthylazine	214	173, 216
Surrogate standards		
$^{13}C_6$-alpha-BHC	189	187, 225
d_{10}-Chlorpyrifos	324	260, 326
$^{13}C_6$-Permethrin (*cis/trans*)	189	163, 127
$^{13}C_3$-Simazine	204	189, 176

Table 9. Run conditions for the Saturn 2000 gas chromatography/mass spectrometry (GC/MS) system.

[psi, pounds per square inch; dpm, degrees per minute; SIS, selected ion storage; m/z, mass/charge ratio; µamps, microamperes, a unit of charge; ev, electronvolts, a voltage measurement that describes the gain on the electron multiplier of the mass spectrometer]

Injection conditions:	Splitless injection, pressure pulse of 50 psi for 1.5 minutes
Injection temperature:	275°C
Oven program:	80°C, hold for 0.5 min, 80 to 120°C @ 10 dpm 120 to 200°C @ 3 dpm, hold for 5 minutes 200 to 219°C, hold for 5 minutes 219 to 300°C @ 10 dpm, hold for 10 minutes
GC/MS conditions for most of the run:	Range SIS, collecting 90 to 450 m/z, emission current = 15 µamps
For permethrin, cypermethrin, cyfluthrin, esfenvalerate, lambda cyhalothrin and azinphos-methyl:	True SIS – only quantification and confirmation ions collected, electron multiplier + 300 ev offset, emission current 45 µamps
Analytical column:	CPSIL 8-MS (Varian Corporation), 30 m × 0.25 mm, 0.5 µm phase thickness

Calibration of instrument response to each pesticide was made using an eight-point standard curve that spanned the range of sample concentrations. Standards were purchased from Supelco Inc. (Bellefonte, Pa.). In addition to the standard curve, a mid-level standard was run every six injections to verify that the response was within 10 percent of the standard curve. If compounds in the mid-level standard fell outside of this response window, the samples were reinjected. Each sample was analyzed twice, and replicate injections that had a greater than 25 percent variability were reanalyzed.

A list of current-use organochlorine and pesticide analytes are presented in tables *4* and *8*. Compounds were quantified using internal standards (see *table 8*). Recovery of the terbuthylazine surrogate was used to assess the efficiency of each water extraction. Recoveries of the surrogate standards (^{13}C-labeled α-BHC, simazine, permethrin, and d_{10}-chlorpyrifos) were monitored to check for matrix interference and procedural recoveries in the sediment method.

Sediment Organic Carbon Analysis

Sediments were analyzed for organic carbon content using a Perkin Elmer CHNS/O analyzer (Perkin Elmer Corporation, Norwalk, Conn.). Sediments were weighed into 5 × 9 mm silver boats (Costech Analytical Technologies, Valencia, Calif.), exposed to concentrated hydrochloric acid fumes in a dessicator for 24 hours (to remove carbonate minerals), dried to constant weight, and then combusted at 925°C. Acetanilimide was used for instrument calibration of elemental carbon and nitrogen. Purified products of high temperature combustion (CO_2 for carbon [C]) and N_2, (the gaseous form of the element nitrogen [N]) were detected using a thermal conductivity detector.

Trace Elements and Selected Inorganic Constituents

Suspended sediments collected during the fall 2001 sampling period were analyzed by the USGS National Water Quality Laboratory in Denver, Colo., using methods described in Arbogast (1996) and Briggs (1999). Instrumental analysis was performed by inductively coupled argon-plasma emission spectrometry.

Analysis Results and Discussion

Field Parameters, DOC, and Streamflows

Specific conductance and temperature were measured in the field at all sites and times during sampling (*table 10*). Samples also were collected at the time of sampling, and specific conductance and pH were measured at the USGS California District Laboratory in Sacramento. The measurements indicate a slight trend of increasing pH from the outlet sites to the off-shore sites, from approximately 7.3 pH units to 8.3. The gradient of conductance (measured as a surrogate for salinity) was extremely high and varied by a factor of more than 10 between the rivers and the Salton Sea Basin. Salinity in the Salton Sea Basin is discussed in depth by Schroeder and others (2002); Schroeder and others (1993); and Setmire and others, (1993).

DOC was measured at all sites during the fall 2001 sampling period. Concentrations were elevated at all the sites and differed by a factor of 10 between the outlet and the off-shore sites. Values ranged from a low of 5.2 mg/L at the Whitewater River outlet site to 61 mg/L at the New River off-shore site. Values for the near-shore sites were either intermediate between these two extremes, as in the case of the Alamo and New Rivers, or similar in concentration to the off-shore sites, as in the case of the Whitewater River. DOC concentrations in samples from the off-shore sites were fairly uniform. DOC concentrations at the New River outlet and the off-shore sites measured in fall 2002 were slightly higher than those in 2001, although were within an order of magnitude.

Daily mean streamflows during the 2001 and 2002 sampling events were similar to flows for the 42-year period of record for the New and Alamo Rivers (*fig. 2*) (U.S. Geological Survey, 2001). For the Whitewater River, streamflows were approximately 40 percent lower than the 42-year average.

Dissolved Pesticide Concentrations

Dissolved pesticide concentrations ranged from below detection limit (1.7 ng/L) to 3,800 ng/L, with the highest concentrations detected at the outlet and the near-shore sites (tables *11–13*). Generally, the compounds with the greatest concentrations and frequency were those pesticides applied in the largest quantities, and include atrazine, chlorpyrifos, dacthal, diazinon, eptam, malathion, pendimethalin, and trifluralin (*table 1*).

Table 10. Water parameters measured at sampling sites in the Salton Sea Basin, California, during fall 2001, spring 2002, and fall 2002.

[°C, degrees Celsius, µS/cm, microsiemens per centimeter at 25°C. DOC, dissolved organic carbon concentration in mg/L as carbon. mg/L, milligram per liter. pH, specific conductance, and DOC were measured in the laboratory; temperature was measured in the field. —, no data]

Parameter	Alamo River			New River			Whitewater River		
	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore
Fall 2001									
Temp (°C)	28.9	28.0	29.8	26.1	26.4	29.2	22.0	25.3	31.9
pH (standard units)	7.4	7.8	8.1	7.8	7.6	8.1	7.7	7.8	7.8
Specific conductance (µS/cm)	3,080	11,500	53,300	3,800	34,500	53,800	1,900	53,200	53,200
DOC (mg/L)	6.3	11.6	50	6.6	33.6	53	5.2	52	52
Spring 2002									
Temp (°C)	14.6	—	16.7	—	—	—	—	16.4	—
pH (standard units)	7.3	7.8		6.9	7.6	8.0	7.8	7.4	
Specific conductance (µS/cm)	26,000	39,600	57,100	4,100	20,900	37,700	2,160	53,900	52,500
DOC (mg/L)	—	—	—	—	—	—	—	—	—
Fall 2002									
Temp (°C)	28.9	28.0	29.8	26.1	26.4	29.2	22.0	25.3	31.9
pH (standard units)	7.4	7.9	8.4	7.5	8.1	8.3	7.4	8.1	8.3
Specific conductance (µS/cm)	3,300	9,210	32,600	3,930	16,340	32,700	2,140	9,810	32,300
DOC (mg/L)	—	—	—	9.1		61	—	—	—

Table 11. Pesticide concentrations in water samples collected from sampling sites at the Alamo, New, and Whitewater rivers in the Salton Sea Basin, California, fall 2001.

[Values are reported as nanograms per liter. Concentrations are the mean of duplicate injections. Water samples also were analyzed for alachlor, azinphos-methyl, butylate, cyanazine, diethylatyl-ethyl, ethafluralin, fonofos, hexazinone, methidathion, methyl parathion, metolachlor, molinate, napropamide, oxyfluorfen, pebulate, phosmet, piperonyl butoxide, sulfotep, and thiobencarb, which were not detected during this sampling period. nd, not detected]

Pesticide	Alamo River			New River			Whitewater River		
	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore
Atrazine	nd	14.9	165	8.4	78.6	145	nd	151	144
Carbaryl	56.4	44.4	nd	nd	nd	nd	nd	nd	nd
Carbofuran	nd	nd	nd	34.8	nd	nd	nd	nd	nd
Chlorpyrifos	161	87.7	nd	44.3	15.0	nd	nd	nd	nd
Cycloate	9.3	34.1	nd	nd	nd	nd	9.6	nd	nd
Dacthal	94.3	328	9.4	26.1	30.6	5.6	38.1	9.8	9.0
Diazinon	789	936	9.1	213.4	34.8	nd	32.4	8.5	9.3
EPTC (eptam)	418	3,830	84.9	3,490	1,300	17.9	102	51.0	46.2
Malathion	340	36.5	nd	585	nd	nd	43.2	nd	nd
Pendimethalin	59.5	nd	nd	nd	nd	nd	nd	nd	nd
Simazine	nd	nd	21.0	nd	nd	nd	nd	nd	nd
Trifluralin	37.4	37.6	nd	35.0	27.3	nd	22.5	nd	nd

Table 12. Pesticide concentrations in water samples collected from sampling sites at the Alamo, New, and Whitewater rivers in the Salton Sea Basin, California, spring 2002.

[Values are reported as nanograms per liter. Water samples were analyzed for alachlor, azinphos-methyl, butylate, carbaryl, cyanazine, cycloate, diethatyl-ethyl, ethalfluralin, fonofos, hexazinone, methidathion, methyl parathion, metolachlor, molinate, napropamide, pebulate, phosmet, piperonyl butoxide, simazine, sulfotep, and thiobencarb, which were not detected during this sampling period. nd, not detected; ( ), concentration below detection limit]

Pesticide	Alamo River			New River			Whitewater River		
	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore
Atrazine	630	128	128	434	66.4	124	(2.1)	128	119
Carbofuran	530	18.9	nd	nd	nd	nd	nd	nd	56.2
Chlorpyrifos	73.1	nd	nd	20.7	9.5	nd	nd	nd	nd
Dacthal	47.0	8.9	nd	31.7	15.2	6.9	8.5	nd	6.1
Diazinon	(3.4)	nd	nd	22.7	13.8	nd	8.53	nd	nd
EPTC (eptam)	50.6	53.8	50.2	nd	nd	nd	34.0	30.1	35.7
Malathion	1,100	nd	nd	253	90.0	nd	nd	nd	nd
Oxyflurofen	30.3	nd	nd	nd	nd	nd	nd	nd	nd
Pendimethalin	156	nd	nd	65.3	27.3	nd	20.0	nd	nd
Trifluralin	600	15.8	nd	215	80.3	nd	10.5	nd	nd

Table 13. Pesticide concentrations in water samples collected from sampling sites at the Alamo, New, and Whitewater rivers in the Salton Sea Basin, California, fall 2002.

