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Pesticide Concentrations in Water and in Suspended and Bottom Sediments in the New and Alamo Rivers, Salton Sea Watershed, California, April 2003

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

In cooperation with the California State Regional Water Quality Control Board

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Conversion Factors, Abbreviations, and Acronyms

| Multiply | By | To obtain |
|---|----------------------------|--|
| centimeter (cm) | 0.3937 | inch (in.) |
| cubic centimeter (cm ³) | 0.06102 | cubic inch (in ³) |
| cubic foot per second (ft ³ /s) | 0.02832 | cubic meter per second (m ³ /s) |
| gram (g) | 0.03527 | ounce, avoirdupois (oz) |
| kilometer (km) | 0.6214 | mile (mi) |
| liter (L) | 1.057 | quart (qt) |
| meter (m) | 3.281 | foot (ft) |
| millimeter (mm) | 0.03937 | inch (in.) |
| nanogram (ng) | 0.03527(10 ⁻⁹) | ounce, avoirdupois (oz) |
| pound per square inch (lb/in ²) | 6.895 | kilopascal (kPa) |

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

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

Abbreviations and Acronyms

| | |
|------------------|--|
| Å | angstrom |
| CO ₂ | carbon dioxide |
| D | detected |
| DO | dissolved oxygen |
| GC/MS | gas chromatography/mass spectrometry |
| GPC/HPLC | gel permeation/high pressure liquid chromatography |
| MASE | microwave-assisted solvent extraction |
| min | minute |
| mL | milliliter |
| mm | millimeter |
| N ₂ | nitrogen gas |
| ng | nanogram |
| nm | nanometer |
| NWQL | National Water Quality Laboratory |
| OC | organic carbon |
| <i>p,p'</i> -DDD | Dichlorodiphenyldichloroethane |
| <i>p,p'</i> -DDE | Dichlorodiphenyldichloroethylene |
| <i>p,p'</i> -DDT | Dichlorodiphenyltrichloroethane |
| rpm | revolutions per minute |
| SIM | selected ion monitoring |
| SIS | selected ion storage |
| SPE | solid phase extraction |
| SSC | suspended sediment concentration |
| USGS | U.S. Geological Survey |
| UV | ultraviolet |
| V | volt |
| w | watts |
| μL | microliter |
| μm | micrometer |
| μS | microsiemens |

Pesticide Concentrations in Water and in Suspended and Bottom Sediments in the New and Alamo Rivers, Salton Sea Watershed, California, April 2003

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

Abstract

This report contains pesticide concentration data for water, and suspended and bed sediment samples collected in April 2003 from twelve sites along the New and Alamo Rivers in the Salton Sea watershed, in southeastern California. The study was done in collaboration with the California State Regional Water Quality Control Board, Colorado River Region, to assess inputs of current-use pesticides associated with water and sediment into the New and Alamo Rivers. Five sites along the New River and seven sites along the Alamo River, downstream of major agricultural drains, were selected and covered the lengths of the rivers from the international boundary to approximately 1.5 km from the river mouths. Sampling from bridges occurred at seven of the twelve sites. At these sites, streamflow measurements were taken. These same sites were also characterized for cross-stream homogeneity by measuring dissolved oxygen, pH, specific conductance, temperature, and suspended solids concentration at several vertical (depths) and horizontal (cross-stream) points across the river.

Large volume water samples (200–300 L) were collected for isolation of suspended sediments by flow-through centrifugation. Water from the outflow of the flow-through centrifuge was sampled for the determination of aqueous pesticide concentrations. In addition, bottom sediments were sampled at each site. Current-use pesticides and legacy organochlorine compounds (*p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD) were extracted from sediments and measured via gas chromatography/mass spectrometry (GC/MS). Organic carbon and percentage of fines were also determined for suspended and bottom sediments.

Cross-stream transects of dissolved constituents and suspended sediments showed that the rivers were fairly homogeneous at the sites sampled. Streamflow was higher at the outlet sites, with the Alamo River having higher flow (1,240 ft³/s) than the New River (798 ft³/s).

Twelve current-use pesticides, one legacy organochlorine compound (*p,p'*-DDE), and the additive piperonyl butoxide were detected in water samples. Trifluralin was found in the

highest concentration of all detected compounds (68.5–599 ng/L) at all sites in both rivers, except for the international boundary sites. Atrazine was also detected in high concentration (51.0–285 ng/L) at several sites. The outlet sites had among the highest numbers of pesticides detected and the international boundary sites had the lowest numbers of pesticides detected for both rivers. The numbers of pesticides detected were greater for the Alamo River than for the New River.

Six current-use pesticides and two legacy organochlorines (*p,p'*-DDE and *p,p'*-DDD) were found associated with suspended and bed sediments. The DDT metabolite *p,p'*-DDE was detected in all suspended and bed sediments from the Alamo River, but only at two sites in the New River. Dacthal, chlorpyrifos, pendimethalin, and trifluralin were the most commonly detected current-use pesticides. Trifluralin was the compound found in the highest concentrations in suspended (14.5–120 ng/g) and bed (1.9–9.0 ng/g) sediments. The sites along the Alamo River had more frequent detections of pesticides in suspended and bed sediments when compared with the New River sites. The greatest number of pesticides that were detected in suspended sediments (seven) were in the samples from the Sinclair Road and Harris Road sites. For bottom sediments, the Alamo River outlet site had the greatest number of pesticide detections (eight).

Introduction

The Salton Sea watershed in southeastern California is an intensely cultivated area, owing to its sunny climate and supply of irrigation water, which is carried from the Colorado River to this area via the All American Canal. Concerns about water quality resulting from pesticide use led to a need for a survey of pesticide concentrations in the New and Alamo Rivers. This report presents the results of analyses of current-use pesticides and DDTs in water, suspended sediments, and bed sediments from 12 sites along the New and Alamo Rivers, extending from the international boundary to approximately 1.5 km upriver from where the rivers discharge into the Salton

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Sea Basin. In addition, results of stream discharge measurements made at selected sites, and river cross-sectional measurements of dissolved oxygen, specific conductance, temperature, pH, and suspended solids concentration are presented. Particle size and organic carbon concentrations are presented for suspended and bed sediments.

Hydrographic Setting

The New and Alamo Rivers are located in Imperial County in the southeastern corner of California. This area is characterized by an arid, desert-like climate, with hot temperatures (up to 52°C) and low rainfall (5–8 cm/year, Eccles, 1979). Irrigation water, derived from the Colorado River and delivered to the Imperial Valley via the All American Canal, provides a steady source of water and supports intensive agricultural activity. The Alamo River begins as a small stream near the U.S.–Mexico border adjacent to the All American Canal and flows northward approximately 97 km where it discharges into the southern end of the Salton Sea. The New River originates in the Colorado River delta in the Mexicali Valley, Mexico, and flows northward approximately the same distance as the Alamo River (108 km), where it also discharges into the southern end of the Salton Sea. Flow from both rivers consists of a high percentage of irrigation runoff; the Alamo River consists almost entirely of irrigation return flow (Setmire, 1984; Schroeder and others, 1988; and de Vlaming and others, 2000). Daily mean flows over the last 40-year period ranged from 45.0 to 1,140 ft³/s for the Alamo River, and from 456 to 758 ft³/s for the New River (U.S. Geological Survey, 2001).

Purpose and Scope

The purpose of this report is to present results of pesticide analyses of water, suspended sediment, and bed sediment from 12 sampling stations along the New and Alamo Rivers, extending from the U.S.–Mexico border to approximately 1.5 km upstream from the river mouths. The percentage of organic carbon and percentage of fines were also determined in suspended and bed sediments, and are presented. Measurements of dissolved oxygen (DO), specific conductance, suspended sediment concentration (SSC), and temperature were made in cross-stream transects at seven of the twelve sites, along with concurrent stream discharge measurements. These data, along with specific conductivity, temperature, pH, DO, and SSC measurements from point samples at the other five sites are presented.

