USGS
science for a changing world

Perpared in cooperation with the National Park Service

Level 1 Water-Quality Inventory of Baseline Levels of Pesticides in Urban Creeks—Golden Gate National Recreation Area and the Presidio of San Francisco, California

Data Series 338

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

Front cover; clockwise from top left:
Hydrologist sampling Redwood Creek in the northern portion of Golden Gate Recreation Area (photo credit: Michelle Hladik, USGS).
Chemist sampling Tennessee Hollow Creek in the Presidio of San Francisco (photo credit: James Orlando, USGS).
Nyhan Creek located in the northern portion of Golden Gate Recreation Area (photo credit: James Orlando, USGS).
Sanchez Creek located in the southern portion of Golden Gate Recreation Area (photo credit: Michelle Hladik, USGS).

Level 1 Water-Quality Inventory of Baseline Levels of Pesticides in Urban Creeks—Golden Gate National Recreation Area and the Presidio of San Francisco, California

By Michelle L. Hladik and James L. Orlando

Prepared in cooperation with the National Park Service

Data Series 338

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

U.S. Department of the Interior
DIRK KEMPTHORNE, Secretary

U.S. Geological Survey
Mark D. Myers, Director

U.S. Geological Survey, Reston, Virginia: 2008

For product and ordering information:
World Wide Web: http://www.usgs.gov/pubprod
Telephone: 1-888-ASK-USGS

For more information on the USGS--the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment:
World Wide Web: http://www.usgs.gov
Telephone: 1-888-ASK-USGS

Suggested reference:
Hladik, M.L., and Orlando, J.L., 2008, Level 1 water-quality inventory of baseline levels of pesticides in urban creeks—Golden Gate National Recreation Area and the Presidio of San Francisco, California: U.S. Geological Survey Data Series 338, 14 p.

Contents

Figures

Tables

Abbreviations and Acronyms

(additional information or clarification given in parentheses)

3,4-DCA	3,4-dichloroaniline
DCM	dichloromethane
DCPA	dacthal
p,*p*′-DDD	dichlorodiphenyldichloroethane
p,*p*′-DDE	dichlorodiphenyldichloroethylene
p,*p*′-DDT	dichlorodiphenyltrichloroethane
dms	degrees, minutes, seconds
DPR	Department of Pesticide Regulation
EPTC	*S*-ethyl dipropylthiocarbamate
GC/MS	gas chromatograph/mass spectrometer
GOGA	Golden Gate National Recreation Area
GPC/HPLC	gel-permeation chromatography/high-performance liquid chromatography
HCl	hydrochloric acid
MASE	microwave-assisted solvent extraction
MDL	method detection limit
nd	not detected
N_2	nitrogen gas
NPS	National Park Service
PAH	polycyclic aromatic hydrocarbon
PBO	piperonyl butoxide
PCA	pentachloroanisole
PCNB	pentachloronitrobenzene
PRES	Presidio of San Francisco
rpm	revolutions per minute
SPE	solid-phase extraction
SD	standard deviation
SWRCB	State Water Resources Control Board
USGS	U.S. Geological Survey
v/v	volume-to-volume
WRD	Water Resources Division (NPS)

Units of Measurement

cm	centimeter
g	gram
L	liter
L/min	liter per minute
lb	pound
m	meter
µg/kg	micrograms per kilogram
µm	micrometer
µL	microliter
µS/cm	microsiemens per centimeter
mi	mile
mi^2	square mile
mg	milligram
mL	milliliter
mL/min	milliliter per minute
ng	nanogram
ng/g	nanogram per gram
ng/L	nanogram per liter

Notes

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

$$°F = (1.8 \times °C) + 32$$

Chemical concentrations in water are reported in units of nanograms per liter (ng/L). Chemical concentrations in sediment are reported in units of nanograms per gram of dry weight sediment (ng/g).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25°C).

Use of liter (L) as a special name for cubic decimeter (dm^3) is restricted to the measurement of liquids and gases.

Level 1 Water-Quality Inventory of Baseline Levels of Pesticides in Urban Creeks—Golden Gate National Recreation Area and the Presidio of San Francisco, California

By Michelle L. Hladik and James L. Orlando

Abstract

To characterize baseline water-quality levels of pesticides in Golden Gate National Recreation Area and the Presidio of San Francisco, the U.S. Geological Survey collected and analyzed surface-water and bed-sediment samples at 10 creeks during February, April, and July 2006. Pesticide data were obtained using previously developed methods. Samples from sites in the Presidio were analyzed only for pyrethroid insecticides, whereas the remaining samples were analyzed for pyrethroids and additional current and historical-use pesticides. Pesticide concentrations were low in both the water (below 30 ng/L) and sediment (below 3 ng/g). The pyrethroid bifenthrin was detected in water samples from two sites at concentrations below 2 ng/L. Other compounds detected in water included the herbicides dacthal (DCPA) and prometryn, the insecticide fipronil, the insecticide degradates *p*,*p*′-DDE and fipronil sulfone, and the fungicides cyproconazole, myclobutanil and tetraconazole. The only pesticides detected in the sediment samples were *p*,*p*′-DDT and its degradates (*p*,*p*′-DDD and *p*,*p*′-DDE). Pesticide information from the samples collected can provide a reference point for future sampling and can help National Park Service managers assess the water quality of the urban creeks.