[Values are reported as nanograms per liter. Concentrations are the mean of duplicate injections. Water samples were analyzed for alachlor, azinphos-methyl, butylate, cyanazine, diethatyl-ethyl, ethalfluralin, fonofos, hexazinone, malathion, methidathion, methyl parathion, metolachlor, molinate, pebulate, phosmet, piperonyl buto w detection limit]

Pesticide	Alamo River			New River			Whitewater River		
	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore
Atrazine	19.7	160	108	nd	110	110	14.3	88.0	110
Carbaryl	(2.2)	(2.7)	nd	19.3	nd	nd	nd	nd	nd
Carbofuran	9.7	7.8	25.7	nd	37.9	nd	(2.2)	40.2	31.7
Chlorpyrifos	41.7	19.0	nd	7.0	nd	nd	(1.7)	nd	nd
Cycloate	6.1	10.4	nd	nd	nd	nd	nd	nd	nd
Dacthal	60.3	94.0	nd	6.7	3.2	3.2	110	9.0	3.6
Diazinon	970	48.0	nd	22.6	8.8	(3.0)	12.8	6.4	nd
EPTC (eptam)	52.9	24.9	13.0	22.3	24.5	22.5	100	24.5	10.7
Napropamide	nd	nd	nd	35.9	nd	nd	nd	nd	nd
Oxyfluorfen	5.5	(2.0)	nd	nd	nd	nd	nd	nd	nd
Pendimethalin	6.1	7.2	nd	nd	nd	nd	61.9	nd	nd
Simazine	nd	nd	nd	nd	nd	nd	(6.5)	nd	nd
Trifluralin	4.6	5.5	nd	12.4	nd	nd	(1.5)	nd	nd

A total of 14 current-use pesticides were detected in water. Eptam was detected at the highest concentrations of all the pesticides (3,490 and 3,830 ng/L) at the New River outlet site and at the Alamo River near-shore site, respectively, during fall 2001 (*table 11*). The concentration of malathion was elevated at the Alamo River outlet site, especially during spring 2002, with a concentration of 1,100 ng/L (*table 12*). At the Alamo River outlet and near-shore sites, diazinon concentrations were elevated in both fall 2001 and fall 2002 (tables *11* and *13*). Diazinon was implicated as a major cause of toxicity to test organisms in standardized aquatic toxicity tests of water collected from the Alamo River (deVlaming and others, 2000). Concentrations of pesticides in the Alamo River were within an order of magnitude of those reported in Crepeau and others (2000), who sampled monthly during 1996. However, concentrations of eptam, which in 1996 were reported as high as 13,000 ng/L and often exceeded 1,000 ng/L, were comparable (3,800 ng/L) only with the fall 2001 concentrations. During the spring and fall of 2002, concentrations were only 13 to 100 ng/L. It should be noted, however, that sampling by Crepeau and others (2000) was done much more fre-quently (monthly) so sampling of a maximum or a "peak" concentration was more likely.

Although there was little difference in the concentrations of the compounds detected between spring and fall, dissolved concentrations of these pesticides varied between seasons. Concentrations of diazinon were elevated in fall 2001 and fall 2002 relative to concentrations in spring 2002. Other pesticides that were higher in the fall compared with those in the spring were dacthal and eptam (*fig. 3*). Pesticides that were higher in the spring included atrazine, carbofuran, and trifluralin. Similar seasonal trends were observed by Crepeau and others (2000). These seasonal patterns in dissolved concentration also are reflected in the pesticide-use patterns for 2001 in *table 1*, in which the amounts of pesticides applied are separated into two groups representing application periods prior to and during sampling: winter/early spring (November–March) and late spring/fall (April–October, *table 1*). Because the 2002 pesticide-use data from the California Department of Pesticide Regulation was not yet available during the writing of this report, the only direct comparison between pesticide use and dissolved concentration that could be made was for fall 2001. The most abundantly detected pesticides shown in *fig. 3A* (chlorpyrifos, dacthal, diazinon, and eptam) were among the most abundantly used pesticides during April 2000 to October 2001 (*table 1*). Futhermore, aqueous concentrations of these compounds were higher during the fall 2001 sampling period than during the spring 2002 sampling period, which parallels pesticide applications for the previous winter/early spring 2001 application period (*table 1*) compared with those for the late spring/fall application period (*table 1*). Atrazine, carbofuran, and trifluralin, which were detected in high concentrations in spring (March) 2002 (*fig. 3B*), were used more heavily prior to and during the previous spring application period when compared with use during late spring/fall 2001 (*table 1*).

Dissolved pesticide concentrations in the Alamo River were higher during the fall 2001 sampling period relative to those during the fall 2002 sampling period (with the exception of diazinon which had similar concentrations). Pesticide concentrations in the New and the Alamo Rivers generally were higher than concentrations in the Whitewater River during fall 2001 and spring 2002 (*fig. 3*).

In fall 2002, concentrations of dacthal, eptam, and pendimethalin were higher at the Whitewater River outlet site compared with concentrations at the outlet sites of the other two rivers (*fig. 3*). Diazinon concentrations were highest at all three sites for the Alamo River (*table 13*). More pesticides were detected in the Alamo and New Rivers than were detected in the Whitewater River. Concentrations of most of the dissolved pesticides were highest at the outlet sites of all three rivers during the fall 2001 sampling period, consistent with an upstream source (*fig. 4*). However, concentrations of some compounds were elevated at the nearshore sites, such as those for carbaryl in the Alamo River (*fig. 4A*) and dacthal and trifluralin in the New River (*fig. 4B*). Concentrations in 2001 also were elevated at the off-shore sites for atrazine in the Alamo River and diazinon in the New River. Similar trends were seen for some pesticides in spring 2002 and fall 2002 (tables *12* and *13*). Since the source of the pesticides presumably is not constant, but rather more episodic and tied to application times, high concentration pulses move through the watershed over time. With only a single timepoint sampling, it is difficult to explain why concentration patterns along the transects differ among pesticides, but it may be due to different use patterns for different pesticides.

Suspended-Sediment Concentration, Particle Size, and Organic Carbon Content

Concentrations of suspended sediments were higher in the Alamo and New Rivers relative to concentrations in the much smaller Whitewater River (*fig. 5*, *table 14*), and decreased in all three rivers from the river outlet to the off-shore sites (*fig. 5*). The percentage of fine-grained material (less than 62 µm) did not change appreciably from outlet sites to the off-shore sites. These trends are in agreement with historical trends described in Setmire and others (1990, 1993) and Schroeder and others (1993).

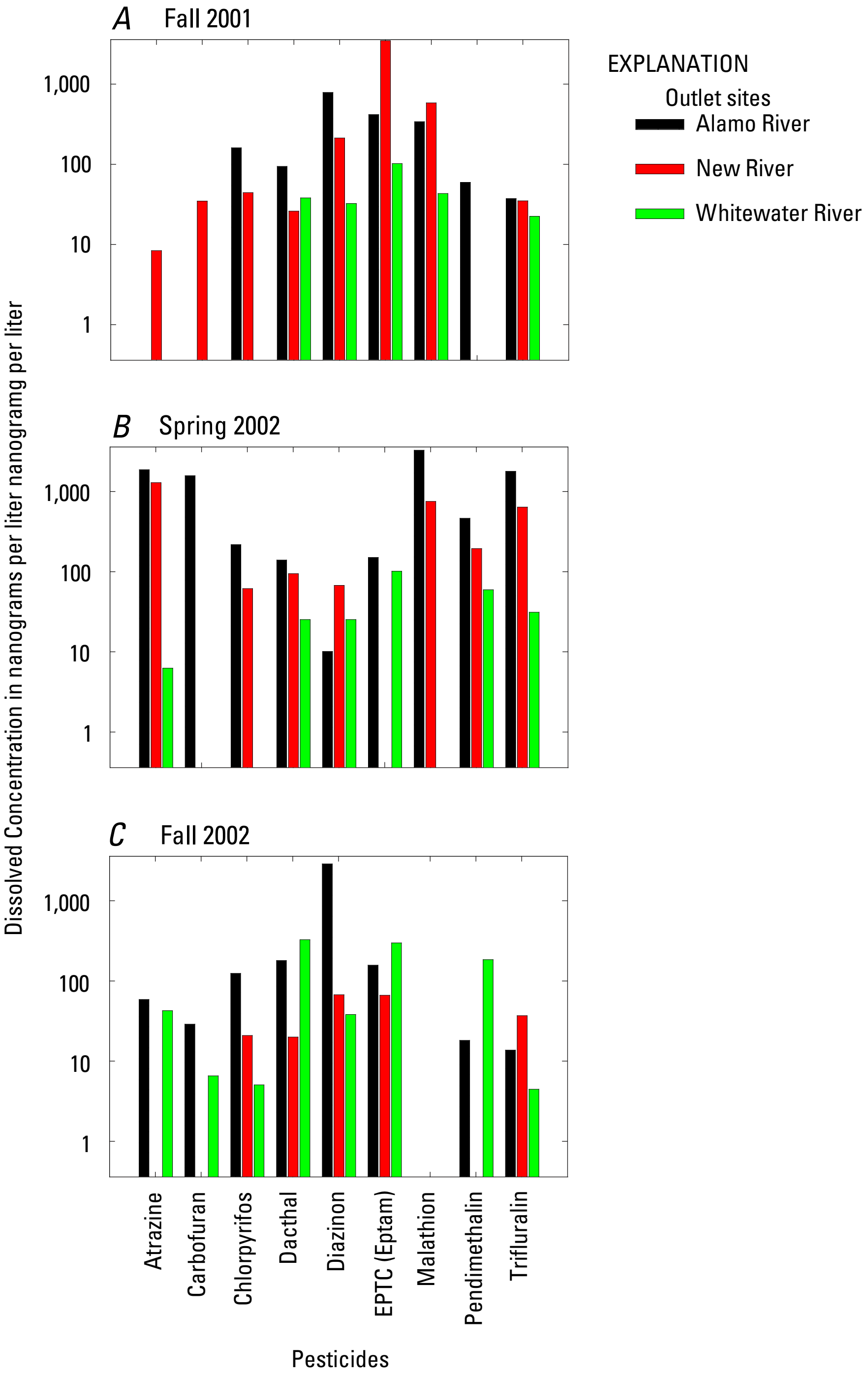

Figure 3. Dissolved concentrations of selected pesticides at the outlet sites of the New, Alamo, and Whitewater rivers during (*A*) Fall 2001, (*B*) Spring 2002, and (*C*) Fall 2002.