Sample Collection Methods

Seven sites along the Alamo River and five sites along the New River were selected as sampling stations, beginning at

the U.S. side of the international boundary, to approximately 1.5 km from where each river discharges into the Salton Sea (*fig. 1*). Stations were chosen to be proximate (and downstream from) inputs from agricultural drains, as well as for continuity with other sampling programs being managed by the California State Water Control Board. Site coordinates are listed in *table 1*. At each site, large volume water samples (approximately 200 L) were collected for isolation of sufficient quantities of suspended material for sediment-associated pesticide analysis and concurrent analysis of aqueous pesticide concentrations. In addition, 500 mL samples were taken for quantification of SSC. Measurements of DO, pH, specific conductance, and temperature were made at each site by deploying a YSI model 556 hand-held multiparameter meter (YSI International, Dayton, OH), calibrated prior to each use.

At seven of these sites (sampled at bridges and one cableway), cross-stream heterogeneity was characterized by measuring DO, pH, specific conductance, SSC, and temperature at several evenly spaced points along the width of the river and at several depths (*table 1*). In addition, streamflow measurements were made at these sites, using established U.S. Geological Survey methods (Buchanan and Somers, 1969). Depth-integrated sampling for SSC was made using a D-77 isokinetic sampler at five vertical transects, each representing 20 percent of the flow. Positions of these transects were determined using the results of the streamflow measurements.

At the other five sites, the lack of a bridge, cableway, or other means to safely traverse the river precluded sampling across the river. At these sites, point samples were taken at a distance of 2–3 m from the river bank at a depth of 0.5 m for determination of SSC and collection large volume water samples. Measurements of DO, specific conductivity, and temperature were made at these sites, using the multiparameter meter at the same location and depth.

Large Volume Water Samples

Large volume water samples were collected at a total of twelve sites along the New and Alamo Rivers (*fig. 1*). These samples were collected using a large peristaltic pump powered by a portable generator and equipped with a single stainless steel and Teflon inlet hose. Sample water was pumped directly into precleaned and prerinsed 20 L stainless steel kegs for transport. The stainless steel kegs were cleaned with deionized water, methanol, and acetone prior to each use. Immediately prior to sample collection, each keg was rinsed with sample water three times before collecting the sample. Total sample volumes varied with each site, but were between 200–300 L. Time for sample collection was approximately 30 min.

At seven of the sites, sampling was performed by establishing three vertical transects across the river, each representing 33 percent of the total flow (as determined by the discharge measurements) and pumping water at several depths (10, 30, 50, 70, and 90 percent of the total depth) at each tran-

sect. Samples for SSC measurements were collected with the D-77 isokinetic sampler, as described in the previous section.

At the remaining five sites, water was sampled from a single point in the river approximately 3 m from the river bank and at a depth of 0.5 m, by affixing the sampling hose to an extendable pole (maximum length 3.6 m). Station-specific sampling details are summarized in *table 1*. Station coordinates were determined using a handheld global positioning system device (Garmin GPS 12, Garmin International Inc., Olathe, KS). Additional samples were collected for measurements of SSC and percentage of fines (diameter less than 62 μm). For these samples, water was pumped into precleaned 500 mL clear glass bottles during the large volume sample collection.

Isolation of Suspended Sediments

Suspended sediments were isolated by pumping the large volume water samples through a flow-through centrifuge (Westfalia model KA-2, Westfalia Corporation, Odele, FRG), after transport of the kegs to the Sonny Bono Wildlife

Refuge, adjacent to the Salton Sea (*fig. 1*). Water (200–300 L) was pumped at a flow rate of 2 L/min through the centrifuge, which operated at 9,500 G (G is the dimensionless ratio of the acceleration due to centrifugal force divided by the acceleration due to gravity). The 2 L/min flow-rate has been shown to be the optimal influent rate for efficient capture of a wide variety of grain sizes and suspended solids concentrations (Horowitz and others, 1989). Following centrifugation, the solid phase and sediment slurry were carefully removed from each of the concentric centrifuge bowls. Water in the bowls was used to rinse the solid particles off all of the bowl surfaces. The resulting sediment slurry was stored refrigerated in precleaned glass bottles and transported back to the USGS's Organic Chemistry Laboratory in Sacramento. In the laboratory the suspended material was further dewatered by centrifuging in 200 mL-size stainless steel centrifuge bottles for 20 min at 10,000 rpm in a high speed refrigerated centrifuge (Sorvall RC-5B centrifuge, DuPont Company, Wilmington, DE). The water was decanted and the remaining solid material removed from the centrifuge bottles and stored frozen in precleaned glass screw-cap bottles until analysis.

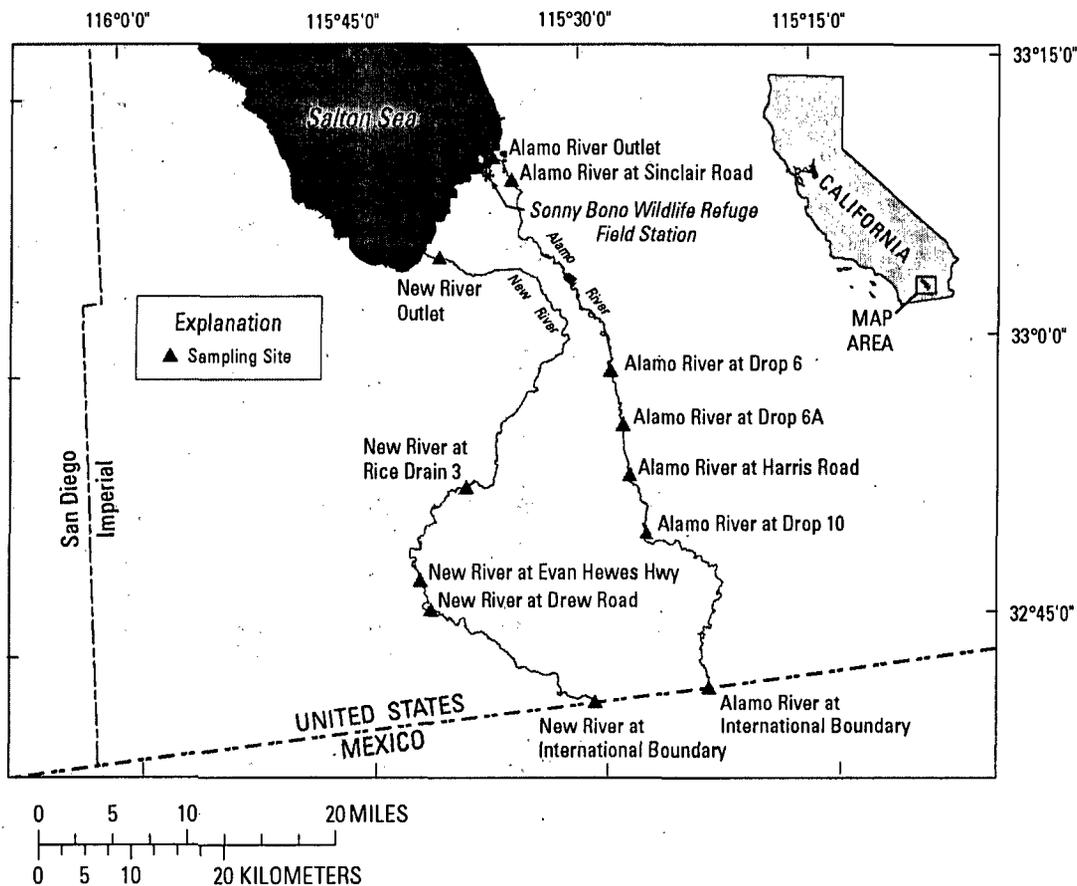


Figure 1. Location of sampling sites along the New and Alamo Rivers, Salton Sea watershed, Imperial County, California.