Introduction

The Level 1 inventory is part of a nationwide program by the National Park Service (NPS) Water Resources Division (WRD) to develop baseline water-quality information for key water bodies at NPS units throughout the United States. Key water bodies for Level 1 purposes are defined as those waters that are essential to the cultural, historical, or natural resource management themes of the unit, or that provide habitats for threatened or endangered plants and animals.

The objective of this water-quality inventory was to obtain data on pesticide concentrations in key water bodies of the Golden Gate National Recreation Area (GOGA). GOGA comprises approximately 75,000 acres of coastal lands north and south of the entrance to San Francisco Bay and includes the Presidio of San Francisco (PRES), a former U.S. Army installation (fig. 1). The water-quality data obtained during this study will provide baseline information to enable evaluation of the need for future monitoring.

In 1998, all urban creeks in the San Francisco Bay area were added to the Clean Water Act Section 303d list because of known or suspected diazinon impairment (U.S. Environmental Protection Agency, 2002), and as of 2006, Coyote Creek and Rodeo Creek remain on the list (State Water Resources Control Board, 2006). Diazinon is an organophosphorus insecticide used on lawns, fruits, and vegetables. This pesticide has since been partially “phased out” and has not been available for purchase for residential use since late 2004 (U.S. Environmental Protection Agency, 2004). Diazinon use is declining and is being replaced by other pesticides such as pyrethroids (TDC Environmental, 2005). There are currently seven pyrethroid pesticides that are the new focus of the San Francisco Bay Regional Water Quality Control Board’s Water Quality Attainment Strategy (Johnson, 2004). These pyrethroids include bifenthrin, cyfluthrin, λ-cyhalothrin, cypermethrin, deltamethrin, esfenvalerate, and permethrin.

In GOGA, there is concern regarding pesticide (especially pyrethroid) use within, as well as adjacent to parklands. Pyrethroid pesticides can be harmful to aquatic life including the endangered coho salmon (*Oncorhynchus kisutch*) and tidewater goby (*Eucyclogobius newberryi*), as well as the threatened California red-legged frog (*Rana aurora draytonii*) and steelhead trout (*Oncorhynchus mykiss*) (U.S. Fish and Wildlife Service, 2007). Soils, sediments, surface water, and ground water in some areas within GOGA and PRES have been tested for pesticides through the Presidio remediation program; however, many surface waters have not been tested for pesticides. Knowledge of the baseline condition of streams with regard to pesticides is a critical need for resource management.

Figure 1. Sites in Golden Gate National Recreation Area and the Presidio of San Francisco, California.
(NPS, National Park Service)

Pesticide Use in GOGA and PRES

While the NPS has records of pesticides applied in GOGA and PRES, historically and currently, there is very little knowledge about the occurrence of these pesticides in water and sediment. With regard to the pyrethroids, permethrin and resmethrin have documented uses on parklands (Mary Cooprider, National Park Service, written commun., 2005).

In addition to the NPS database on pesticide application, data can also be obtained from the California Department of Pesticide Regulation (DPR) as to which pesticides were applied by registered pesticide applicators in and around GOGA and PRES, with the latest data being available for 2005 (California Department of Pesticide Regulation, 2005). The DPR database includes pesticide applications by the township, range, and section for fixed locations such as agricultural sites, or merely by county when applied for nonagricultural purposes, such as structural pest control, landscape and roadside maintenance, or similar uses.

The 2005 database contains no records of pesticides applied specifically within the watersheds of the sites sampled in this study. However, the database does show that significant amounts of pesticides were applied to nonagricultural sites within the counties occupied by the sampling sites. Specifically, 52,892 lb of pesticides were applied in Marin County, where four of the sites are located (Coyote Creek, Nyhan Creek, Redwood Creek, and Rodeo Creek), 23,479 lb were applied in San Francisco County, where four of the sites are located (Crissy Marsh, Dragonfly Creek, Lobos Creek, and Tennessee Hollow Creek), and 179,791 lb were applied in San Mateo County, where the Milagra Creek and Sanchez Creek sites are located. These data indicate that pesticides are applied within or immediately adjacent to the parklands evaluated in this study. Additionally, whereas the DPR database tracks use by registered pesticide applicators (such as to specific crops or for structural pest control), it does not track the use of pesticide by nonprofessionals (for example, homeowners) where the application of pyrethroids is likely to be significant (TDC Environmental, 2005).

Project Design

This project was a collaboration between the NPS and the U.S. Geological Survey (USGS) in 2006 that was designed to measure baseline levels of pesticides in key water bodies located within Golden Gate National Recreation area (including the Presidio of San Francisco). Sampling locations were selected through consultation with NPS and Presidio Trust personnel. Sampling design and all field work was conducted by the USGS. A variety of pesticide classes were analyzed by the USGS in surface water and in bed sediments using methods previously developed by the USGS.

Surface waters and bed sediments were sampled during a one-day period on three separate occasions during this study. The first sampling event occurred in February, the second in April, and the third in June, to detect any pesticides that had been applied during the winter, spring, and summer, respectively.