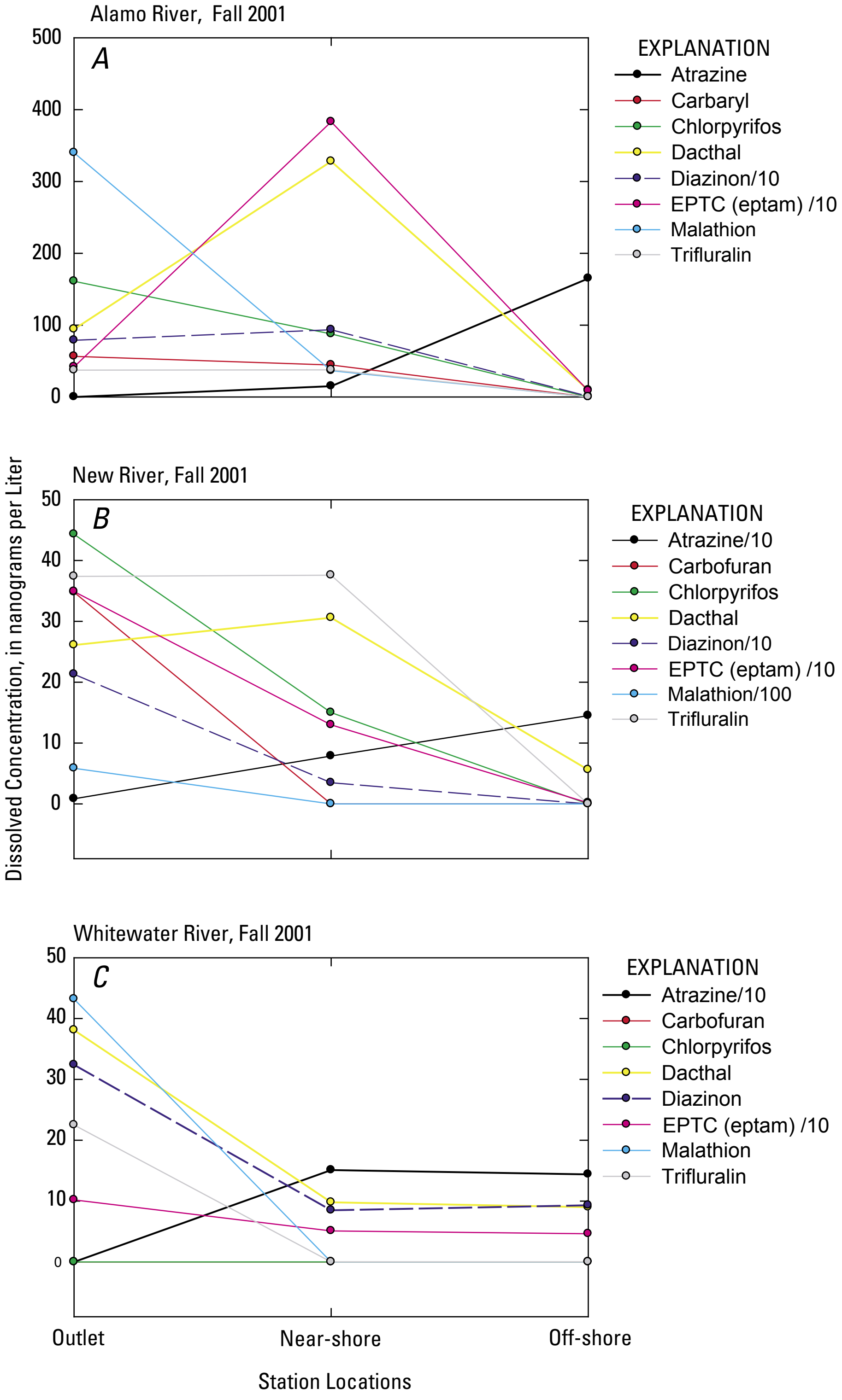

Figure 4. Dissolved concentrations of representative current-use pesticides at three sampling sites along the (*A*) Alamo, (*B*) New, and (*C*) Whitewater rivers in the Salton Sea Basin, California, Fall 2001.

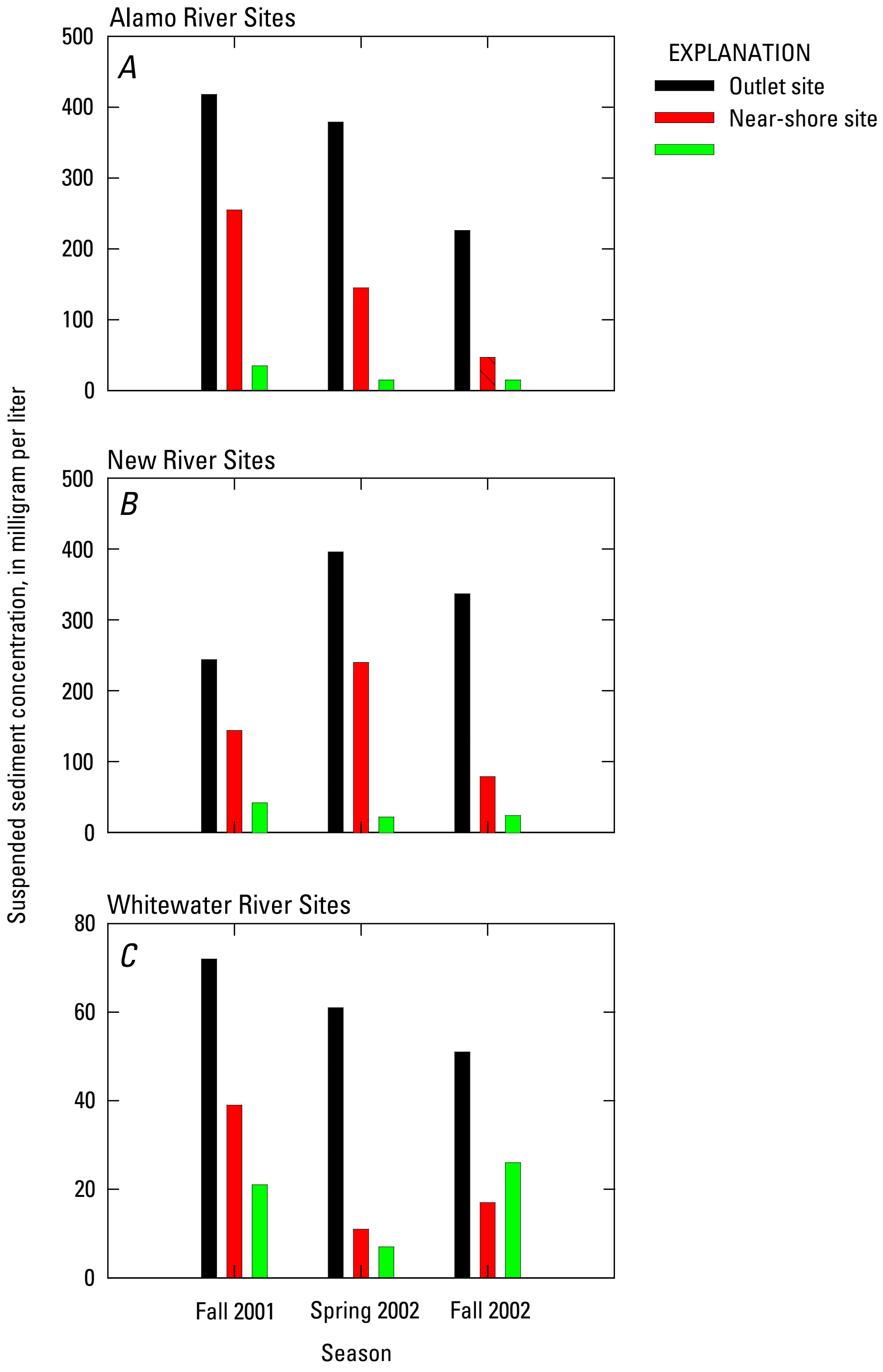

Figure 5. Pesticides concentrations on suspended sediment from the outlet, near-shore, and off-shore sampling sites in the Salton Sea Basin, in the (*A*) Alamo, (*B*) New, and (*C*) Whitewater rivers in fall 2001, spring 2002, and fall 2002.

Table 14. Suspended-sediment concentrations and percentage of fine-grained materials in water from sampling sites at the Alamo, New, and Whitewater rivers in the Salton Sea Basin, California, during fall 2001, spring 2002, and fall 2002.

[mg/L, milligram per liter. Fines, percent particles less than 62 micrometer. *, not analyzed]

Sampling site	Fall 2001		Spring 2002		Fall 2002	
	Concentration (mg/L)	Fines	Concentration (mg/L)	Fines	Concentration (mg/L)	Fines
Alamo River outlet	418	80	379	91	226	84
Alamo River near-shore	255	88	145	95	47	86
Alamo River off-shore	35	76	15	96	15	81
New River outlet	245	97	397	77	338	80
New River near-shore (near surface)	145	48	241	84	80	84
New River near-shore (near bottom)	89	70	*	*	36	65
New River off-shore	43	86	23	91	25	83
Whitewater River outlet	72	82	61	66	51	48
Whitewater River near-shore	39	66	11	77	17	57
Whitewater River off-shore	21	79	7	67	26	91

Organic carbon concentrations in suspended sediment collected from the river (outlet) sites ranged from 0.93 to 5.4 percent (*table 15*); the Whitewater River outlet site consistently had the highest organic carbon content. Suspended sediment at all the off-shore sites consisted of a high percentage of algal-derived detritus, which is reflected in extrordinarily high percent organic carbon concentrations. The Whitewater River near-shore site also had extremely high organic carbon concentrations (28.8 to 42.7 percent), unlike concentrations at the near-shore sites of the other two rivers. This is consistent with the lower outflow from the Whitewater River, which results in a smaller riverine influence at the near-shore site.

Molar ratios of carbon to nitrogen in off-shore samples also suggest a biogenic origin for the suspended material. Ratio values ranged from 1.1 to 8.0 in off-shore suspended solids, which overlaps the traditional Redfield ratio for organic matter of 105:15, or about 7:1 (Chester, 1990). Although this number has been revised and refined for specific environments over the years, the fairly high percent nitrogen in these samples (5.1 to 6.7 percent) suggests that the suspended sediment is primarily of organic and autocthonous origin, as opposed to clastic (mineral) material deposited from the rivers. Finally, visual observations of intense algal blooms (red and green) during sample collection and the appearance (and smell) of the dewatered material support the assertion that suspended sediment in the sea consisted of highly organic material of algal origin.

Pesticides Associated With Suspended Sediments

Pesticide concentrations in suspended sediments ranged from the limits of detection (1–3 ng/g) to 106 ng/g (tables *16–18*). The most frequently detected pesticides were those used in the highest amounts; they included chlorpyrifos and trifluralin. These compounds also were detected frequently in water (tables *11–13*) as were dacthal and eptam (table 1). Other pesticides, such as carbaryl, carbofuran, diazinon, oxyflurofen, and pendimethalin were detected in only a few of the suspended-sediment samples. The only organochlorine pesticide consistently detected on suspended sediments was *p,p′*-DDE, a metabolite of DDT.

Differences in the concentration and occurrence of pesticides by season were not as prononounced as the differences in the water samples, and were similar to those for dissolved concentrations. Diazinon, which had the highest dissolved concentrations in the fall, also was detected in suspended sediments in the fall. The maximum dissolved concentrations of dacthal and eptam were measured in fall 2001; dacthal and eptam concentrations also were high in suspended sediment in fall 2001 (*fig. 6*). Eptam was not detected during the spring and the fall 2002 sampling periods, which probably is due, in part, to the higher detection limits for eptam in suspended sediments (0.7 ng/g, or parts per million) compared with the limits for water (4 ng/L, or parts per trillion). Similarly, trifluralin concentrations were highest in water samples collected during the spring sampling period, but also were high in in suspended sediments from the New and Alamo Rivers (*fig. 6*). Suspended sediments are likely a combination of recent input from agricultural drainage and older resuspended bottom sediment, which may partly obscure concentration trends in suspended sediment associated with ongoing pesticide use.

The Alamo River had more detections and higher concentrations of pesticides associated with suspended solids than the New and Whitewater Rivers. In some instances pesticide concentrations were higher at the outlet sites than at the near-shore sites (for example, trifluralin was higher at the outlet site of the Alamo River during spring 2002). In some instances pesticide concentrations at the near-shore sites were similar or exceeded pesticide concentrations at the outlet sites, which is consistent with the downstream transport of pesticides on suspended particles into the near-shore environment (*fig. 6*). The fact that pesticides typically were not detected in suspended sediment collected from the off-shore sites may have been due to dilution of river-derived suspended sediment by algal material formed in the Salton Sea. An equally important and related factor is that the high concentrations of algal material in these samples caused matrix interference that prevented detection of pesticides and caused low recoveries of spiked surrogates, as discussed in the “Quality Assurance/Quality Control” subsection of the “Sediment Analysis” section.

Organic Carbon and Pesticides Associated With Bed Sediments

Organic carbon (OC) concentrations in bed sediments collected from the river outlet sites ranged from 0.25 to 1.17 percent and were much lower than OC concentrations in suspended sediments (*table 15*). OC concentrations in off-shore sediments were as high as 6.23 percent, although there was considerable variability between sites owing, in part, to differences in bottom sediment and the presence of algal detritus. The highest OC concentrations found were in bottom sediments collected from the off-shore site of the Whitewater River.