Table 1. Sampling sites and location coordinates for the New and Alamo River sampling stations, California

[Horizontal datum NAD 83; SSC, suspended sediment concentration; for point samples the large volume pump was utilized, for integrated samples the D-77 sampler was utilized]

| Official Site Name | USGS Station Number | Alamo River Stations | Latitude | Longitude | Sampling Location | SSC Sampling | Bottom Sediment Sampling |
|---|---------------------|---------------------------|-------------|--------------|-------------------|-------------------|--------------------------|
| Alamo River at International Boundary | 324032115220501 | International Boundary | 32° 40' 30" | 115° 22' 13" | drain | point sample | Eckman (5 grabs) |
| Alamo River at Drop 10 near Holtville | 324935115260201 | Drop 10 | 32° 49' 35" | 115° 26' 5" | river bank | point sample | Eckman (5 grabs) |
| Alamo River at Harris Road near Imperial | 325259115270801 | Drop 8 (Harris Road) | 32° 52' 59" | 115° 27' 7" | bridge | integrated sample | Eckman (3 grabs) |
| Alamo River at Drop 6A near Brawley | 32555115272601 | Drop 6A | 32° 55' 55" | 115° 27' 26" | river bank | point sample | Eckman (2 grabs) |
| Alamo River at Drop 6 near Brawley | 325911115280401 | Drop 6 | 32° 59' 11" | 115° 28' 8" | river bank | point sample | Teflon corer (10 cores) |
| Alamo River at Drop 3 near Calipatria | 10254670 | Sinclair Road. (Drop 3) | 33° 10' 36" | 115° 34' 34" | bridge | integrated sample | Eckman (2 grabs) |
| Alamo River near Niland | 10254730 | Garst Road (Outlet site) | 33° 11' 57" | 115° 35' 50" | bridge | integrated sample | Eckman (3 grabs) |
| | | New River Stations | | | | | |
| New River at International Boundary at Calexico | 10254970 | International Boundary | 32° 39' 57" | 115° 30' 8" | bridge | integrated sample | Eckman (3 grabs) |
| New River at Drew Road near Seeley | 324542115412501 | Drew Road | 32° 45' 42" | 115° 41' 25" | bridge | integrated sample | Eckman (5 grabs) |
| | 324728115420101 | Evanhews Road | 32° 47' 29" | 115° 42' 6" | bridge | integrated sample | Eckman (2 grabs) |
| New River at Rice Drain 3 near Imperial | 325243115383701 | Rice Drain 3 | 32° 52' 36" | 115° 39' 3" | river bank | point sample | Teflon corer (9 cores) |
| New River near Westmorland | 10255550 | Outlet (cable-way) site | 33° 6' 17" | 115° 39' 49" | cableway | integrated sample | Eckman (4 grabs) |

Water Samples for Aqueous Pesticide Analysis

Samples for the determination of aqueous pesticide concentrations were collected in 1-L amber glass bottles from the outlet of the Westfalia flow-through centrifuge, following centrifugation of each large volume sample. For each station, composites were taken by sampling approximately 50–100 mL from each of the 10–15 containers collected per station. Samples were refrigerated at 20°C immediately after collection and were processed within 24 hours of collection by extraction with solid phase extraction (SPE) cartridges, as described in the Water Analysis subsection of the Laboratory Methods section of this report.

Bed Sediment

Bed sediment samples were collected concurrently with water sampling at each of the twelve sites. Samples were collected using either a 23-cm Eckman grab sampler or a 5-cm diameter, Teflon-barreled hand corer. Wherever possible, an attempt was made to sample the river bottom in quiescent, settling areas, such as immediately downstream and adjacent to bridge structures. Multiple grabs were required for a total collection volume of approximately 0.5 L at each site. Samples were taken only from the top 2 cm of undisturbed sediment collected in each grab. Multiple core samples (5–7) or Eckman grab samples (2–3) were composited to make a sample. Sediment was scooped into cleaned, 0.5 L, glass mason jars using a stainless steel spoon. Samples were transported on ice back to the Sonny Bono Wildlife Refuge where they were frozen at –4°C within 4 hours of collection, and transported on ice back to the USGS's Organic Chemistry Laboratory in Sacramento, where they were kept frozen until analysis.

Laboratory Methods

Water Analysis

Pesticides were extracted from water samples using solid phase extraction (SPE) cartridges. Prior to sample extraction, the volume of water was measured, and 100 µL of 2 ng/µL surrogate (terbuthylazine) was spiked into the sample. The water was then pumped through a precleaned and conditioned C8 SPE cartridge (Varian Bond-Elut, 500 mg, 300 cc size barrel, Varian Analytical Corporation, Walnut Creek, CA) using 12 V ceramic-piston metering pumps. To condition the cartridges, 3 mL of methanol followed by 3 mL of organic-free water was passed through each cartridge. The cartridge was then kept wet with water until the extraction step. After the extraction, excess water was removed from the cartridge by pass-

ing air through it with a luer-lock syringe. Cartridges were labeled, kept refrigerated, and sent to Sacramento for storage within three days of collection. Upon receipt of samples in Sacramento, the cartridges were further dried with CO₂ for at least one hour. Cartridges were stored frozen until analysis, which did not exceed the established holding time of two months (Crepeau and others, 2000).

Samples were eluted from the SPE cartridges using 9 mL of ethyl acetate, reduced in volume to 500 µL via evaporation with a stream of nitrogen gas (N-evap, Organomation Associates, Kansas City, MO), and had appropriate concentrations of internal standards added. The internal standards used were d₁₀-acenaphthene, d₁₀ phenanthrene, and d₁₀-pyrene. Extracts were reduced to a final volume of 200 µL and analyzed via gas chromatography/mass spectrometry (GC/MS). Full details of the extraction method are provided in Crepeau and others (2000).

Quality Assurance and Quality Control for Water Samples

Quality assurance samples for water included laboratory and field blanks, matrix spike samples, and confirmatory analyses performed by the USGS's National Water Quality Laboratory (NWQL) in Denver, CO, on three replicate samples. Laboratory blanks (two replicates) consisted of 1 L of deionized water, carried through the water extraction and analysis procedure described above. Field blanks (three replicates) were 1-L samples of deionized water pumped through the Westfalia flow-through centrifuge and carried through the entire procedure.

No compounds were detected in laboratory blanks processed in Sacramento. However, field blanks processed at the Sonny Bono Wildlife refuge had concentrations below method detection limits of trifluralin (1.6–1.8 ng/L) and diazinon (2.3–3.2 ng/L). One field blank, taken near the end of the sampling period (April 15, 2003) was found to have a concentration of diazinon above the method detection limit (19.8 ng/L).

Method detection limits for water samples ranged between 0.6 and 11.1 ng/L (table 2). Recoveries of the terbuthylazine surrogate from water samples ranged from 88.7 to 124 percent, and averaged 97.5 ± 12 percent (mean ± standard deviation). Mean recoveries of water matrix spikes (5 samples) ranged between 44 and 101 percent with an overall mean recovery of 80.8 ± 18 percent. Lower recoveries of the pyrethroid compounds (51.8 percent) lowered the overall mean recovery. Recoveries of detected compounds ranged from 66.4 to 113 percent and averaged 90.1 ± 11 percent.

Concentrations in samples analyzed at the Sacramento laboratory agreed with samples analyzed at the NWQL laboratory in Denver (three replicates) to within 25 percent.

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Table 2. Method detection limits for pesticides analyzed in water samples

[ng/L, nanograms per liter]

| Pesticide | Method Detection Limit (ng/L) |
|---------------------------------|-------------------------------|
| Alachlor ¹ | 2.1 |
| Atrazine | 4.2 |
| Azinphos-methyl ¹ | 11.1 |
| Butylate ¹ | 1.8 |
| Carbaryl ¹ | 4.2 |
| Carbofuran | 3.3 |
| Chlorpyrifos | 4.2 |
| Cycloate ¹ | 1.5 |
| Dacthal | 1.2 |
| Diazinon | 3.6 |
| Diethatyl-ethyl ¹ | 3.6 |
| Eptam | 4.5 |
| Ethalfuralin ¹ | 2.4 |
| Hexazinone | 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 | 0.6 |
| Pendimethalin | 2.4 |
| Phosmet ¹ | 4.2 |
| Piperonyl butoxide ¹ | 3.3 |
| Simazine | 6.9 |
| Thiobencarb ¹ | 3.9 |
| Trifluralin | 3.0 |

¹ Pesticide not detected in any water samples during any sampling period.