Purpose and Scope

This report describes the methods and procedures used during sampling and analysis of pesticides at sites within GOGA (fig. 1) and presents water-quality and sediment-quality data for samples collected during the study. Concentrations of 61 pesticides and degradates were analyzed in 27 water samples. Total organic carbon and concentrations of 41 pesticides and degradates were analyzed in 30 sediment samples. In addition, Method detection limits (MDLs) are presented for pesticides that were analyzed in water and sediment as part of this study. During this study, the USGS was responsible for the design of the field sampling, collection of surface-water and sediment samples, and all analyses of the samples. Water and sediment samples were analyzed for pesticides and total organic carbon at the USGS's California Water Science Center organic chemistry laboratory in Sacramento, California (hereinafter, "Sacramento Laboratory").

Acknowledgments

The authors would like to thank Tania Pollak of the Presidio Trust, and Mary Cooprider, Brannon Ketcham, and Tamara Williams with the NPS for providing guidance in selecting sites and helping with sample locations.

Study Design and Methodology

Selection of Sampling Sites

Ten sampling sites were chosen within GOGA. These included four sites (Coyote Creek, Nyhan Creek, Redwood Creek, and Rodeo Creek) located north of the entrance to San Francisco Bay, four sites (Crissy Marsh, Dragonfly Creek, Lobos Creek, and Tennessee Hollow Creek) within the Presidio of San Francisco, and two sites (Milagra Creek and Sanchez Creek) located in urban areas south of San Francisco (table 1, fig. 1). Sites were selected from input by NPS and Presidio Trust personnel and were chosen using the "key water body" criteria defined for the Level 1 inventory program. The upstream watersheds for each of the sites sampled are primarily NPS lands.

Table 1. Surface water and sediment sampling sites in Golden Gate National Recreation Area and the Presidio of San Francisco, California, and sample matrices collected.

[Horizontal Datum is NAD 83. dms, degrees (°), minutes (‘), seconds (″); GOGA, Golden Gate National Recreation Area; NPS, National Park Service; Presidio Trust, manages Presidio lands; no., number; PRES, Presidio of San Francisco; USGS, U.S. Geological Survey]

Site name [USGS official site name]	Management	USGS site identification no.	Latitude (dms)	Longitude (dms)	Sample matrix collected
North GOGA					
Coyote Creek [Coyote Creek near Marin City]	NPS	375243122324501	37°52′43″	122°32′45″	Water, bed sediment
Nyhan Creek [Nyhan Creek at Marin City]	NPS	375213122313901	37°52′13″	122°31′39″	Water, bed sediment
Redwood Creek [Redwood Creek at Muir Beach near Tamapais Valley]	NPS	11460152	37°51′48″	122°34′31″	Water, bed sediment
Rodeo Creek [Gerbode Valley Creek near Sausalito]	NPS	11460110	37°50′01″	122°31′14″	Water, bed sediment
PRES					
Crissy Marsh [Crissy Marsh at San Francisco]	NPS	374816122271501	37°48′16″	122°27′15″	Depositional sediment
Dragonfly Creek [Dragonfly Creek at San Francisco]	Presidio Trust	374801122281501	37°48′01″	122°28′15″	Water, bed sediment
Lobos Creek [Lobos Creek]	NPS and Presidio Trust	374715122285601	37°47′15″	122°28′56″	Water, bed sediment
Tennessee Hollow [Tennessee Hollow Creek at San Francisco]	Presidio Trust	374808122271401	37°48'08″	122°27'15″	Water, bed sediment
South GOGA					
Milagra Creek [Milagra Creek near Pacific Manor]	NPS	373842122290301	37°38′42″	122°29′03″	Water, bed sediment
Sanchez Creek [Sanchez Creek at Pacifica]	NPS	373718122292701	37°37′17″	122°29′27″	Water, bed sediment

Watersheds for sites in the northern portion of GOGA (north of the entrance to San Francisco Bay) are fairly stable and functional, supporting threatened coho salmon and steelhead trout. However, these stream systems are affected by historical or current agricultural activities, as well as by dispersed urban development. Coyote Creek drains the town of Mill Valley and the eastern slopes of Mount Tamalpais (Cooprider, 2004). The Coyote Creek sampling site is located near the northeastern border of NPS lands, upstream of Mill Valley (fig. 2). The watershed upstream of the site (216 acres) is almost entirely within NPS lands. Nyhan Creek drains an approximately 750-acre watershed into the southeast of Mill Valley (fig. 2). Sampling on Nyhan Creek was conducted immediately downstream of the confluence of Oakwood Valley Creek and the border of NPS lands (fig. 2). Water flow in Coyote and Nyhan Creeks varied and was very low during drier periods of the sampling effort. The Rodeo Creek watershed (2,000 acres) is located entirely within GOGA lands (fig. 2). Rodeo Creek flows approximately east to west, includes a North Fork and South Fork, and drains into Rodeo Lagoon. Developments located within the drainage include NPS housing, a stable riding operation, and Fort Cronkhite (Cooprider, 2004). Sampling for Rodeo Creek was conducted from a footbridge upstream of Rodeo Lagoon. Redwood Creek has the largest drainage of all sites sampled, at over 4,700 acres, and its headwaters include Muir Woods National Monument. The watershed for Redwood Creek drains the south side of Mount Tamalpais, where it is fed by three major and seven minor tributaries (Cooprider, 2004). The sampling site for Redwood Creek is located at a road bridge approximately 0.5 mi upstream of Muir Beach. Discharge at the Redwood Creek site can be high during storm events, causing lowland flooding, as occurred during January 2006.