Eighteen pesticides were detected in bed sediments, primarily at the outlet sites (tables *16–18*). In general, the pesticides detected were the same pesticides detected in the suspended sediments. These pesticides were applied in large amounts to fields in the study area; they include pesticides such as chlorpyrifos, dacthal, diazinon, and eptam (*table 1*). The greatest amount of pesticide detections and the highest concentrations were at the Alamo River outlet site in spring 2002. Concentrations of the same pesticides also were measured in spring 2002 at the Alamo River near-shore site and at the New River outlet and near-shore sites. In fall 2001, pesticide detections were more sporadic and concentrations were lower than those in spring 2002. More compounds were detected at the Alamo River outlet site in fall 2002 than in fall

Table 15. Percentage of organic carbon in suspended sediments and bed sediments from sampling sites at the Alamo, New, and Whitewater rivers in the Salton Sea Basin, California, during fall 2001, spring 2002, and fall 2002.

[*, not analyzed]

Sampling site	Organic carbon		
	Fall 2001	Spring 2002	Fall 2002
	Suspended sediments		
Alamo River outlet	0.93	1.55	1.15
Alamo River near-shore	1.20	11.1	3.49
Alamo River off-shore	28.4	35.9	27.1
New River outlet	1.74	1.90	1.33
New River near-shore	2.71	4.41	5.31
New River off-shore	40.2	*	35.1
Whitewater River outlet	3.99	5.45	4.78
Whitewater River near-shore	42.7	28.8	33.6
Whitewater River off-shore	43.7	36.6	41.9
	Bed sediments		
Alamo River outlet	0.56	1.17	0.49
Alamo River near-shore	1.04	1.26	1.39
Alamo River off-shore	.38	.36	.60
New River outlet	.37	.47	.25
New River near-shore	.94	.25	1.83
New River off-shore	.78	1.39	.83
Whitewater River outlet	.46	1.13	.46
Whitewater River near-shore	*	1.65	.94
Whitewater River off-shore	4.25	3.25	6.23

2001 but concentrations were lower than those in spring. For the Whitewater River, more pesticides were detected at the outlet site during the two fall sampling periods than those that were detected during the spring sampling period.

In several instances, concentrations of pesticides (for example, dacthal, eptam, and trifluralin) in the Alamo River in spring and fall 2002 were higher in the suspended sediments and lower or not detected in the bed sediments (tables *16–18*). In other instances, they were similar, suggesting that pesticides in the suspended solids pool may come from more than one source (for example, from agricultural drainage and resuspension of bottom material). Bottom sediments from near-shore sites in the New and Alamo Rivers for fall 2001 had pesticide concentrations that were higher than those at the outlet sites, consistent with the settling of river-derived particles at the near-shore sites (*table 16*). Detections of pesticides in bottom sediment from the Whitewater River were much lower than detections for the New and Alamo Rivers.

The metabolite *p,p′*-DDE was consistently detected in bed sediments from the outlet and the near-shore sites of all three rivers, with concentrations as much as 64 ng/g at the outlet sites. *p,p′*-DDD also was detected, although not as frequently. Concentrations of DDE and DDD at the outlet sites of all three rivers were similar to those reported in Setmire and others (1990).

Table 16. Pesticide concentrations in suspended and bed sediments collected from sampling sites at the Alamo, New, and Whitewater rivers in the Salton Sea Basin, California, fall 2001.

[Values are reported as nanograms per gram. nd, not detected; D, detected but quantitation uncertain; ( ), concentration below detection limit. Sediments were also analyzed for alachlor, atrazine, azinphos-methyl, cyanazine, cycloate, cypermethrin, endosulfan, esfenvalerate, ethalfluralin, fonofos, hexazinone, malathion, methidathion, methyl parathion, metolachlor, molinate, napropamide, oxyflurofen, pebulate, pendimethalin, phosmet, piperonyl butoxide, prometryn, simazine, sulfotep and thiobencarb, which were not detected during this sampling period]

Pesticide	Alamo River			New River			Whitewater River		
	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore
Suspended sediments									
Chlorpyrifos	50.0	63.9	nd	30.4	nd	nd	nd	nd	nd
Dacthal	17.7	38.2	nd	nd	nd	nd	nd	nd	nd
Diazinon	11.8	12.5	nd	nd	nd	nd	nd	nd	nd
EPTC (eptam)	6.6	9.2	nd	4.9	nd	nd	nd	nd	nd
Permethrin	18.7	8.7	nd	D	nd	nd	nd	nd	nd
Trifluralin	9.7	12.2	nd	4.6	6.8	nd	(0.4)	nd	nd
p,p′-DDD	6.8	nd	nd	nd	nd	nd	3.8	nd	nd
p,p′-DDE	84.8	72.7	nd	22.6	25.4	nd	62.5	nd	nd
p,p′-DDT	9.5	9.8	nd	nd	nd	nd	nd	nd	nd
Bed sediments									
Bifenthrin	nd	nd	nd	nd	nd	nd	7.5	nd	nd
Carbaryl	(0.8)	nd	nd	nd	nd	nd	nd	nd	nd
Carbofuran	(2.3)	nd	nd	nd	(1.9)	nd	nd	nd	nd
Chlorpyrifos	nd	10.5	nd	10.2	27.7	nd	nd	nd	nd
Dacthal	nd	7.9	nd	nd	nd	nd	3.7	nd	nd
Diazinon	nd	4.9	nd	nd	nd	nd	nd	1.9	nd
Diethylatyl-ethyl	nd	nd	nd	nd	nd	nd	1.85	nd	nd
EPTC (eptam)	nd	(2.3)	nd	(3.9)	nd	nd	Nd	nd	nd
lambda-Cyhalothrin	nd	nd	nd	nd	nd	nd	11.2	nd	nd
Permethrin	nd	8.5	nd	7.9	D	nd	Nd	nd	nd
Prometryn	nd	nd	nd	nd	nd	nd	4.2	nd	nd
Trifluralin	nd	(.7)	nd	(1.2)	(1.9)	nd	(.6)	(.5)	nd
p,p′-DDD	nd	nd	nd	nd	93.9	nd	Nd	nd	nd
p,p′-DDE	14.4	31.5	nd	17.6	23.6	nd	6.2	nd	nd
p,p′-DDT	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table 17. Pesticide concentrations in suspended and bed sediments collected from sampling sites at the Alamo, New, and Whitewater rivers in the Salton Sea Basin, California, spring 2002.

[Values are reported as nanograms per gram. nd, not detected; D, detected but quantiitation uncertain; (), concentration below detection limit. Sediments were analyzed for alachlor, atrazine, azinphos-methyl, bifenthrin, butylate, cyanazine, cycloate, cypermethrin, diethylatyl-ethyl, endosulfan, ethalfluralin, hexazinone, lambda-cyhalothrin, malathion, methyl parathion, metolachlor, molinate, napropamide, pebulate, phosmet, piperonyl butoxide, prometryn, simazine, sulfotep and thiobencarb, which were not detected during this sampling period]

Pesticide	Alamo River			New River			Whitewater River		
	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore
Suspended sediments									
Carbaryl	nd	nd	43.6	nd	nd	nd	nd	nd	nd
Carbofuran	nd	nd	nd	nd	nd	nd	5.1	nd	nd
Dacthal	7.1	nd	nd	nd	nd	nd	2.2	nd	nd
Diazinon	nd	nd	nd	nd	nd	nd	2.0	nd	nd
EPTC (eptam)	(3.7)	nd	nd	5.6	nd	nd	nd	nd	nd
Esfenvalerate	nd	2.9	nd	nd	nd	nd	nd	nd	nd
Fonofos	nd	nd	nd	nd	nd	nd	(2.4)	nd	nd
Methidathion	nd	nd	nd	34.3	nd	nd	nd	nd	nd
Oxyfluorfen	19.7	nd	nd	nd	nd	nd	nd	nd	nd
Pendimethalin	42.4	nd	nd	nd	nd	nd	nd	nd	nd
Permethrin	nd	D	nd	nd	D	nd	D	nd	nd
Trifluralin	106.4	19.2	nd	33.3	62.5	nd	(.6)	nd	nd
p,*p*′-DDD	4.9	nd	nd	nd	nd	nd	nd	nd	nd
p,*p*′-DDE	101	nd	nd	58.2	14.9	nd	31.7	nd	nd
p,*p*′-DDT	nd	nd	nd	nd	nd	nd	nd	nd	nd
Bed sediments									
Chlorpyrifos	30.3	16.9	nd	5.5	2.9	nd	nd	nd	nd
Dacthal	10.5	9.1	nd	1.9	nd	nd	nd	nd	nd
Diazinon	2.1	nd	nd	nd	nd	nd	nd	nd	nd
EPTC (eptam)	6.4	6.7	nd	2.5	nd	nd	nd	nd	nd
Oxyfluorfen	89.5	nd	nd	nd	nd	nd	nd	nd	nd
Pendimethalin	77.5	nd	nd	nd	nd	nd	nd	nd	nd
Permethrin	12.0	nd	nd	4.2	6.8	nd	nd	nd	nd
Trifluralin	37.2	7.1	2.5	5.0	12.8	2.0	nd	nd	nd
p,*p*′-DDD	8.0	7.1	nd	nd	nd	nd	3.5	12.8	nd
p,*p*′-DDE	63.8	55.8	2.1	14.0	9.3	3.7	14.9	8.3	nd
p,*p*′-DDT	5.8	nd	nd	nd	nd	nd	nd	nd	nd

Table 18. Pesticide concentrations in suspended and bed sediments collected from the Alamo, New, and Whitewater rivers in the Salton Sea Basin, California, fall 2002.

[Values are reported as nanograms per gram. nd, not detected; D, detected but quantitation uncertain; ( ), concentration below detection limit, New River near-shore site, sample collected from above the halocline. Sediments were analyzed for the following pesticides that were not detected during this sampling period: atrazine, azinphos-methyl, bifenthrin, butylate, cyanazine, cycloate, cypermethrin, endosulfan, esfenvalerate, ethalfluralin, fonofos, hexazinone, malathion, methidathion, methylparation, molinate, napropamide, oxyflurofen, pebulate, permethrin, phosmet, piperonyl butoxide, prometryn, simazine, sulfotep and thiobencarb]

Pesticide	Alamo River			New River			Whitewater River		
	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore
Suspended sediments									
Carbaryl	nd	nd	nd	nd	nd	89.5	nd	nd	nd
Carbofuran	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chlorpyrifos	12.3	nd	nd	nd	nd	nd	nd	nd	nd
Dacthal	7.2	8.9	nd	nd	3.9	nd	nd	nd	nd
Diazinon	11.4	nd	nd	nd	nd	nd	nd	nd	nd
Diethylatyl-ethyl	2.7	nd	nd	nd	nd	nd	nd	nd	nd
EPTC (eptam)	4.8	nd	nd	nd	nd	nd	nd	nd	nd
lambda-Cyhalothrin	16.8	nd	nd	nd	nd	nd	nd	nd	nd
Metolachlor	7.8	nd	nd	nd	nd	nd	nd	nd	nd
Pendimethalin	nd	nd	nd	nd	nd	nd	36.2	nd	nd
Trifluralin	3.1	8.6	nd	18.2	(.4)	nd	nd	nd	nd
p,*p*′-DDD	nd	nd	nd	nd	nd	nd	nd	nd	nd
p,*p*′-DDE	54.2	D	nd	40.3	5.8	nd	29.2	nd	nd
p,*p*′-DDT	nd	nd	nd	nd	nd	nd	nd	nd	nd
Bed sediments									
Alachlor	7.9	nd	nd	nd	nd	nd	4.4	nd	nd
Carbofuran	8.2	nd	nd	nd	nd	nd	nd	nd	nd
Chlorpyrifos	11.1	nd	nd	nd	nd	nd	nd	nd	nd
Dacthal	3.9	nd	nd	4.5	nd	nd	3.7	nd	nd
Diethylatyl-ethyl	9.0	nd	nd	nd	15.1	nd	1.8	nd	nd
Metolachlor	7.9	nd	nd	nd	11.9	nd	5.2	nd	nd
Trifluralin	2.6	nd	nd	3.5	nd	nd	nd	nd	nd
p,*p*′-DDD	13.6	nd	nd	nd	nd	nd	nd	nd	nd
p,*p*′-DDE	48.0	31.7	nd	11.5	4.9	nd	6.2	(2.3)	nd
p,*p*′-DDT	nd	nd	nd	nd	nd	nd	nd	nd	nd