Sediment Analysis

Extractions of sediment samples were performed using microwave-assisted solvent extraction (MASE). The MASE system was a MSP 1000 (CEM Corporation, Matthews, NC). Wet sediments were used, both 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-g of sediment,

dry weight were extracted per sample. The percentage of water in the sample was determined by weighing wet sediments, drying at 70°C, and reweighing to a constant dry weight. A wet weight equivalent to 5-g dry was calculated for each sample after determining the percentage of water.

After the wet sediments were weighed into teflon extraction vessels, a surrogate solution containing 400 ng each of *d*₁₄-trifluralin, (*di-n*-propyl-*D*₁₄) ¹³C₆-permethrin (phenoxy-¹³C₆, *cis/trans* mixture), ¹³C₁₂-4'-DDE (ring-¹³C₁₂, [(*p*, *p'*-dichlorodiphenyl dichloroethylene)], and *d*₁₀-chlorpyrifos (diethyl-*D*₁₀, [Cambridge Isotope Laboratories, Inc, Andover, MA]) was spiked to each sample. The sediments were extracted twice with 30 mL of a methylene chloride-acetone mixture (50:50 v/v) for 20 min per extraction. The MSP 1000 was operated at 75 percent of maximum power (maximum power = 950 w), and samples in the MASE extractor reached temperatures of 120°C and pressures of 150 lb/in². Because of excessive matrix interference, eight replicates were re-extracted under less energy-intensive conditions (80°C and 70 lb/in² pressure).

Extracts were decanted into separatory funnels containing 200 mL of deionized, organic-free water. The mixture was shaken, and the methylene chloride removed. The aqueous phase was extracted twice more with two volumes of methylene chloride (2 × 30 mL). 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 passage through an SPE column consisting of 500 mg of activated carbon (6 cm³ size barrel, Restek Corporation, Bellefonte, PA) followed by elution with 10 mL of methylene chloride. In selected cases, richly colored extracts were reduced again to 1 mL and placed onto another SPE column containing 300 mg of florisil (Supelco Corporation, Bellefonte, PA) and eluted with 10 mL of a 50:50 mixture of methylene chloride and ethyl acetate.

Samples were then solvent-exchanged to ethyl acetate, reduced in volume to 0.5 mL via nitrogen evaporation and further purified using gel permeation/high pressure liquid chromatography (GPC/HPLC). The sample was injected onto a Perkin Elmer HPLC consisting of a PE 410 4-stage pump and an LC-95 UV fixed wavelength detector (Perkin Elmer Corporation, Norwalk, CT). The analytical column was a gel permeation column from Polymer Laboratories (Amherst, MA). Column dimensions were 300 × 7.5 mm and the packing was polydivylbenzene (10 mm, 50 Å pore size). The mobile phase was ethyl acetate pumped at 1 mL/min. The size of the collection window was verified daily using pesticide standards and monitored at a wavelength of 254 nm. GPC/HPLC provided additional matrix cleanup, especially with elimination of elemental sulfur, which is a major co-extractant that interferes with GC/MS instrument analysis.

After GPC/HPLC, the sample extract (now at 9 mL volume) was reduced to approximately 500 µL, internal standards (the same as for the water samples) added, and brought to a final volume of 500 µL via N₂ evaporation for GC/MS analy-

sis. In the case of extremely colored extracts, the sample was brought to a volume of 1 mL prior to GC/MS analysis.

Quality Assurance and Quality Control for Sediment Samples

Samples processed for quality control included sediment matrix spikes and laboratory blanks. For sediment matrix spikes, a mixture containing 400 ng of each pesticide analyte was spiked to two suspended and two bed sediments, and the sediments were extracted and analyzed, as described above.

Sediment laboratory blanks (two replicates) consisted of cleaned Teflon vessels that were extracted twice with solvent (30 mL of a 50:50 mixture of acetone and methylene chloride v:v) using the MASE system. Extracts were brought through the entire sediment sample preparation procedure, reduced to 500 μ L, and analyzed by GC/MS. No analytes were detected in sediment laboratory blanks.

Method detection limits for the sediment procedure were determined by spiking seven replicate sediment samples with a pesticide mix containing 50 ng of each pesticide analyte. The sediment used was collected from an agricultural drain along the Sacramento River in northern California. Detection limits were calculated by multiplying the standard deviation of the mean concentration of each analyte by the corresponding value of Student's *t* test ($p = 0.05$ at $n - 1$ degrees of freedom, from Sokal and Rohlf, 1981). Detection limits for all pesticides ranged from 0.5 to 7.9 ng/g (table 3).

Recoveries of the d_{14} -trifluralin surrogate ranged from 50.5 to 120 percent with recovery of 88.3 ± 21.0 percent (mean \pm standard deviation). Recovery of the d_{10} -chlorpyrifos surrogate ranged from 43.9 to 116.9 percent with a mean recovery of 87.1 ± 17.3 percent. Recovery of $^{13}C_{12}$ -4,4' DDE ranged from 60.3 to 143 percent with an average of 96.0 ± 25.4 percent. Recovery of $^{13}C_6$ -permethrin ranged from 45.7 to 188 percent with an overall mean recovery of 95.0 ± 37.5 percent.

Recovery of pesticides from four matrix spike samples ranged from 58.7 to 133 percent with a mean recovery of 84.9 ± 23.8 percent. Matrix interference in suspended sediment samples from the New River international boundary, Alamo River international boundary, and New River at Drew Road sites led to low surrogate recoveries (these data are not included in the above summary calculations). Consequently, concentration data from these sites are considered as estimates only and have been flagged with an 'E' qualifier in the data tables. Poor chromatography of carbaryl and azinphos methyl led to high, but variable recoveries in spiked samples (these compounds were not included in the above calculations). Neither carbaryl nor azinphos methyl was detected in water or sediment samples.

Table 3. Method detection limits for current-use pesticides and DDTs¹ in sediments

| [ng/g, nanograms per gram] | |
|---------------------------------|-------------------------------|
| Pesticide | Method Detection Limit (ng/g) |
| Alachlor ² | 1.1 |
| Atrazine ² | 0.6 |
| Azinphos-methyl ² | 7.6 |
| Bifenthrin | 0.9 |
| Butylate ² | 0.5 |
| Carbaryl ² | 1.2 |
| Carbofuran ² | 3.0 |
| Chlorpyrifos | 1.5 |
| Cycloate ² | 1.8 |
| Cyfluthrin ² | 7.9 |
| Cypermethrin ² | 5.6 |
| Dacthal | 0.6 |
| Diazinon ² | 1.5 |
| Diethatyl-ethyl ² | 1.2 |
| Eptam | 0.7 |
| Esfenvalerate ² | 1.4 |
| Ethalfuralin ² | 1.9 |
| Hexazinone ² | 3.2 |
| lambda-Cyhalothrin ² | 0.5 |
| Malathion ² | 1.5 |
| Methidathion ² | 3.4 |
| Methyl parathion ² | 1.6 |
| Metolachlor ² | 1.0 |
| Molinate ² | 2.0 |
| Napropamide ² | 1.6 |
| Oxyfluorfen ² | 6.1 |
| Pebulate | 0.8 |
| Pendimethalin | 4.0 |
| Permethrin ² | 1.4 |
| Phosmet ² | 0.8 |
| Piperonyl butoxide ³ | 1.2 |
| Prometryn ² | 1.8 |
| Simazine ² | 2.1 |
| Thiobencarb ² | 4.4 |
| Trifluralin | 1.4 |
| <i>p,p'</i> -DDD | 2.9 |
| <i>p,p'</i> -DDE | 3.7 |
| <i>p,p'</i> -DDT | 3.9 |

¹ Refers to *p,p'*-DDT and the metabolites *p,p'*-DDD and *p,p'*-DDE.