Sites located in the Presidio of San Francisco are in an area that is highly urbanized and has limited surface-water resources. Four sites were sampled in this area (fig. 3). Dragonfly Creek (also referred to as “Fort Scott Creek”) drains an approximately 50-acre watershed entirely within the Presidio and is fed by a perennial spring. This site was located near the Presidio native plant nursery, upstream of the point where Dragonfly Creek is diverted into an underground concrete channel. The Tennessee Hollow Creek watershed is approximately 300 acres and extends partially outside NPS lands. The creek was sampled at the downstream end of a section “daylighted” during a restoration project completed in 2005, and before it returns below ground (in a concrete channel). Crissy Marsh is a tidal marsh restoration project along San Francisco Bay adjacent to Crissy Field (a former airfield; Cooprider, 2004). This site, just below the outflow of Tennessee Hollow Creek into Crissy Marsh, was sampled for depositional sediment. Lobos Creek is the only above-ground stream located within the city of San Francisco and forms part of the southern boundary of the Presidio (fig. 3). The creek is the drinking-water source for the Presidio, and is partly diverted into the Presidio Water Treatment plant at Baker Beach (Cooprider, 2004). At the point of sampling (upstream of the water treatment plant), Lobos Creek drains an approximately 50-acre watershed.

Figure 2. Sites in northern portion of Golden Gate National Recreation Area, California. NM, National Monument; NPS, National Park Service.

Two water bodies in highly urbanized areas (Milagra Creek and Sanchez Creek) were chosen for sampling in the southern area of GOGA (fig. 4). These small watersheds (460 and 690 acres, respectively) flow through predominantly residential areas in the towns of Pacific Manor and Pacifica. Both creeks are channelized and concrete-lined, and (or) built as culverts, outside of NPS lands. Milagra Creek was sampled at the point where it leaves NPS lands before it enters a culvert in a residential area. Sanchez Creek, bordered by the Sharp Park Golf Course, was sampled where it leaves the golf course and re-enters parklands.

Sample Collection

Surface Water

Surface-water samples were collected for analysis of pesticides at all sites except Crissy Marsh. Water flow and channel depth were used to determine the sampling method. For those sites with low flow and narrow, shallow channels (Coyote Creek, Nyhan Creek, Dragonfly Creek, Tennessee Hollow Creek, and Milagra Creek), “grab” samples were collected mid-channel by dipping a 1-L baked, amber-glass bottle below the water surface. Samples from Lobos Creek, Rodeo Creek, Redwood Creek, and Sanchez Creek, which had higher flows and were wider and deeper, were collected as integrated samples (width and depth) using a Teflon bottle attached to a wading rod (Wilde and Radtke, 1998). Immediately after sampling, the water was transferred from the Teflon bottle into a 1-L baked amber-glass bottle. Water flow in Tennessee Hollow Creek was very low during the February and April sampling events, and as a result, water was collected using a small peristaltic pump, with Teflon tubing, to pump the water directly into a 1-L baked amber-glass bottle. All samples were immediately placed on ice for transport to the USGS Sacramento Laboratory where they were refrigerated prior to processing for analysis. Analysis occurred within 24 hours of sampling.