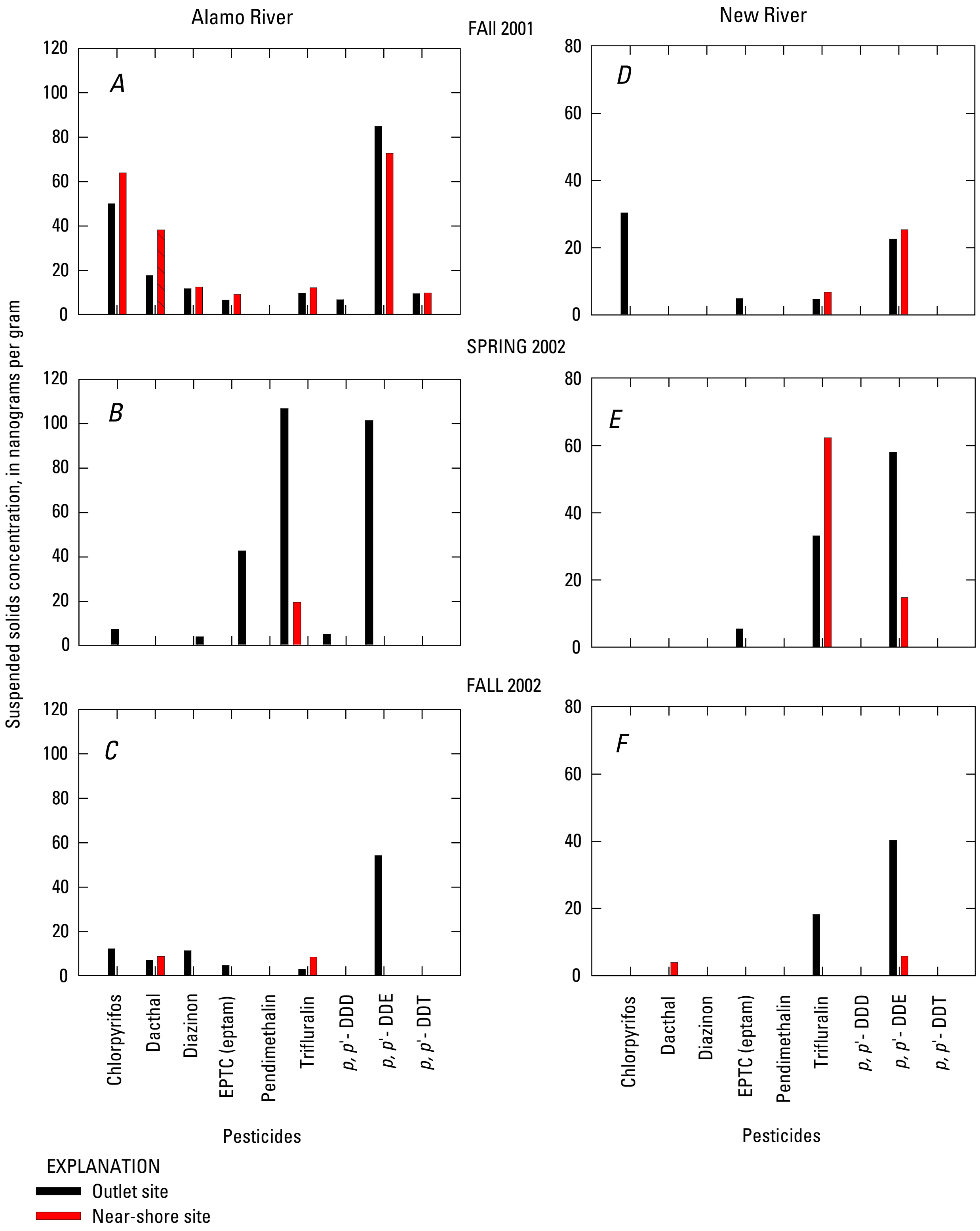

Figure 6. Pesticides concentrations on selected suspended sediments from the Alamo River outlet and near-shore sites in the Salton Sea Basin, California, in (*A*) fall 2001, (*B*) Spring 2002, and (*C*) fall 2002 and from the New River outlet and near-shore sites in (*D*) fall 2001, (*E*) spring 2002, and (*F*) fall 2002.

Distribution of Pesticides between Water, Suspended Solids, and Bed Sediments

There was a high amount of overlap among water, suspended solids, and bed sediments matrices in terms of the pesticides detected. Carbaryl, carbofuran, chlorpyrifos, dacthal, diazinon, eptam, and trifluralin, among the pesticides applied most heavily in the Salton Sea watershed, were often found in all three matrices, especially at the outlet and near-shore sampling sites. Pesticides found only in sediments included lambda-cyhalothrin, metolachlor, and permethrin. Those detected only in water included atrazine, cycloate, malathion, napropamide, and simazine (*table 19*).

The physical-chemical properties of the pesticides detected in water and sediments are listed in *table 19*. If the physical-chemical properties of pesticide compounds are the main control on the distribution and partitioning of pesticides between sediments and water, one would not expect compounds with high water solubility and low log K_{oc} values (the logarithm of the organic carbon:water partition coefficient) to become associated with sediments, and vice versa.

To examine the influence of the physical-chemical properties of pesticides on the distribution of compounds between water and sediments, predictions of dissolved concentrations based on equilibrium partitioning were made. If the pesticide concentrations in sediment are in equilibrium with the surrounding water, one should be able to predict aqueous concentrations using the measured sediment concentration and the solid:solution partitioning coefficient, K_d (from Schwarzenbach and others, 1993). K_d is defined as the concentration ratio of sediment: water

$$K_d = \frac{C_s}{C_W} \quad ,$$

where

C_s is the concentration in sediment (mg/kg)

C_W is the concentration in water (mg/L).

Organic chemicals are believed to associate most strongly with the organic carbon (OC) portion of sediment aggregates, and so the distribution of organic compounds between sediments and water can be modeled using an organic carbon to water partition coefficient K_{oc}, which is defined as follows:

$$K_{OC} = \frac{C_{OC}\left(mg \bullet Kg^{-1}_{OC}\right)}{C_W\left(mg \bullet L^{-1}_{WATER}\right)} \quad ,$$

where

C_s is the concentration of a compound in the organic carbon sediment pool (mg/kg of OC)

C_w is the concentration of a compound in water (mg/L).

Equations for calculating equilibrium partitioning are derived from first principles in Schwarzenbach and others (1993). There are several ways of determining K_{oc}, both theoretical (through relations established between K_{oc} and other physical-chemical constants) and experimental. These values have been compiled in several references, including Mackay and others (1997). The equations for K_d and K_{oc} can be related by defining C_s (concentration of a compound in sediment) as the product of the fraction of organic material in the sediment (f_{OC}) multiplied by the concentration of the pesticide in the sediment organic carbon pool (C_{oc}):

$$C_S = f_{OC} \bullet C_{OC} \quad ,$$

The equation for K_d now becomes

$$K_d = \frac{f_{OC} \bullet C_{OC}}{C_W} = f_{OC} \bullet K_{OC} \quad ,$$

Solving for C_w is now possible if one knows the value of K_{oc} for the specific compound, the concentration of the pesticide in the sediment, and the organic carbon (OC) concentration in the sediment:

$$C_W = \frac{C_S}{K_d} = \frac{f_{OC} \bullet C_{OC}}{K_d}$$

The terms described in the above model and their units are presented in *table 20*, and an example calculation is presented in *table 21*.

Measured aqueous pesticide concentrations in samples from the Alamo, New, and Whitewater River sampling sites for fall 2001 and predicted concentrations based on suspended and bed sediment pesticide concentrations are given in table 22. Predicted aqueous values, which were determined using suspended-sediment concentrations generally were much higher than the measured aqueous values illustrating that suspended-sediment concentrations are above equilibrium with the surrounding water. One exception to this trend was for eptam. Predicted aqueous concentrations were higher than the measured aqueous concentrations at the Alamo River outlet site, similar at the Alamo River near-shore site, and lower at the New River outlet site. Predicted aqueous concentrations of trifluralin were similar to the measured aqueous concentrations at the Whitewater River outlet site, but they were higher than the measured concentrations at four other sites (*table 22*).

Despite the above inconsistencies, it is clear that partitioning alone does not control pesticide distribution between water and suspended sediments. Bergamaschi and others (2001) noted this same phenomenon in the Sacramento and San Joaquin Rivers in northern California. They postulated that elevated concentrations of pesticides associated with suspended sediments in rivers are due to fresh sediments entering the rivers from surrounding agricultural fields during storm runoff. Domalgalski and Kuivila (1993) also noted this phenomenon for diazinon associated with suspended sediments in San Francisco Bay.

Table 19. Pesticides detected in water, suspended sediments, and bed sediments in the Salton Sea Basin, California, and key physical-chemical descriptors.

[Matrix designations: W, water; BS, bed sediment; SS, suspended sediment. mg/L, milligram per liter. na, not available. K_{oc}, the organic carbon-water partition coefficient. Data are from Mackay and others (1997)]

Pesticides	Matrix	Molecular weight	Water solubility (mg/L)	Log K_{oc}
Atrazine	W	215.68	30	2.2
Bifenthrin	BS	422.9	.1	5.11−5.48
Butylate	SS, BS	217.38	45	2.73
Carbaryl	W, SS, BS	201.22	104	2.5
Carbofuran	W, SS, BS	221.3	[1]350,700	2.1
Cycloate	W	215.4	75-95	2.6
Chlorpyrifos	W, SS, BS	350.6	.3, 1.1	3.78
Cyfluthrin	SS, BS	434.3	0.0012−0.003, 2	4 −5.13
Dacthal	W, SS, BS	332.0	.50	3.78
Diazinon	W, SS, BS	304.36	40	2.76
Diethylatyl-ethyl	SS, BS	311.8	105	3.15
EPTC (eptam)	W, SS, BS	189.31	365	2.38
Esfenvalerate	SS	419.9	.002	3.72
lambda−Cyhalothrin	BS	449.9	5.00×10^{-3}	na
Malathion	W	330.36	145	3.25
Oxyflurofen	W, SS, BS	361.7	.1	2.63−2.80
Napropamide	W	271.4	73	2.48−2.85
Pendimethalin	W, SS, BS	281.3	.3	1.48−3.70
Permethrin	SS, BS	391.3	1.53×10^{-5}	4.8
Simazine	W	201.67	5.0	2.14
Trifluralin	W, SS, BS	335.5	.3, variable	3.63

[1] Multiple values are reported in the literature and listed here.

Another factor contributing to the disequilibrium between water and sediment pesticide concentrations is that, over time, pesticides associated with sediment can become increasingly resistant to desorption into water. Because in many cases pesticides are applied directly to agricultural soil, a portion of the pesticides can become incorporated into the soil matrix and form associations (including chemical bonds) that can cause the pesticides to become resistant to desorption when the soil enters the aqueous environment. This desorption-resistant fraction, called the bound residue fraction in soils, has been described by several researchers (Calderbank, 1989; Führ and Ophoff, 1996; Lerch and others, 1997).