² Compounds not detected in suspended or bed sediments during the sampling period.

³ A pesticide synergist added to pesticide formulations.

Instrument Analysis

Water and sediment extracts were analyzed for pesticides with a Saturn 2000 GC/MS ion trap system (Varian, Inc., Walnut Creek, CA). Run conditions are listed in *table 4*. The instrument was operated in full scan mode during most of the run. However, later in the instrument run, selected ion storage (SIS), which is equivalent to selected ion monitoring (SIM) on a quadrupole instrument, was utilized to optimize sensitivity for select analytes.

Calibration of instrument response was made with an eight-point standard curve that spanned the range of sample concentrations. Standards were purchased from Supelco Inc. (Bellefonte, PA). In addition, 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 check standard fell outside of this response window, the samples were re-injected. Each sample was injected twice, and concentrations were calculated from the mean of the two injections. If the concentrations from replicate injections had greater than a 25 percent difference, the data were reported, but were flagged with a 'D' qualifier in the data table, indicating that the compound was detected, but the concentration is uncertain because of high variability of replicate injections.

Sediment Organic Carbon Analysis

Sediments were analyzed for organic carbon content using a Perkin Elmer CHNS/O analyzer (Perkin Elmer Corporation, Norwalk, CT). Sediments were weighed in 5 × 9 mm silver boats, (Costech Analytical Technologies, Valencia, CA) exposed to concentrated hydrochloric acid fumes in a desiccator for 24 hours (to remove carbonate minerals), dried at 70°C to constant weight, and then combusted at 925°C. Acetanilimide was used for instrument calibration of elemental carbon and nitrogen.

Grain-Size Analysis

The percentage of sand and percentage of fines were determined on suspended sediments by the USGS laboratory in Marina, CA, using standard methods (Guy, 1969). The percentage of fines is defined as the fraction of sediment that passes through a 63 µm mesh sieve. A similar process was used for bed sediments in USGS's Sacramento Hydrologic Research Laboratory, except the mesh size of the sieve was 53 µm. Percentages were calculated on a dry weight basis for both types of sediments.

Table 4. Run conditions for the Saturn 2000 GC/MS system

[dpm, degrees per minute; PSI, pounds per square inch; °C, degrees Celsius; SIS, selected ion storage; m/z, mass/charge ratio; µamps, microamperes, a unit of charge; ev, electronvolts, a measurement of the gain on the MS electron multiplier; mm, millimeter; min, minute; µm, micrometer]

| | |
|--|--|
| Injection Conditions: | splitless injection, pressure pulse of 50 psi for 1.5 min. |
| Injection Temperature | 275°C |
| Oven Program: | 80°C, hold for 0.5 minutes, 80°C-120°C at 10 dpm 120°C – 200°C at 3 dpm, hold for 5 min. 200°C – 219°C, hold for 5 min. 219°C – 300°C at 10 dpm, hold for 10 min. |
| GC/MS conditions for most of the run: | range SIS, collecting 90 – 450 m/z, emission current = 15 µamps |
| For permethrin, cypermethrin, cyfluthrin, esfenvalerate, lambda cyhalothrin and azinphos-methyl: | true SIS – only quantitation and confirmatory ions collected, electron multiplier +300 ev offset, emission current 45 µamps |
| analytical column: | CPSIL 8-MS (Varian Corp) analytical column, 30m x 0.25 mm, 0.5 µm phase thickness |

Results

Station Characteristics

Station coordinates and the types of samples collected at each station are presented in *table 1*. The discharge measurements determined at the bridge sites are presented in *tables 5* and *6*. Also detailed in *tables 5* and *6* is the cross-stream characterization of dissolved constituents (DO, pH, and specific conductance), as well as temperature, for the Alamo and New Rivers bridge sites, respectively. The percentage of fines and SSC percentage of fines from the cross-stream transects are presented in *tables 7* and *8*. At the Drew Road site on the New River, DO concentrations differed by a factor of two (*table 6*), with the right bank having the lowest concentrations. SSC and percentage of fines also differed across the stream, with SSC lower in the middle of the stream, and percentage of fines having a maxima 11.3 m from the right bank (*table 8*).

Aqueous Pesticide Concentrations

Aqueous pesticide concentrations for both rivers are presented in *table 9*. Atrazine, chlorpyrifos, dacthal, eptam, hexazinone, malathion, oxyfluorfen, pendimethalin, and trifluralin were found at concentrations that were at least twice the method detection limit in at least one site in the Alamo River. Pesticide compounds, listed in order of decreasing detection frequency are as follows: {dacthal, eptam, trifluralin} > {atrazine, carbofuran, malathion, pendimethalin} > {*p,p'*-DDE} > {oxyfluorfen} > {bifenthrin, hexazinone, metolachlor, piperonyl butoxide and prometryn}. Trifluralin was found in the highest concentration of all detected compounds (207–599 ng/L), at six of the seven sites. Atrazine was also detected at relatively high concentrations (107–285 ng/L) at five of the seven sites. Only eptam was detected at the international boundary site (28.7 ng/L).

Fewer pesticides were detected in the water samples from the New River (*table 9*). Concentrations of atrazine, diazinon, malathion, and trifluralin were ten times above method detection limits at two or more New River sites. Diazinon was detected at all sites in concentrations that ranged from 21.5 to 95.8 ng/L. Atrazine was detected at four of the five sites, with a high concentration at the Evan Hewes Highway site (232 ng/L) and elevated concentrations (25.6–86.6 ng/L) at the remaining sites (atrazine was not detected at the international boundary site). Chlorpyrifos was also detected at three of the five sites in concentrations that ranged from 14.8 to 18.7 ng/L. Only diazinon was detected at the international boundary site, at a concentration of 74.1 ng/L.

Table 5. Summary of total discharge measurements and measurements of dissolved constituents and temperature from the Alamo River transects.

[ft³/s, cubic feet per second; m, meters; °C, degrees Celsius; µS/cm, microsiemens per centimeter; mg/L, milligrams per liter]