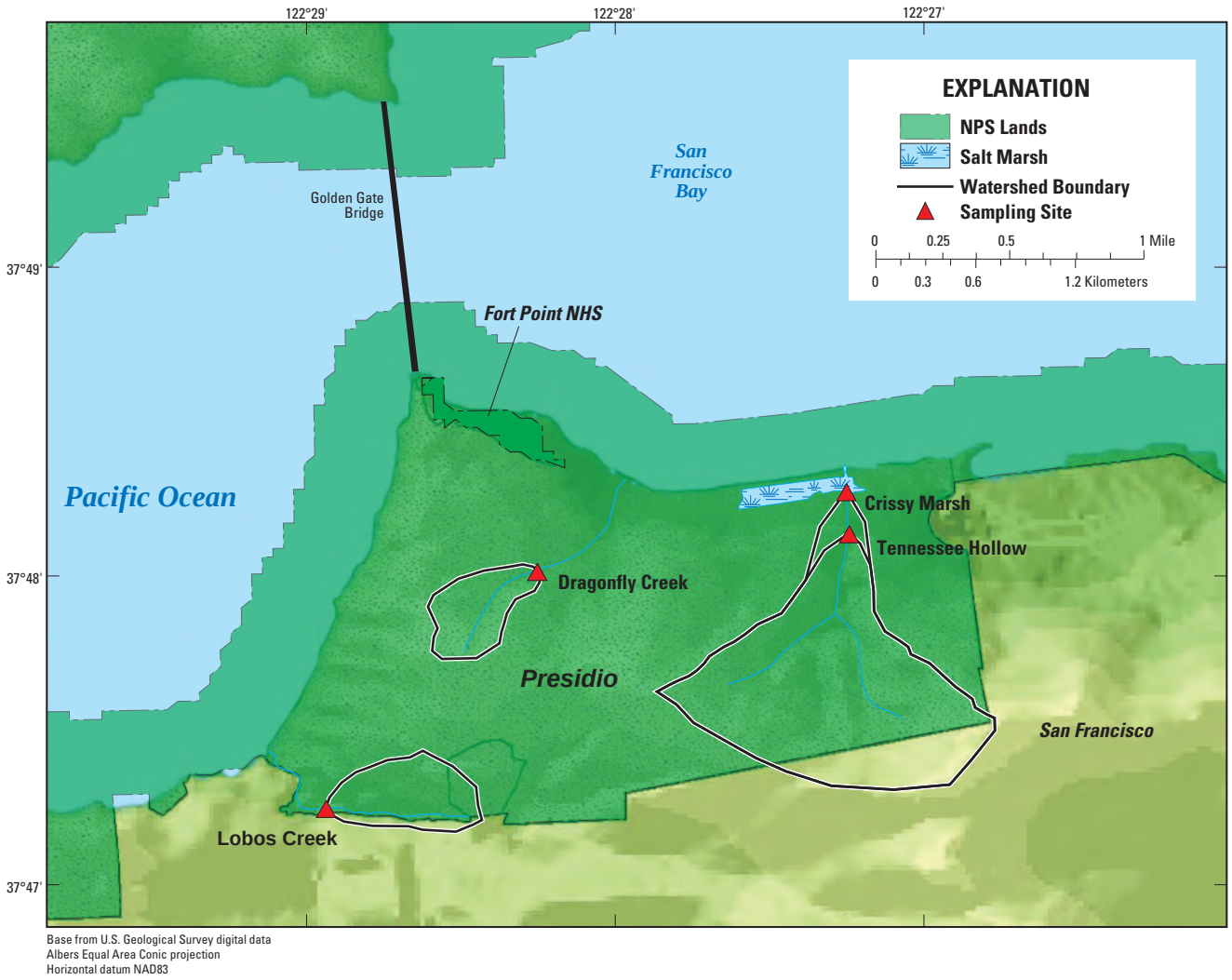

Figure 3. Sites in the Presidio of San Francisco, California. NHS, National Historic Site; NPS, National Park Service.

Sediment

At all sites except Crissy Marsh, bed-sediment samples were collected in areas of active deposition, using a stainless-steel scoop to transfer the top 2 cm of undisturbed stream bottom into 500-mL, pre-cleaned, baked glass jars. At the Crissy Marsh site, depositional sediment was collected using an Ekman grab sampler, and the top 2 cm were transferred to a 500-mL, pre-cleaned glass jar using a stainless-steel scoop. Samples were then transported on ice to the USGS Sacramento Laboratory and were stored frozen at –20°C until analysis (which occurred within 6 months).

Measurement of Water-Quality Parameters

To characterize the water from which the samples were collected, specific conductance, pH, and temperature of the water were measured in the field using two handheld instruments (Cole Parmer Model 141-61 and Orion Model 250A, respectively), following methods described in the USGS National Field Manual (Wilde and Radtke, 1998).

Pesticide Analysis

Dissolved Pesticides

Water samples were filtered through baked 0.7-µm, glass-fiber filters within 24 hours of collection. Dissolved pesticide surrogates, ring-$^{13}C_3$-atrazine and diethyl-d_{10} diazinon (Cambridge Isotope Laboratories Inc., Andover, Massachusetts), were added to each sample (for a final concentration of 100 ng/L) to provide quantitative data on extraction efficiency and analyte recovery. The samples were extracted onto Oasis HLB (6 cc, 200 mg; Waters Corporation, Milford, Massachusetts) solid-phase extraction (SPE) cartridges. The cartridges were eluted using 12 mL of ethyl acetate and concentrated to 0.2 mL for analysis. Deuterated polycyclic aromatic hydrocarbon (PAH) compounds (40 µL)