For bed sediments, a comparison of sediment and aqueous concentrations did not show a consistent trend. For many pesticides, predicted aqueous concentrations were higher than measured concentrations by a factor of only two or less and often were below measured concentrations. This was consistently true for eptam and trifluralin, which differ markedly in aqueous solubility and log K_{oc}. Bed sediments presumably have a longer residence time in the watershed compared with suspended sediments, and so have had a longer time to come into equilibrium with the surrounding water. Degradative processes can also confound predictions based on the partitioning model. Finally, it should be realized that there is much variability in reported values of K_{oc}. Although the use of K_{oc} as a predictor of sorption for hydrophobic chemicals assumes an independence of the structure of the sorbing compound (as long as it is non-polar and hydrophobic) and the type of organic carbon present in the system (Boethling and Mackay, 2000), literature values can vary for some compounds as much as 50 percent. This can be a function of different methods of determining K_{oc}, as well as different sorbing properties of the test soil carbon. An in depth discussion of the limitations of the use of K_{oc} can be found in Boethling and Mackay (2000) as well as in Swarzenbach and others (1993).

Table 20. Definition of terms used in equilibrium portioning calculations.

[mg/kg, milligrams per kilogram; mg/L, milligram per liter; g OC/g, grams of organic carbon per gram]

Term	Definition	Units
C_{OC}	Concentration of pesticide in sediment organic carbon	$\mathrm{mg/kg_{OC}}$
C_S	Concentration of compound in sediment	mg/kg dry weight
C_W	Concentration of compound in water	mg/L
f_{OC}	Fraction of organic carbon in sediment	g OC/g sediment dry weight
K_d	Sediment to water partition coefficient	$\mathrm{(mg/kg_{sediment})/(mg/L_{water})}$
K_{OC}	Sediment to organic carbon partition coefficient	$\mathrm{(mg/kg_{OC})/(mg/L_{water})}$

Table 21. Example calculation of an aqueous concentration of chlorpyrifos, based on equilibrium partitioning and measured values of suspended sediment organic carbon and chlorpyrifos concentration from the Alamo River outlet site in the Salton Sea Basin, California, fall 2001.

[CHN, carbon hydrogen, nitrogen]

Example calculation: $C_W = (f_{OC} \bullet C_{OC})/K_d$

Alamo River suspended sediment, fall 2001

Compound	Log K_{OC}[1]	K_{OC}[2]	f_{OC}[3] (g OC/g sed)	K_d[4]	C_s[5] (ng/g dry weight)	C_{OC}[6] (ng/g OC)	C_{OC}[7] (mg/kg OC)	C_W[8] (mg/L)	C_W[9] (ng/L)
CHLORPYRIFOS	3.78	6025.6	0.0093	56.0	50	5376	5.38	0.0009	892

[1] Organic carbon:water partition coefficient (Mackay and others, 1997).

[2] $K_{OC} = 10^{(\mathrm{LogK}_{OC})}$.

[3] f_{OC} = fraction of sediment organic carbon (measured by CHN analysis).

[4] K_d = sediment:water partition coefficient for chlorpyrifos = $f_{OC} \times K_{OC}$.

[5] C_s = Sediment chlorpyrifos concentration (in ng/g sediment dry weight).

[6] C_{OC} = Sediment concentration of chlorpyrifos in sediment organic carbon: ng/g OC – (ng/g sediment dry weight)/(f_{OC}).

[7] Units conversion: mg/kg = (ng/g)/1,000.

[8] C_w = Predicted aqueous concentration (mg/L).

[9] Units conversion: ng/L = (mg/L)*1,000,000.

Table 22. Predicted and measured aqueous concentrations in suspended sediments and bed sediments from the outlet and near-shore sites of the Alamo, New, and Whitewater rivers in the Salton Sea Basin, California, fall 2001.

[ng/L, nanogram per liter. nd, not detected]

Pesticides	Suspended sediment		Bed sediment	
	Predicted (ng/L)	Measured (ng/L)	Predicted (ng/L)	Measured (ng/L)
Alamo River outlet				
Carbaryl	nd	nd	452	56.4
Chlorpyrifos	892	161	nd	nd
EPTC (eptam)	2,958	418	nd	nd
Trifluralin	245	37.4	nd	nd
Alamo River near-shore				
Chlorpyrifos	884	87.7	168	87.7
Dacthal	528	328	126	328
Diazinon	1,810	936	819	936
EPTC (eptam)	3,196	3,830	922	3,830
Trifluralin	238	37.6	16	37.6
New River outlet				
Chlorpyrifos	290	44.3	458	44.3
EPTC (eptam)	1,174	3,490	4,394	3,490
Trifluralin	62.0	35.0	76.0	35.0
New River near-shore				
Carbaryl	nd	nd	1,850	<4
Chlorpyrifos	nd	nd	489	15.0
EPTC (eptam)	nd	nd	1,774	1,300
Trifluralin	58.8	27.3	47.4	27.3
Whitewater River outlet				
Dacthal	nd	nd	133	38.1
Trifluralin	17.6	22.5	31	22.5
Whitewater River near-shore				
Diazinon	nd	nd	200	8.5
Trifluralin	nd	nd	7.1	<3

Although the distribution of pesticides between water and sediments was not quantitatively predictable based on physical-chemical properties, the presence or absence of pesticides in sediments, along with concentration patterns, appeared to be due to a combination of the physical-chemical properties of pesticides and pesticide-use patterns. Trifluralin, which has a relatively low solubility (0.3 mg/L) and a relatively high log K_{oc} (3.6) compared with the other pesticides in *table 19*, was detected in sediment samples from all three sampling periods. Use of trifluralin was high in the watershed in 2001 (277,604 lbs); concentration patterns matched the pesticide-use patterns, with higher suspended-sediment concentrations during the spring 2002 sampling period relative to those during the fall 2001 and fall 2002 sampling periods, and higher pesticide use during the winter/early spring 2001 (November 2000 through March 2001) application period compared with use during the late spring/fall 2001 (April 2000 through October 2001) application period (tables *1*, *17*, *16*, and 18, respectively). Chlorpyrifos, which has a low solubility ($1.2 - 3 \times 10^{-3}$ mg/L) and high log K_{oc} (3.78), had high use during the fall 2001 application period (74,048 lbs); however, it was detected in sediment samples only during the fall. Use of chlopyrifos, although high, was half that for trifluralin between November 2000 and October 2001 (total of 101,368 lbs). Dacthal, which had an overall lower use (42,799 lbs) than chlorpyrifos and similar physical-chemical properties, was detected consistently and at the highest concentrations during both fall sampling periods (also the time of highest use) in the Alamo River. Permethrin, despite being used in far lower quantities (10,961 lbs) than chlorpyrifos, dacthal, and trifluralin, was detected in sediments but not in water during fall 2001 and spring 2001. This was not surprising given its extremely low water solubility (1×10^{-5} mg/L) and high log K_{oc} value (4.8). Variable recoveries of the pyrethroid compounds from SPE cartridges cannot be discounted as a reason that none of these compounds were detected in water.

Compounds having high aqueous solubility and a low tendency to partition onto sediments (for example, compounds with a low log K_{oc} value) were detected occasionally in the sediment samples. Eptam, with a high aqueous solubility (365 mg/L), a low log K_{oc} value (2.38), and extremely high use (106,569 lbs) was detected frequently in the sediment samples, although at low concentrations (below detection limits to 9.2 ng/g). Atrazine, with a lower aqueous solubility (30 mg/L) but a similar log K_{oc} (2.2), was detected only in water (*table 19*). The amount of atrazine applied in the watershed (19,208 lbs) was much lower than that for eptam. Malathion was used in larger quantities (122,730 lbs) than was eptam during November 2000 through October 2001. Malathion has a lower aqueous solubility and a higher log K_{oc} value and therefore a greater tendency to partition onto sediments; but it was not detected in the sediment samples, which contradicts observations for the other pesticides. The distribution of pesticides between water and suspended and bed sediments appears to be a complicated function of pesticide use, physical-chemical properties, and the residence time of sediments in the watershed.

Distribution of Pesticides between Colloidal and Truly Dissolved Fractions

The distribution of pesticides between the colloidal (retentate) and the “truly dissolved” (filtrate) fractions of the ultrafiltered water are presented in *table 23*. The term truly dissolved is used here to distinguish these concentrations from aqueous concentrations in water that has not been separated into colloidal, retentate, and filtrate fractions. For the sample collected from the New River outlet station in fall 2002, 4.7 to 25 percent of the pesticides detected were associated with the retentate (colloidal) fraction. These pesticides included atrazine, carbofuran, dacthal, diazinon, eptam, molinate, and napropamide. All the atrazine in this sample appeared to be associated with the colloidal fraction, although the concentration was below the method detection limit (2 ng/µL), which makes this high percentage somewhat suspect. In the sample collected from New River off-shore site, between 4.7 and 18.2 percent of the pesticides carbofuran, diazinon, and eptam were associated with the colloidal (retentate) fraction. Fonofos, which was completely found in the retentate fraction, had a very low concentration (4.8 ng/L) and, so again, the distribution is suspect. All the detectable atrazine (99 ng/L) is associated with the filtrate (truly dissolved) fraction in the New River off-shore sample.

Pesticide concentrations in the ultrafiltered samples (with the filtrate and retentate fractions combined) and the filtered water extracted by SPE are shown in *table 24*. Although there are differences between the two samples, the concentrations of many of the pesticides are within a factor of two.

A limited amount of samples were analyzed for this study. From this work, however, it can be noted that a measurable percentage of dissolved pesticides appear to be associated with colloids, which may have implications for the fate of dissolved pesticides (flocculation of colloid-associated pesticides at higher salinities) and pesticide bioavailability (lower bioavailability with greater colloidal complexation) and is worthy of further study.

Metals and Other Inorganic Constituents on Suspended Solids

Metals associated with continental crustal materials, such as iron (Fe), aluminum (Al), titanium (Ti), barium (Ba), chromium (Cr), and vanadium (V) were elevated in suspended sediments from the river outlet sites relative to those from the off-shore sites owing to the dilution off-shore by large amounts of organic-rich particulate material (*table 25*). Cadmium (Cd), copper (Cu), and zinc (Zn) are more soluble and have greater potential for release from sediments and redistribution in the environment (Boehm and others, 1987; Allen, 1995), including bioaccumulation into organisms. The concentrations of these metals were more evenly distributed between the river outlet sites and the off-shore sites in the Alamo and New River transects. Although the metals were higher in concentration in suspended sediments at the outlet sites, the difference in concentrations between the river outlet sites and the off-shore sites differed by a factor of 2 or less. Differences in concentrations in metals derived from the continental crust were factors of 10 or greater between the river outlet sites and the off-shore sites. Differences in concentrations between the river outlet sites and the off-shore sites for the Whitewater River were a often a factor of 10 or greater for both continental crust-derived elements and the more biologically active trace metals. Selenium (Se), which also can become remobilized from sediments, was elevated in the off-shore suspended sediments relative to suspended sediments in the river outlet sediments by factors of 10 or greater for all three transects.

Table 23. Percent distribution of pesticides between colloidal (retentate) and dissolved (filtrate) fractions of ultrafiltered water from the New River outlet and off-shore sites, Salton Sea Basin, California, September 2002.