| Distance From Right Bank (m) | Depth (m) | Temperature (°C) | Specific Conductivity (µS/cm) | Dissolved Oxygen (mg/L) | pH |
|--|-----------|------------------|-------------------------------|-------------------------|-----|
| Alamo River at Harris Road Total discharge = 440 ft³/s | | | | | |
| 1.2 | 0.6 | 19.1 | 2,660 | 9.8 | 7.6 |
| 3.7 | 0.9 | 20.0 | 2,660 | 9.9 | 7.6 |
| 6.1 | 0.9 | 20.0 | 2,660 | 10.1 | 7.6 |
| 6.1 | 1.8 | 20.0 | 2,660 | 10.0 | 7.6 |
| 8.5 | 0.9 | 20.0 | 2,660 | 10.2 | 7.6 |
| 8.5 | 1.8 | 20.0 | 2,660 | 10.2 | 7.6 |
| 12.2 | 0.9 | 20.0 | 2,660 | 10.2 | 7.6 |
| 12.2 | 1.8 | 20.0 | 2,660 | 10.1 | 7.6 |
| 16.5 | 0.9 | 20.0 | 2,670 | 10.1 | 7.6 |
| 16.5 | 2.1 | 20.0 | 2,660 | 10.0 | 7.6 |
| 20.7 | 0.9 | 20.1 | 2,660 | 9.9 | 7.6 |
| 20.7 | 1.5 | 20.1 | 2,660 | 9.8 | 7.6 |
| 23.2 | 0.9 | 20.1 | 2,660 | 9.8 | 7.6 |
| Alamo River at Sinclair Road Total discharge = 1,140 ft³/s | | | | | |
| 3.0 | 0.9 | 19.0 | 3,500 | 10.7 | 7.8 |
| 5.5 | 0.9 | 19.1 | 2,530 | 10.6 | 7.8 |
| 5.5 | 2.4 | 19.2 | 2,510 | 10.5 | 7.7 |
| 9.1 | 0.9 | 19.2 | 2,560 | 10.7 | 7.7 |
| 9.1 | 2.4 | 19.2 | 2,560 | 10.6 | 7.7 |
| 12.8 | 0.9 | 19.2 | 2,560 | 11.2 | 7.8 |
| 12.8 | 2.4 | 19.2 | 2,560 | 10.7 | 7.8 |
| 16.5 | 0.9 | 19.2 | 2,560 | 10.7 | 7.8 |
| 16.5 | 2.4 | 19.2 | 2,560 | 10.9 | 7.8 |
| 20.1 | 0.9 | 19.2 | 2,560 | 10.7 | 7.8 |
| 20.1 | 2.4 | 19.2 | 2,560 | 10.6 | 7.8 |
| 23.8 | 0.9 | 19.2 | 2,560 | 11.5 | 7.8 |
| 23.8 | 2.4 | 19.2 | 2,560 | 11.0 | 7.8 |
| Alamo River at Garst Road Total discharge = 1,244 ft³/s | | | | | |
| 3.7 | 0.6 | 19.0 | 2,580 | 9.5 | 7.8 |
| 7.3 | 0.9 | 19.0 | 2,590 | 9.5 | 7.1 |
| 7.3 | 2.4 | 19.0 | 2,590 | 9.4 | 7.7 |
| 10.4 | 0.9 | 19.0 | 2,590 | 9.5 | 7.7 |
| 10.4 | 2.4 | 19.0 | 2,590 | 9.5 | 7.7 |
| 14.6 | 0.9 | 19.1 | 2,590 | 9.4 | 7.7 |
| 14.6 | 2.4 | 19.1 | 2,590 | 9.4 | 7.7 |
| 18.9 | 0.9 | 19.1 | 2,590 | 9.5 | 7.7 |
| 18.9 | 2.4 | 19.1 | 2,580 | 9.5 | 7.7 |
| 21.3 | 0.9 | 19.1 | 2,580 | 9.5 | 7.7 |
| 21.3 | 2.4 | 19.1 | 2,580 | 9.4 | 7.7 |
| 25.6 | 0.9 | 19.2 | 2,580 | 9.4 | 7.7 |

10 Pesticide Concentrations in Water and in Suspended and Bottom Sediments in the New and Alamo Rivers

Table 6. Summary of total discharge measurements and measurements of dissolved constituents and temperature from the New River transects

[ft³/s, cubic feet per second; m, meters; °C, degrees Celsius; μS/cm, microsiemens per centimeter; mg/L, milligrams per liter]

| Distance From Right Bank (m) | Depth (m) | Temperature (°C) | Specific Conductance (μS/cm) | DO (mg/L) | pH |
|--|-----------|------------------|------------------------------|-----------|-----|
| New River at International Boundary | | | | | |
| Total Discharge = 177 ft ³ /s | | | | | |
| 1.2 | 0.30 | 20.0 | 5,350 | 0.9 | 7.6 |
| 3.0 | 0.91 | 20.0 | 5,350 | 0.8 | 7.6 |
| 4.9 | 0.91 | 19.9 | 5,350 | 0.9 | 7.6 |
| 6.7 | 0.91 | 19.9 | 5,350 | 0.9 | 7.6 |
| 8.5 | 0.91 | 19.9 | 5,350 | 0.9 | 7.6 |
| New River at Drew Road Total Discharge = 362 ft³/s | | | | | |
| 4.9 | 0.9 | 20.6 | 4,490 | 0.4 | 7.6 |
| 7.3 | 0.9 | 20.6 | 4,490 | 0.3 | 7.6 |
| 7.3 | 1.5 | 20.6 | 4,490 | 0.5 | 7.6 |
| 9.8 | 0.9 | 20.6 | 4,500 | 0.5 | 7.6 |
| 9.8 | 2.4 | 20.6 | 4,490 | 0.5 | 7.6 |
| 12.8 | 0.9 | 20.6 | 4,500 | 0.6 | 7.6 |
| 12.8 | 1.8 | 20.7 | 4,500 | 0.8 | 7.6 |
| 15.8 | 0.6 | 20.7 | 4,500 | 0.8 | 7.6 |
| New River at Evanhwes Highway¹ | | | | | |
| 1.5 | 0.9 | 19.7 | 4,800 | 1.1 | 7.5 |
| 4.6 | 0.6 | 19.7 | 4,820 | 1.1 | 7.5 |
| 7.6 | 0.9 | 19.7 | 4,810 | 1.1 | 7.5 |
| 10.7 | 0.9 | 19.7 | 4,810 | 1.1 | 7.5 |
| New River at Outlet Total Discharge = 798 ft³/s | | | | | |
| 3.7 | 0.6 | 20.6 | 3,630 | 7.5 | 7.4 |
| 7.9 | 0.9 | 20.7 | 3,640 | 7.4 | 7.5 |
| 10.7 | 0.9 | 20.7 | 3,640 | 7.4 | 7.5 |
| 15.2 | 0.9 | 20.7 | 3,650 | 7.4 | 7.5 |
| 15.2 | 1.8 | 20.7 | 3,610 | 7.1 | 7.5 |
| 20.1 | 0.9 | 20.7 | 3,640 | 7.3 | 7.5 |
| 20.1 | 1.8 | 20.7 | 3,620 | 7.2 | 7.5 |
| 22.3 | 0.9 | 20.8 | 3,650 | 7.2 | 7.5 |
| 22.3 | 2.4 | 20.8 | 3,640 | 7.2 | 7.5 |
| 25.0 | 0.9 | 20.8 | 3,660 | 7.2 | 7.5 |
| 25.0 | 2.4 | 20.8 | 3,660 | 7.2 | 7.5 |

¹ Discharge measurements not performed at this site.

Table 7. Concentration and composition of suspended solids from depth-integrated samples, taken from the Alamo River in cross-stream transects and point samples

[mg/L, milligrams per liter]

| Distance From Right Bank ¹ | Fines (in percent) | Sand (in percent) | Concentration (mg/L) |
|--|--------------------|-------------------|----------------------|
| Alamo River at International Boundary | | | |
| 3 | 53 | 47 | 27 |
| Alamo River at Drop 10 | | | |
| 3 | 81 | 19 | 318 |
| Alamo River at Harris Road | | | |
| 5.8 | 75 | 25 | 355 |
| 10.7 | 80 | 20 | 344 |
| 12.8 | 78 | 22 | 344 |
| 14.9 | 79 | 21 | 343 |
| 18.3 | 76 | 24 | 365 |
| Alamo River at Drop 6A | | | |
| 3 | 80 | 20 | 312 |
| Alamo River at Drop 6 | | | |
| 3 | 77 | 23 | 372 |
| Alamo River at Sinclair Road | | | |
| 6.4 | 81 | 19 | 456 |
| 11.0 | 65 | 35 | 737 |
| 14.3 | 82 | 18 | 457 |
| 17.1 | 89 | 11 | 414 |
| 18.0 | 84 | 16 | 443 |
| Alamo River at Outlet | | | |
| 5.5 | 83 | 17 | 384 |
| 9.4 | 74 | 26 | 483 |
| 15.2 | 86 | 14 | 352 |
| 19.5 | 74 | 26 | 417 |
| 22.6 | 74 | 26 | 457 |

¹ When facing downstream.