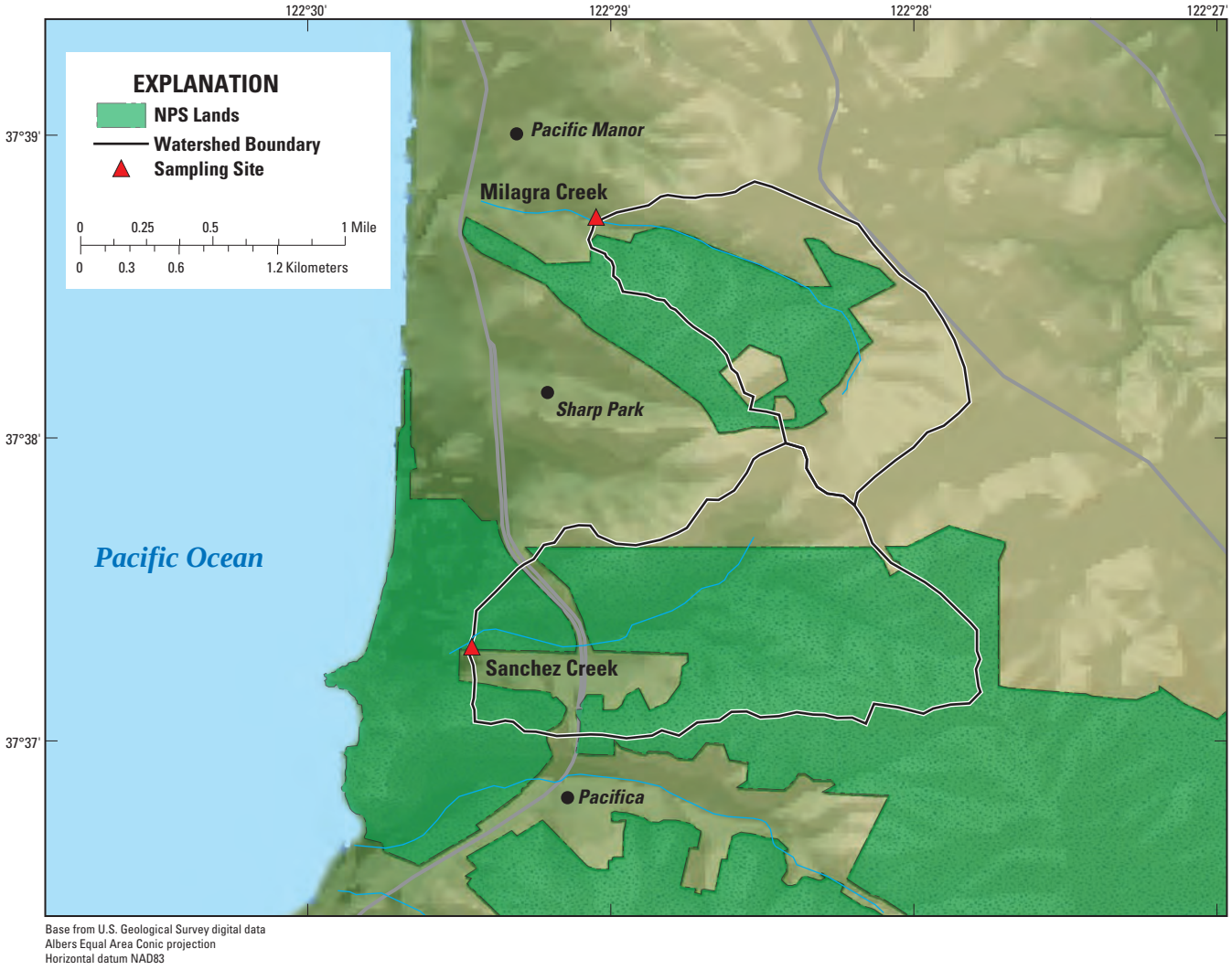

Figure 4. Sites in southern portion of Golden Gate National Recreation Area, California. NPS, National Park Service.

were used as an internal standard and included the PAHs d_{10}-acenaphthene, d_{10}-phenanthrene, and d_{10}-pyrene (Cambridge Isotope Laboratories Inc.). All extracts were analyzed for pesticides using a Varian Saturn 2000 gas chromatograph/mass spectrometer (GC/MS) with ion trap detection. Details of the analytical method are described in Hladik and others (2008). PRES samples were analyzed only for pyrethroids, whereas GOGA samples were analyzed for other pesticides in addition to the pyrethroids (table 2).

Sediment-Associated Pesticides

Sediment samples were extracted wet and analyzed using the method described by Smalling and others (2005) with one additional analyte (resmethrin) added to the list. Approximately 5–9 g of sediment (dry weight) was fortified with a surrogate recovery solution containing 200 ng of di-*N*-propyl-d_{14} trifluralin, dimethyl-d_6 chlorpyrifos, ring-$^{13}C_{12}$ *p,p′*-DDE, and phenoxy-$^{13}C_6$ *cis*-permethrin (Cambridge Isotope Laboratories, Inc.). The amount of moisture in the sediment was adjusted to 50 percent prior to microwave-assisted solvent extraction (MASE) by adding up to 4.0 mL of organic-free deionized water, depending on the moisture content of each sediment sample. The sediment samples were extracted two times with a mixture of dichloromethane (DCM) and acetone (50:50 v/v) using a CEM MSP-1000 microwave sample preparation system (Matthews, North Carolina).

Table 2. Method detection limits for pesticides analyzed in surface waters, and pesticide-use patterns in the study area, Golden Gate National Recreation Area and the Presidio of San Francisco, California.