[All values are in percent. nd, not detected]

Analyte	New River outlet		New River off-shore	
	Filtrate	Retentate	Filtrate	Retentate
Atrazine	nd	100	100	nd
Butylate	100	nd	nd	nd
Carbaryl	93	7	nd	nd
Carbofuran	88	12	82	18
Dacthal	82	18	nd	nd
Diazinon	74	26	92	8
Disulfoton	nd	nd	nd	nd
EPTC (eptam)	87	13	95	5
Fenamiphos	nd	nd	nd	nd
Fonofos	100	nd	nd	100
Methyl parathion	100	nd	nd	nd
Metolachlor	100	nd	nd	nd
Molinate	86	14	nd	nd
Napropamide	89	11	nd	nd
Pebulate	nd	nd	nd	nd

Table 24. Pesticide concentrations in the combined fractions of ultrafiltered water extracted by liquid-liquid partitioning (40L) to solid-phase extraction extracted water (1L), New River outlet and off-shore sites in the Salton Sea Basin, California, fall 2002.

[Values in parenthesis are below detection limit. SPE, solid-phase extraction. ng/L, nanogram per liter; nd, not detected]

Pesticides	New River outlet		New River off-shore	
	Ultrafiltered water (ng/L)	SPE-extracted water (ng/L)	Ultrafiltered water (ng/L)	SPE-extracted water (ng/L)
Atrazine	2.0	12.6	99.4	99.0
Bifenthrin	nd	6.9	nd	nd
Carbaryl	10.0	19.3	nd	nd
Carbofuran	16.7	5.4	52.4	nd
Chlorpyrifos	nd	7.02	nd	nd
Cyfluthrin	29.2	14.9	nd	nd
Dacthal	1.1	6.7	nd	2.6
Diazinon	12.2	22.6	8.5	(3.0)
Diethylatyl-ethyl	nd	nd	5.8	nd
EPTC(eptam)	8.5	22.3	12.6	15.0
Fonofos	nd	nd	4.8	nd
Metolachlor	2.4	nd	nd	nd
Molinate	10.8	nd	nd	nd
Napropamide	20.6	35.8	nd	nd
Piperonyl butoxide	1.5	6.1	nd	nd
Trifluralin	(.1)	12.4	nd	nd

Table 25. Element concentrations in suspended sediment from samples from the Alamo, New, and Whitewater rivers in the Salton Sea Basin, California, fall 2001.

[Concentrations are in micrograms per gram dry sediment weight, except for boldface values, which are in percent. Eu, Au, Ho, Nd, S, Ta, Sn, Yb and total carbon were not analyzed. <, less than]

Element	Alamo River			New River			Whitewater River		
	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore	Outlet	Near-shore	Off-shore
Aluminum (Al)	**7.8**	**8.4**	**0.46**	**6.7**	**6.8**	**0.14**	**7.9**	**0.13**	**0.11**
Antimony (Sb)	.71	.82	.2	.76	.62	.02	.62	.02	<.02
Arsenic (As)	8.3	9.2	17	9.1	9.1	30	11	27	27
Barium (Ba)	490	460	34	520	480	19	630	14	13
Beryllium (Be)	1.9	2.1	.18	2	1.8	.04	2	.03	.03
Bismuth (Bi)	<.005	<.005	<.005	.17	.12	<.005	.84	.1	<.005
Cadmium (Cd)	.4	.44	.18	.45	.4	.12	.36	.15	.09
Calcium (Ca)	**5.5**	**5.8**	**1.2**	**5.1**	**4.8**	**.88**	**5.5**	**.51**	**.54**
Cerium (Ce)	63	71	3.4	67	62	1.2	85	.7	.8
Chromium (Cr)	120	70	60	57	110	28	83	7.9	8.2
Cobalt (Co)	10	11	2.8	9.9	9.5	4.5	19	5.9	4.5
Copper (Cu)	28	34	16	37	31	18	69	7.9	8
Gallium (Ga)	15	17	.91	15	14	.27	21	.27	.27
Iron (Fe)	**2.9**	**3.3**	**.2**	**3**	**2.6**	**.071**	**5.2**	**.056**	**.051**
Lanthanum (La)	33	37	2.2	35	32	.7	45	.5	.5
Lead (Pb)	22	24	27	23	23	15	27	2.5	1.9
Lithium (Li)	44	51	22	46	43	15	44	12	15
Magnesium (Mg)	**2**	**2.1**	**.42**	**2.1**	**2**	**.36**	**2.3**	**.4**	**.45**
Manganese (Mn)	670	700	250	650	740	140	1,200	170	120
Mercury (Hg)	.04	.04	.06	.07	.07	.05	.08	.03	.04
Molybdenum (Mo)	6.3	1.3	3	2.5	6.5	2.3	4.1	1.1	1
Nickel (Ni)	51	34	22	30	43	11	36	6	6
Niobium (Nb)	18	20	<2	17	12	<2	26	<2	<2
Phosphorous (P)	**.11**	**.13**	**.48**	**.2**	**.24**	**.54**	**.29**	**.6**	**.55**
Potassium (K)	**2**	**2.1**	**.42**	**2.1**	**2**	**.36**	**2.3**	**.4**	**.45**
Scandium (Sc)	11	12	.9	11	9.5	<.3	16	<.3	<.3
Selenium (Se)	.7	1	8.7	1	1.4	16	1	14	11
Silver (Ag)	<3	<3	<3	<3	<3	<3	<3	<3	<3
Sodium (Na)	**.54**	**.52**	**6.4**	**.6**	**1.6**	**4.6**	**1.3**	**3.8**	**4.7**
Strontium (Sr)	320	340	230	320	280	200	500	150	140
Thallium (Tl)	3,100	3,600	170	3,400	3,000	50	6,200	50	40
Thorium (Th)	11	12	.52	11	10	.18	15	.13	.09
Titanium (Ti)	.62	.68	.01	.65	.61	<.003	.77	<.003	<.003
Uranium (U)	3	3.6	5.7	3.3	3	4.7	4.4	1.2	1.2
Vanadium (V)	78	90	16	80	69	23	110	17	16
Yttrium (Y)	23	25	1.6	27	30	.5	26	<.3	.3
Zinc (An)	86	100	92	120	100	62	190	27	27
Total Organic Carbon	**.9**	**1.2**	**30**	**1.7**	**2.7**	**39**	**3.6**	**39**	**38**
Total Inorganic Carbon	**7.8**	**8.4**	**.46**	**6.7**	**6.8**	**.14**	**1.1**	**.02**	**.02**

Ratios were calculated to demonstrate the enrichment of certain metals in off-shore algae. This was done by normalizing metal concentrations to a single constituent associated with the riverine contribution of continental crust materials (in this case aluminum) and calculating the ratio of off-shore particulate concentrations to riverine particulate concentrations for each constituent. The resulting ratio is a measure of the degree to which metals and other constituents are concentrated in the off-shore suspended particulates and, by inference, enriched in algae. The use of enrichment ratios is described in more detail in Schroeder (1985, 1995) and Schroeder and others (1988).

The enrichment ratio values for trace metals and other inorganic constituents are presented in *table 26*. Those elements associated with aluminosilicate materials, such as the rare earth elements (for example, lanthanum), had ratios of approximately 1 (no enrichment). A number of constituents that are important in biological metabolism, such as calcium and potassium, as well as magnesium and zinc, had ratios of 6 to 18. Elements known as "heavy metals" such as copper, chromium, lead, nickel, and mercury have been shown to accumulate in phytoplankton (Fisher, 1986; Luoma and others, 1998) and had ratios between 10 and 30. Phosphorous, an essential nutrient, had a very high enrichment ratio (140), which is consistent with the observation that off-shore suspended sediment contained a high percentage of algal material. Selenium had a ratio value that was the same order of magnitude as phosphorous. Arsenic also had a very high enrichment value.

Table 26. Element enrichment ratios for suspended sediment from the Salton Sea Basin, California, fall 2001.

[*, value not calculated because too many concentrations were below the detection limit. ~, about]

Element	Symbol	Enrichment ratio
Antimony	Sb	3
Arsenic	As	120
Barium	Ba	1.5
Beryllium	Be	1.2
Bismuth	Bi	*
Cadmium	Cd	14
Calcium	Ca	6.2
Cerium	Ce	.8
Chromium	Cr	11
Cobalt	Co	15
Copper	Cu	14
Gallium	Ga	.9
Iron	Fe	1
Lanthanum	La	.9
Lead	Pb	19
Lithium	Li	15
Magnesium	Mg	16
Manganese	Mn	8
Mercury	Hg	30
Molybdenum	Mo	18
Nickel	Ni	31
Niobium	Nb	*
Phosphorus	P	140
Potassium	K	8.1
Scandium	Sc	~1.3
Selenium	Se	550
Silver	Ag	*
Strontium	Sr	21
Thallium	Tl	.3
Thorium	Th	.7
Titanium	Ti	.7
Uranium	U	40
Vanadium	V	8.8
Yttrium	Y	1
Zinc	Zn	18

Summary and Conclusions

Current-use pesticides were detected in water, suspended sediments, and bed sediments collected from the Salton Sea Basin, California, during the fall 2001, spring 2002, and fall 2002 sampling periods. Dissolved concentrations were similar to concentrations reported in previous studies, which were shown to cause toxicity to aquatic organisms. Differences in pesticide concentrations between spring and fall most likely reflect pesticide use during the application periods. Aqueous pesticide concentrations along the transects (river outlet, near-shore delta, and off-shore sites) for many pesticides were highest at the outlet sites compared with concentrations at the near-shore and off-shore sites, which reflects dilution of the river water by water from the Salton Sea. However, there were also instances where aqueous concentrations of some compounds were similar or higher at the near-shore and off-shore sites than at the outlet sites, which may have been due to the transport of concentration pulses into the Salton Sea. The number of pesticides detected and their concentrations generally were higher in samples from the New and Alamo Rivers than those in the samples from the Whitewater River. Overall concentrations were higher in fall 2001 than in spring 2002 and fall 2002. A measurable fraction (10–25 percent) of pesticides were determined to be associated with colloidal material isolated by ultrafiltration.

The concentration of current-use pesticides in sediments ranged from 1 to 106 ng/g. There were differences between rivers in terms of the numbers of pesticides detected and their concentrations; the New and Alamo Rivers had more compounds that had higher concentrations in suspended and bed sediments than did the Whitewater River for both suspended and bed sediments. An exception was DDE, which was found in similar concentrations in bed sediments from all three rivers. Seasonal trends for pesticides associated with suspended sediments were not as pronounced as those for the dissolved concentrations, although they were similar for a few pesticides, notably chlorpyrifos, which had higher sediment concentrations in fall 2001, and trifluralin, which had higher concentrations in spring 2002. In the Alamo River, suspended sediment pesticide concentrations were nearly as high or higher at the near-shore site compared with concentrations at the outlet site; this may have been due to the transport of a pulse of sediment from the river (outlet) site to the near-shore site. Elevated concentrations of pesticides in suspended sediments at the near-shore sites compared with concentrations at the outlet sites also were seen for fewer compounds in the Alamo and New Rivers in spring 2002 and fall 2002. There was no consistent detection of pesticides in suspended or bed sediments from the off-shore sites, which also had the highest degree of matrix interference.

As with water, the pesticides detected in sediments were the pesticides most heavily used in the watershed; thus, the differences in concentration between seasons were at least partly related to pesticide-use patterns. Chlorpyrifos, dacthal, and eptam, used heavily during fall 2001, were detected in suspended sediments. Trifluralin, used heavily during spring 2001, was detected at high concentrations in spring 2002. Concentrations of pesticides on suspended sediments generally were above equilibrium with the water; this may be due to the presence of a sediment-associated pesticide fraction that is resistant to desorption. Concentrations in bed sediment were closer to equilibrium, which partly may be due to the longer residence time of bed sediments in the watershed.