Table 8. Concentration and composition of suspended solids from depth-integrated samples, taken from the New River in cross-stream transects, and point samples

[mg/L, milligrams per liter]

| Distance From Right Bank¹ | Fines (in percent) | Sand (in percent) | Concentration (mg/L) |
|---|-------------------------------|------------------------------|---------------------------------|
| New River at International Boundary | | | |
| 1.5 | 51 | 49 | 25 |
| 3.0 | 53 | 47 | 25 |
| 4.6 | 63 | 37 | 26 |
| 5.8 | 49 | 51 | 27 |
| 7.6 | 52 | 48 | 21 |
| New River at Drew Road | | | |
| 4.6 | 66 | 34 | 91 |
| 7.9 | 65 | 35 | 120 |
| 9.8 | 63 | 37 | 119 |
| 11.3 | 88 | 12 | 85 |
| 13.4 | 43 | 57 | 135 |
| New River at Evan Hewes Highway | | | |
| 3.0 | 81 | 19 | 144 |
| New River at Rice Drain | | | |
| 3.0 | 80 | 20 | 286 |
| New River at Outlet | | | |
| 7.3 | 82 | 18 | 283 |
| 14.0 | 77 | 23 | 321 |
| 19.5 | 79 | 21 | 284 |
| 22.9 | 82 | 18 | 274 |
| 25.3 | 86 | 14 | 248 |

¹When facing downstream.

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Table 9. Dissolved concentrations of current-use pesticides, April 2003

[Water samples were analyzed for the following compounds that were not detected during this sampling period: alachlor, azinphos-methyl, butylate, carbaryl, cycloate, diethylatyl-ethyl, ethalfluralin, methidathion, methyl parathion, molinate, napropamide, pebulate, phosmet, simazine, and thiobencarb. ng/L, nanogram per liter; ND, not detected; D, compound detected, but quantitation uncertain because of high variability between replicate injections; a number in parentheses () indicates the value is below the method detection limit; E, concentration is an estimate. Method detection limits were not determined for *p,p'*-DDE in water, and so are considered estimates].

| Alamo River Stations | | | | | | | |
|----------------------|-------------------------------|----------------------|---------------------------|--------------------------------|--------------------|----------------|---------------|
| | International Boundary (ng/L) | Sinclair Road (ng/L) | Drop 6 (ng/L) | Drop 6A (ng/L) | Harris Road (ng/L) | Drop 10 (ng/L) | Outlet (ng/L) |
| Atrazine | ND | 184 | 107 | 181 | 138 | ND | 285 |
| Bifenthrin | ND | ND | ND | ND | 9.5 | ND | ND |
| Carbofuran | ND | 18.8 | 182 | 7.3 | 46.8 | ND | 19.4 |
| Chlorpyrifos | ND | 25.0 | 19.2 | 23.7 | 18.8 | ND | 25.5 |
| Dacthal | ND | 29.1 | 26.1 | 31.2 | 29.3 | 40.9 | 37.7 |
| Diazinon | ND | 4.8 | 5.4 | 2.4 | D | ND | D |
| Eptam | 28.7 | 28.5 | 16.8 | 17.6 | 18.0 | (1.5) | 32.3 |
| Hexazinone | ND | ND | 21.4 | ND | ND | ND | ND |
| Malathion | ND | 142 | 8.6 | 9.7 | 42.8 | ND | 110 |
| Metolachlor | ND | ND | D | ND | ND | ND | ND |
| Oxyfluorfen | ND | ND | 21.7 | D | ND | ND | 14.8 |
| <i>p,p'</i> -DDE | ND | 4.7E | 4.1E | 3.0E | ND | ND | 4.0E |
| Pendimethalin | ND | 50.7 | 52.0 | 37.6 | 29.1 | ND | 52.2 |
| Piperonyl Butoxide | ND | ND | ND | ND | D | ND | ND |
| Prometryn | ND | ND | ND | ND | ND | ND | 6.15 |
| Trifluralin | ND | 409 | 599 | 558 | 477 | 207 | 428 |
| New River Stations | | | | | | | |
| | International Boundary (ng/L) | Drew Road (ng/L) | Evan Hewes Highway (ng/L) | New River at Rice Drain (ng/L) | Outlet (ng/L) | | |
| Atrazine | ND | 86.6 | 232 | 25.6 | 51.0 | | |
| Chlorpyrifos | ND | ND | 14.8 | 18.8 | D | | |
| Dacthal | ND | ND | ND | ND | 10.8 | | |
| Diazinon | 74.1 | D | 30.5 | 37.5 | 21.5 | | |
| Eptam | ND | ND | ND | ND | 46.8 | | |
| Malathion | ND | ND | 52.3 | ND | D | | |
| Pendimethalin | ND | ND | ND | ND | 36.0 | | |
| Piperonyl Butoxide | ND | ND | ND | 9.7 | ND | | |
| Trifluralin | ND | 68.5 D | 97.5 | 167 | 159 | | |

Percentage of Organic Carbon and Percentage of Fines in Suspended and Bed Sediments

Organic carbon and percentage of fines for suspended and bed sediments from the Alamo River are presented in table 10. Mean values of percentage of fines from the cross-stream transects were calculated and are presented here, along with the point samples. Organic carbon concentrations in bed sedi-

ments were lower than suspended sediments by a factor of two to ten. Suspended sediments from both the New and Alamo River international boundary sites had the highest percentage of OC (24 and 14 percent, respectively). For both rivers, the percentage of fines was higher in suspended sediments from the outlet sites compared with the international boundary sites. Much greater variability was seen in the percentage of fines for bed sediments.

Table 10. Percentage of organic carbon and percentage of fines from Alamo and New River suspended and bed sediments[fines for suspended sediments is < 62 μm , for bed sediments is < 53 μm].

| | Organic Carbon (in percent) | Fines (in percent) |
|------------------------------|--------------------------------|-----------------------|
| ALAMO RIVER SEDIMENTS | | |
| Suspended Sediments | | |
| Outlet | 1.0 | 78 |
| Drop 10 | 1.5 | 81 |
| Drop 6 | 1.1 | 77 |
| Drop 6A | 1.1 | 80 |
| Harris Road | 1.8 | 78 |
| Sinclair Road | 1.1 | 20 |
| International Boundary | 14 | 53 |
| Bed Sediments | | |
| Outlet | 0.4 | 54 |
| Drop 10 | 0.7 | < 1.0 |
| Drop 6 | 0.4 | 57 |
| Drop 6A | 0.1 | 38 |
| Harris Road | 0.2 | 28 |
| Sinclair Road | 0.2 | 12 |
| International Boundary | 0.2 | 9.0 |
| NEW RIVER SEDIMENTS | | |
| Suspended Sediments | | |
| Outlet | 1.2 | 81 |
| Rice Drain | 2.7 | 80 |
| Evan Hewes Highway | 5.4 | 81 |
| Drew Road | 8.1 | 65 |
| International Boundary | 24 | 54 |
| Bed Sediments | | |
| Outlet | 0.1 | 20 |
| Rice Drain | 1.4 | 86 |
| Evan Hewes Highway | 0.4 | 24 |
| Drew Road | 0.2 | 21 |
| International Boundary | 2.2 | 56 |

Pesticide Concentrations Associated with Suspended and Bed Sediments

Concentrations of pesticides associated with suspended and bed sediments from the Alamo River sites are presented in *table 11*. Eight pesticide compounds were detected in suspended sediments in the following order of decreasing detection frequency: {*p,p'*-DDE} > {dacthal, trifluralin} > {chlorpyrifos, pendimethalin} > {*p,p'*-DDD} > {*p,p'*-DDT}

> {*p,p'*-DDT, and bifenthrin}. *p,p'*-DDE was detected at all seven sites at concentrations that ranged from D to 113 ng/g. Dacthal was detected at six out of the seven sites (it was not detected at the international boundary site) in concentrations that ranged from 7.3 to 31.9 ng/g. Trifluralin was detected at the same six sites in concentrations that ranged from 16.8 to 120 ng/g. Chlorpyrifos and pendimethalin were detected at five out of seven sites in concentrations that ranged from 8.5 to 13.7 ng/g and 16.5 to 93.2 ng/g, respectively. *p,p'*-DDD was detected at four out of seven sites in concentrations that ranged from 4.4 to 10.9 ng/g. Seven pesticides were detected at the Drop 6, Harris Road, and Sinclair Road sites, five at Drop 6A and the Outlet site, three at Drop 10, and only one at the international boundary site.