[Method detection limits (MDLs) are taken from Hladik and others, 2008. Compound type: D, pesticide degradate; F, fungicide; H, herbicide; I, insecticide; S, synergist. ng/L, nanogram per liter]

Compound	Method detection limit (ng/L)	Compound type	Pesticide-use pattern in study area[1,2]
Anilines			
3,4-DCA	8.3	D	No use (pesticide degradate)
Ethalfluralin	3.0	H	Current registered use
Pendimethalin	2.3	H	Current registered use
Trifluralin	2.1	H	Current registered use, home use
Azoles/Triazoles			
Cyproconazole	11.2	F	Current registered use
Myclobutanil	9.2	F	Current registered use, home use
Propiconazole	8.8	F	Current registered use
Tebuconazole	10.2	F	Current registered use, home use
Tetraconazole	8.2	F	Current registered use
Carbamates			
Carbaryl	6.5	I	Current registered use, home use
Carbofuran	3.1	I	Current registered use
Chloroacetanilides			
Alachlor	1.7	H	Current registered use
Metolachlor	1.5	H	Current registered use
Organochlorines			
PCA	4.7	H	No use (pesticide degradate)
PCNB	3.1	F	Current registered use
p,*p*'-DDD	3.6	D	No use (pesticide degradate)
p,*p*′-DDE	4.1	D	No use (pesticide degradate)
p,*p*′-DDT	4.0	I	Historic Use (prior to 1983)
Organophosphates			
Chlorpyrifos	2.1	I	Current registered use, historic use (1983–1999)
Diazinon	0.9	I	Current registered use, historic use (1983–1999)
Malathion	3.7	I	Current registered use, historic use (1983–1999), home use, mosquito control applications
Methidathion	7.2	I	Current registered use
Methylparathion	3.4	I	Current registered use
Phosmet	4.4	I	Current registered use
Pyrethroids[3]			
Allethrin	6.0	I	Home use
Bifenthrin	4.7	I	Current registered use, home use
Cyfluthrin	5.2	I	Current registered use, home use
λ-Cyhalothrin	2.0	I	Current registered use, home use
Cypermethrin	5.6	I	Current registered use, home use
Deltamethrin	3.5	I	Current registered use, home use
Esfenvalerate	3.9	I	Current registered use, home use
Fenpropathrin	4.1	I	Current registered use, home use
τ-Fluvalinate	5.3	I	Current registered use
Permethrin	3.4	I	Current registered use, historical use (1983–1999), home use, mosquito control applications
Resmethrin	5.7	I	Current registered use, historical use (1983–1999), home use, mosquito control applications
Sumithrin (Phenothrin)	5.1	I	Current registered use, home use, mosquito control applications
Tetramethrin	2.9	I	Home use

Table 2. Method detection limits for pesticides analyzed in surface waters, and pesticide-use patterns in the study area, Golden Gate National Recreation Area and the Presidio of San Francisco, California.—Continued

[Method detection limits (MDLs) are taken from Hladik and others, 2008. Compound type: D, pesticide degradate; F, fungicide; H, herbicide; I, insecticide; S, synergist. ng/L, nanogram per liter]

Compound	Method detection limit (ng/L)	Compound type	Pesticide-use pattern in study area[1,2]
Thiocarbamates			
Butylate	1.8	H	Current registered use
Cycloate	1.1	H	Current registered use
EPTC	1.5	H	Current registered use
Molinate	3.2	H	Current registered use
Pebulate	2.3	H	Current registered use
Thiobencarb	1.9	H	Current registered use
Triazines/Triazones			
Atrazine	2.3	H	Current registered use
Hexazinone	8.4	H	Current registered use
Prometryn	1.8	H	Current registered use
Simazine	5.0	H	Current registered use
Terbuthylazine	1.6	H	Current registered use
Strobilurins			
Azoxystrobin	9.3	F	Current registered use
Trifloxystrobin	3.9	F	Current registered use
Miscellaneous			
Chlorothalonil	12.1	F	Current registered use, home use
DCPA	2.0	H	Current registered use
Fipronil	2.9	I	Current registered use, home use
Fipronil Desulfinyl	1.6	D	No use (pesticide degradate)
Fipronil Sulfide	1.8	D	No use (pesticide degradate)
Fipronil Sulfone	3.5	D	No use (pesticide degradate)
Iprodione	6.5	F	Current registered use
Methoprene	6.4	I	Current registered use, home use, mosquito control applications
Napropamide	8.2	H	Current registered use
Oxyfluorofen	3.1	H	Current registered use, home use
Piperonyl Butoxide (PBO)	2.3	S	Current registered use, home use, mosquito control applications

[1]California Department of Pesticide Regulation (http://www.cdpr.ca.gov/).

[2]TDC Environmental, 2005.

[3]Pyrethroids analyzed for in GOGA and PRES, all other compounds only analyzed in GOGA.

Following extraction, the samples were decanted through glass funnels packed with approximately 30 g of sodium sulfate to remove excess water. Extracts were reduced at 25°C to 0.75 mL under nitrogen gas (N_2). Sediment matrix was removed by passing the sample extract through two stacked SPE cartridges containing different sorbents: a 6-mL, 500-mg, CarboPrep-90 graphitized carbon cartridge (Restek Corporation, Bellefonte, Pennsylvania) was stacked on top of a Sep-Pak Plus alumina A cartridge (Waters Corporation, Milford, Massachusetts). The sample extract was added to the cartridges, rinsed with 10 mL of DCM, which was collected as fraction 1. The carbon SPE was removed and the alumina SPE was eluted with 10 mL of ethyl acetate and DCM (50:50 v/v) and collected as fraction 2. The fractions were then recombined and evaporated under a gentle stream of N_2 to 0.5 mL and exchanged into ethyl acetate. Sulfur was removed using a gel-permeation chromatography/high-pressure liquid chromatography (GPC/HPLC) system. The GPC extracts were reduced under a gentle stream of N_2 to 200 µL and then 40 µL of the deuterated PAH internal standard mix was added. The extracts were analyzed by GC/MS. PRES samples were analyzed only for pyrethroids, whereas GOGA samples included other pesticides in addition to the pyrethroids (table 3).