The concentrations of metals in suspended sediments followed expected trends, with continental crustal materials decreasing in concentration from the river to the off-shore sites. Enrichment ratios provided evidence of elevated concentrations of several metals, most notably selenium, in off-shore suspended sediments, which, based on visual and geochemical characterization, were composed primarily of algae. The high enrichment values for these constituents may represent concentrations of trace metals in the algae within the Salton Sea Basin.

References cited

Allen, H.E. (ed.), 1995, Metal contaminated aquatic sediments: Ann Arbor Press, 292 p.

Arbogast, B.F. (ed.), 1996, Analytical methods manual for the Mineral Resource Surveys Program: U.S. Geological Survey Open-File Report 96-525, 248 p.

Bergamaschi, B.A., Baston, D.S., Crepeau, K.L., and Kuivila, K.M., 1999, Determination of pesticides associated with suspended sediments in the San Joaquin River, California, USA, using gas chromatography-ion trap mass spectrometry: Toxicological and Environmental Chemistry, v. 69, p. 305–319.

Bergamaschi, B.A., Kuivila, K.M., and Fram, M.S., 2001, Pesticides associated with suspended sediments entering San Francisco Bay following the first major storm of water year 1996: Estuaries, v. 24, no. 3, p. 368–380.

Bird, S.M., Fram, M.S., and Crepeau, K.L, 2003, Method of analysis by the U.S. Geological Survey California District Sacramento Laboratory—Determination of dissolved organic carbon in water by high temperature catalytic oxidation, method validation, and quality control practices: U.S. Geological Survey Open-File Report 2003-366, 14 p.

Blanco, E.V., Mahia, P.L., Lorenzo, M.S., Rodriguez, D.P, and Fernandez, E.F., 2000, Optimization of microwave-assisted extraction of hydrocarbons in marine sediments: comparison with the Soxhlet extraction method: Analytical and Bioanalytical Chemistry, v. 366, no. 3, p. 283–288.

Boehm, P., Steinhauer, M., Crecelius, E., Neff, J., and Tuckfield, C., 1987, Beaufort Sea monitoring program: analysis of trace metals and hydrocarbons from outer continental shelf (OCS) activities: Minerals Management Service 87-0072, 263 p.

Boethling, R.S. and Mackay, D., 2000, Handbook of property estimation methods for chemicals: Lewis Publishers, Environmental and Health Sciences, Boca Raton, Fl., 481 p.

Briggs, P.H., and Meier, A.L., 1999, The determination of forty two elements in geological materials by inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 99-166, 15 p.

California Department of Pesticide Regulation, 2001, Pesticide use data for 2001 [digital data]: California Department of Pesticide Regulation, Sacramento, California.

Calderbank, A., 1989, The occurrence and significance of bound pesticide residues in soil: Reviews of Environmental Contamination and Toxicology, v. 108, p. 71–103.

Camel, Valérie, 2000, Microwave-assisted solvent extraction of environmental samples: Trends in Analytical Chemistry, v. 19, no. 4, p. 229–248.

Chester, Roy, 1990, Marine Geochemistry: London, Unwin Hyman, Ltd., 698 p.

Crepeau, K.L., Baker, L.M., and Kuivila, K.M., 2000, Method of analysis and quality-assurance practices for determination of pesticides in water by solid-phase extraction and capillary-column gas chromatography/mass spectrometry at the U.S. Geological Survey California District organic chemistry laboratory, 1996–1999: U.S. Geological Survey Open-File Report 2000-229, 19 p.

Crepeau, K.L., Kuivila, K.M., and Bergamaschi, Brian, 2002, Dissolved pesticides in the Alamo River and the Salton Sea, California, 1996–97: U.S. Geological Survey Open-File Report 2002-232, 7 p.

de Vlaming, Victor, Connor, Valerie, DiGiorgio, Carol, Bailey, H.C., Deanovic, L.A., and Hinton, D.E., 2000, Application of whole effluent toxicity test procedures to ambient water quality assessment: Environmental Toxicology and Chemistry, v. 19, no. 1, p. 42–62.

Domalgalski, J.L., and Kuivila, K.M., 1993, Distributions of pesticides and organic contaminants between water and suspended sediment, San Francisco Bay, California: Estuaries, v. 16, no. 3A, p. 416–426.

Eccles, L.A., 1979, Pesticide residues in agricultural drains, southeastern desert area, California: U.S. Geological Survey Water-Resources Investigations Report 79-16, 60 p.

Fisher, N.S., 1986, On the reactivity of metals for marine phytoplankton: American Society of Limnology and Oceanography, v. 31, no. 2, p. 443–449.

Führ, F., and Ophoff, H., 1996, Pesticide bound residues in soil: Workshop, September 3–4, 1996, Deutsche Forschungsgemeinschaft, ed., by the Senate Commission for the Assessment of Chemicals used in Agriculture, workshop organized by F. Führ and H. Ophoff, Wiley-VCH Verlage, Wenhieim, FRG., 186 p.

Goerlitz, D.F. and Law, L.M., 1971, Note on removal of sulfur interferences from sediment extracts for pesticide analysis: Bulletin of Environmental Contamination and Toxicology, v. 6, p. 9–10.

Guo, Laodong, and Santschi, P.H., 1996, A critical evaluation of the cross-flow ultrafiltration technique for sampling colloidal organic carbon in seawater: Marine Chemistry, v. 55, p. 113–127.

Guo, Laodong, Wen, Liang-Saw, Tang, Ddegui, and Santschi, P.H., 2000, Re-examination of cross-flow ultrafiltration for sampling aquatic colloids: evidence from molecular probes: Marine Chemistry, v. 69, p. 75–90.

Horowitz, A.J., Elrick, K.A., and Hooper, R.C., 1989, A comparison of instrumental dewatering methods for the separation and concentration of suspended sediment for subsequent trace element analysis: Hydrological Processes, v. 2, p. 163–184.

Irwin, G.A., 1971, Water-quality data for selected sites tributary to the Salton Sea, California, August 1969–June 1970: U.S. Geological Survey Open-File Report, 12 p.

Jayaraman, S., Pruell, R.J., and McKinney, R., 2001, Extraction of organic contaminants from marine sediments and tissues using microwave energy: Chemosphere, v. 44, no. 2, p. 181–191.

Jensen, Sören, Renberg, Lars. and Ruetergårdh, Lars, 1977, Residue analysis of sediment and sewage sludge for organochlorines in the presence of elemental sulfur: Analytical Chemistry, v. 49, no. 2, p. 316–318.

Lerch, R.N., Thurman, E.M., and Kruger, E.L., 1997, Mixed-mode sorption of hydroxylated atrazine degradation products to soil: a mechanism for bound residue: Environmental Science and Technology, v. 31, no. 5, p. 1539–1546.

Luoma, S.N., van Geen, A., Lee, B.–G., and Cloern, J.E., 1998, Metal uptake by phytoplankton during a bloom in south San Francisco Bay: implications for metal cycling in estuaries: Limnology and Oceanography, v. 43, no. 5, p. 1007–1016.

Mackay, Donald, Shiu, W.Y., and Ma, K.C., 1997, Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals: Volume V—Pesticide Chemicals: Boca Raton, Fl., Lewis Publishers, 812 p.

Pastor, A., Vasquez, E., Ciscar, R., and de la Guardia, M., 1979, Efficiency of the microwave-assisted extraction of hydrocarbons and pesticides from sediments: Analytica Chimica Acta, v. 344, p. 241–249.

Rees, T.F., Leenheer, J.A., and Ranville, J.F., 1991, Use of a single-bowl continuous-flow centrifuge for dewatering suspended sediments: effect on sediment physical and chemical characteristics: Hydrological Processes, vol. 4, p. 201–204.

Schroeder, R.A., 1985, Sediment accumulation rates in Irondequoit Bay, New York based on lead-210 and cesium-137 geochronology: Northeastern Environmental Science, v. 4, p. 2329.

Schroeder, R.A., 1995, Potential for chemical transport beneath a storm-runoff recharge (retention) basin for an industrial catchment in Fresno, California: U.S. Geological Survey Water-Resources Investigations Report 93-4140, 38 p.

Schroeder, R.A., 1996, Transferability of environmental assessments in the Salton Sea Basin, California, and other irrigated areas in the Western United States to the Aral Sea Basin, Uzbekistan *in* Micklin, P.P., and Williams W.D., eds., The Aral Sea Basin, Proceedings of the NATO Advanced Research Workshop “Critical Scientific Issues of the Aral Sea Basin: State of Knowledge and Future Research Needs,” Taskhent, Uzbekistan, May 2–5, 1994. NATO ASI Series, Partnership Sub-Series 2, Environment, v. 12, Springer Verlag, New York, p. 121–137.

Schroeder, R.A., Orem, W.H., and Kharaka, Y.K., 2002, Chemical evolution of the Salton Sea, California: nutrient and selenium dynamics: Hydrobiologia, v. 473, p. 2345.

Schroeder, R.A., Rivera, A.M., Redfield, B.J., Densmore, J.N., Michel, R.L., Norton, D.R., Audet, D.J., Setmire, J.G., and Goodbred, S.L., 1993, Physical, chemical and biological data for detailed study of irrigation drainage in the Salton Sea area, California, 1988–90: U. S. Geological Survey Open-File Report 93-83, 179 p.

Schroeder, R.A., Setmire, J.G. and Wolfe, J.C., 1988, Trace elements and pesticides in the Salton Sea area, California *in* Proceedings on Planning Now for Irrigation and Drainage: Irrigation Division, American Society of Civil Engineers, Lincoln, Nebraska, July 19–21, 1988, p. 700–707.

Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M., 1993, Environmental Organic Chemistry, John Wiley and Sons, Inc., New York, 681 p.

Setmire, J.G., 1984, Water quality in the New River from Calexico to the Salton Sea Imperial County, California: U.S. Geological Survey Water-Supply Paper 2212: 42 p.

Setmire, J.G., Schroeder, R.A., Densmore, J.N., Goodbred, S.L., Audet, D.J., and Radke, W.R., 1993, Detailed study of water quality, bottom sediment, and biota associated with irrigation drainage in Salton Sea area, California, 1988–90: U.S. Geological Survey Water-Resources Investigations Report 93-4014, 102 p.

Setmire, J.G., and Schroeder, R.A., 1998, Selenium and salinity concerns in the Salton Sea area of California *in* Frankenberger, W.T., Jr., and Engberg, R.A. (eds.), Environmental Chemistry of Selenium: Marcel Dekkar Inc., New York, chap. 12, p. 205221.

Setmire, J.G., Wolfe, J.C., and Stroud, R.K., 1990, Reconnaissance investigation of water quality, bottom sediment, and biota associated with irrigation drainage in the Salton Sea area, California, 1986–87: U.S. Geological Survey Water-Resources Investigations Report 89-4102, 68 p.

Sokal, R.R., and Rohlf, F.J., 1983, Biometry—The principles and practice of statistics in biological research (2d edition): New York, W.H. Freeman and Company, 859 p.

Spencer, W.F., Cliath, M.M., Blair, J.W., and LeMert, R.A., 1985, Transport of pesticides from irrigated fields in surface runoff and tile drain waters: U.S. Department of Agriculture Conservation Research Report 31, 71 p.

U.S. Geological Survey, 2001, National Water Information System (NWISWeb), U.S. Geological Survey, accessed March 15, 2003, at *http://waterdata.usgs.gov/nwis/.*