Eight pesticides were detected on bed sediments from the Alamo River and included in order of decreasing detection frequency: {*p,p'*-DDE} > {chlorpyrifos, trifluralin} > {*p,p'*-DDD, pendimethalin} > {dacthal, eptam} > {pebulate}. *p,p'*-DDE was consistently found on bed sediments from all sites, at concentrations that were a factor of two to ten lower than in suspended sediments (6.2–75.4 ng/g). Chlorpyrifos was detected at five sites in concentrations that ranged from 1.5 to 9.0 ng/g. Concentrations of chlorpyrifos were close (that is, within a factor of two) to those found in the suspended sediments, except at Sinclair Road where concentrations were approximately four times lower. The outlet site had the greatest number of pesticide detections (eight). Drop 10, Drop 6, Drop 6A, and Sinclair Road sites had six compounds detected. The international boundary and Harris Road sites had one compound detected (*p,p'*-DDE).

Concentrations of pesticides associated with suspended and bed sediments from the New River sites are presented in *table 12*. Pesticides detected in suspended sediments, in order of decreasing detection frequency, included {trifluralin} > {*p,p'*-DDE} > {chlorpyrifos, dacthal, pebulate, pendimethalin, and permethrin}. While the concentrations of chlorpyrifos and pebulate were higher than those found in Alamo River suspended sediments, the frequency of detection was much lower. The New River Outlet site had the greatest number of detections (five), followed by the Rice Drain site (three). The Evan Hewes Highway site had two compounds detected, the Drew Road site had only one, and no pesticides were detected at the international boundary site. Regarding the international boundary site, it should be noted that suspended sediment had matrix interference and poor surrogate recoveries. Suspended sediment concentrations of trifluralin were as high as or higher than those found at Alamo River stations (concentrations ranged from 14.5 to 115 ng/g) and were at all sites except for the international boundary site. A high concentration of pebulate (108 ng/g) was found in suspended sediments from the Evan Hewes Highway site, and a lower concentration of pendimethalin (15.7 ng/g) was detected in suspended sediments from the outlet site. The metabolite *p,p'*-DDE was detected

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only at the Rice Drain and outlet stations (concentrations of 22.9 and 33.0 ng/g respectively).

There were fewer pesticides detected on bed sediments in the New River compared with the Alamo River. Chlorpyrifos was detected on bed sediment from the international boundary

site at a concentration of 55.7 ng/g. Other pesticides detected on bed sediments included pebulate (at a concentration of 118 ng/g at the Rice Drain site) and *p,p'*-DDE (9.6 and 13.4 ng/g at the outlet and Evan Hewes Highway sites, respectively).

Table 11. Concentrations of pesticides in Alamo River sediments, April 2003

[Values are in nanograms per gram sediment dry weight. Sediment samples were analyzed for the following compounds that were not detected during this sampling period: alachlor, atrazine, azinphos-methyl, butylate, carbaryl, carbofuran, cycloate, cyfluthrin, cypermethrin, diazinon, diethylatyl-ethyl, esfenvalerate, ethalfuralin, hexazinone, lambda-Cyhalothrin, malathion, methidathion, methyl parathion, metolachlor, molinate, napropamide, oxyfluorfen, phosmet, piperonyl butoxide, prometryn, simazine, thiobencarb, and trifluralin. ng/g, nanogram per gram; ND, not detected; D, compound detected but quantitation uncertain because of high variability between replicate injections; () concentration is below method detection limits; *, concentrations are from replicates that were re-extracted under lower energy conditions in the microwave extractor].

| Pesticide Compounds | International Boundary (ng/g) | Sinclair Road (ng/g) | Harris Road (ng/g) | Drop 6A (ng/g) | Drop 6 (ng/g) | Drop 10 (ng/g) | Outlet (ng/g) |
|----------------------------|-------------------------------|----------------------|--------------------|----------------|---------------|----------------|---------------|
| Suspended Sediments | | | | | | | * |
| Bifenthrin | ND | ND | 1.9 | ND | ND | ND | ND |
| Chlorpyrifos | ND | 10.8 | 13.7 | 9.5 | 8.5 | ND | 11.4 |
| Dacthal | ND | 7.3 | 20.7 | 23.9 | 31.9 | 23.3 | 11.5 |
| <i>p p'</i> -DDD | ND | 7.6 | 7.4 | 10.9 | 4.4 | ND | ND |
| <i>p p'</i> -DDE | 40.5 | 113 | D | D | D | 134 | 113 |
| <i>p p'</i> -DDT | ND | 14.0 | ND | ND | (1.5) | ND | ND |
| pendimethalin | ND | 25.4 | 93.2 | 75.9 | 70.8 | ND | 16.5 |
| trifluralin | ND | 72.4 | 91.5 | 100 | 120 | 16.8 | 20.4 |
| Bed Sediments | | | | | | | * |
| Chlorpyrifos | ND | 2.3 | ND | 5.6 | 7.0 | 1.5 | 9.0 |
| Dacthal | ND | ND | ND | 2.5 | ND | 1.8 | 6.6 |
| Eptam | ND | 1.3 D | ND | ND | 6.7 | ND | 2.4 |
| <i>p p'</i> -DDD | ND | ND | ND | (1.3) | D | (0.56) | 3.5 |
| <i>p p'</i> -DDE | 6.2 | 11.8 | 25.6 | 25.2 | 35.9 | 24.0 | 75.4 |
| Pebulate | ND | ND | ND | ND | 77.3 | ND | 16.6 |
| Pendimethalin | ND | 4.1 | ND | 5.7 | ND | 1.1 | 15.6 |
| Trifluralin | ND | 10.5 | ND | 8.2 | 1.9 | 5.7 | 9.1 |

Table 12. Concentrations of current-use pesticides and DDTs in New River sediments, April 2003

[Sediment samples were analyzed for the following compounds that were not detected during this sampling period: alachlor, atrazine, azinphos-methyl, bifenthrin, butylate, carbaryl, carbofuran, cycloate, cyfluthrin, cypermethrin, diazinon, diethylatyl-ethyl, EPTC, esfenvalerate, ethafluralin, hexazinone, lambda-cyhalothrin, malathion, methidathion, methyl parathion, metolachlor, molinate, napropamide, oxyfluorfen, phosmet, piperonyl butoxide, prometryn, simazine, thiobencarb, *p,p'*-DDD and *p,p'*-DDT. *, concentration are from replicates that were extracted using lower energy conditions in the microwave extractor; ng/g, nanogram per gram; ND, not detected; E, concentration is considered to be an estimate only]

| | International Boundary (ng/g) | Drew Road (ng/g) | Evan Hewes Highway (ng/g) | Rice Drain (ng/g) | Outlet (ng/g) |
|----------------------------|-------------------------------------|---------------------|---------------------------------|----------------------|------------------|
| Suspended Sediments | | | | | |
| Chlorpyrifos | ND | ND | ND | 15.6 | ND |
| Dacthal | ND | ND | ND | ND | 6.5 |
| <i>p,p'</i> -DDE | ND | ND | ND | 22.9 | 33.0 |
| Pebulate | ND | ND | 108 | ND | ND |
| Pendimethalin | ND | ND | ND | ND | 15.7 |
| Trifluralin | ND | 5.8 E | 115 | 113 | 16.1 |
| Permethrin | ND | ND | ND | ND | 9.0 |
| Bed Sediments | | | | | |
| | * | | | * | |
| Chlorpyrifos | 55.7 | ND | ND | ND | ND |
| <i>p,p'</i> -DDE | ND | ND | 8.8 | ND | 6.8 |
| Pebulate | ND | ND | ND | 118 | ND |

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