Table 3. Method detection limits for pesticides analyzed in bed sediments, and pesticide-use patterns in the study area, Golden Gate National Recreation Area and the Presidio of San Francisco, California.

[Method detection limits (MDLs) are taken from Smalling and others, 2005. Compound type: D, pesticide degradate; F, fungicide; H, herbicide; I, insecticide; S, synergist. ng/g, nanogram per gram]

Compound	Method detection limit (ng/g)	Compound type	Pesticide-use pattern in study area[1,2]
Anilines			
Ethalfluralin	1.2	H	Current registered use
Pendimethalin	1.5	H	Current registered use
Trifluralin	1.1	H	Current registered use, home use
Carbamates			
Carbaryl	2.2	I	Current registered use, home use
Carbofuran	5.3	I	Current registered use
Chloroacetanilides			
Alachlor	1.4	H	Current registered use
Metolachlor	1.7	H	Current registered use
Organochlorines			
p,p′-DDD	1.3	D	No use (pesticide degradate)
p,p′-DDE	1.5	D	No use (pesticide degradate)
p,p′-DDT	1.9	I	Historic Use (prior to 1983)
Organophosphates			
Chlorpyrifos	0.8	I	Current registered use, historic use (1983–1999)
Diazinon	0.6	I	Current registered use, historic use (1983–1999)
Malathion	2.2	I	Current registered use, historic use (1983–1999), home use, mosquito control applications
Methidathion	1.5	I	Current registered use
Methylparathion	2.0	I	Current registered use
Phosmet	2.4	I	Current registered use
Pyrethroids[3]			
Bifenthrin	2.3	I	Current registered use, home use
Cyfluthrin	7.9	I	Current registered use, home use
λ-Cyhalothrin	1.6	I	Current registered use, home use
Cypermethrin	5.6	I	Current registered use, home use
Deltamethrin	1.1	I	Current registered use, home use
Esfenvalerate	1.8	I	Current registered use, home use
Fenpropathrin	1.4	I	Current registered use, home use
τ-Fluvalinate	1.1	I	Current registered use
Permethrin	1.2	I	Current registered use, historical use (1983–1999), home use, mosquito control applications
Resmethrin	4.2	I	Current registered use, historical use (1983–1999), home use, mosquito control applications
Sumithrin (Phenothrin)	2.9	I	Current registered use, home use, mosquito control applications
Thiocarbamates			
Butylate	1.1	H	Current registered use
Cycloate	0.8	H	Current registered use
EPTC	1.4	H	Current registered use
Molinate	0.6	H	Current registered use
Pebulate	0.9	H	Current registered use
Thiobencarb	1.6	H	Current registered use

Table 3. Method detection limits for pesticides analyzed in bed sediments, and pesticide-use patterns in the study area, Golden Gate National Recreation Area and the Presidio of San Francisco, California.—Continued

[Method detection limits (MDLs) are taken from Smalling and others, 2005. Compound type: D, pesticide degradate; F, fungicide; H, herbicide; I, insecticide; S, synergist. ng/g, nanogram per gram]

Compound	Method detection limit (ng/g)	Compound type	Pesticide-use pattern in study area[1,2]
Triazines/Triazones			
Atrazine	1.7	H	Current registered use
Hexazinone	2.3	H	Current registered use
Prometryn	1.9	H	Current registered use
Simazine	1.4	H	Current registered use
Miscellaneous			
DCPA	1.5	H	Current registered use
Napropamide	1.1	H	Current registered use
Oxyfluorofen	2.5	H	Current registered use, home use
Piperonyl Butoxide (PBO)	1.3	S	Current registered use, home use, mosquito control applications

[1]California Department of Pesticide Regulation (http://www.cdpr.ca.gov/).

[2]TDC Environmental, 2005.

[3]Pyrethroids analyzed for in GOGA and PRES, all other compounds only analyzed in GOGA.

Quality Control and Quality Assurance

Dissolved pesticide concentrations were validated against a comprehensive set of quality-control parameters, including laboratory and field blanks, replicate samples, matrix spikes, and surrogate recovery. Each quality-control parameter was run for every 10 samples, with the exception of surrogates, which were introduced and analyzed for recovery in each sample. No pesticides were detected in any of the laboratory or field blanks. Replicate samples were within 25 percent agreement for all pesticides detected. Matrix spikes were analyzed with 100 ng of each pesticide (table 2) spiked into a water sample. Recoveries of the matrix spikes ranged from 80 to 120 percent for all of the pesticides analyzed. $^{13}C_3$-atrazine and diethyl-d_{10} diazinon were used as recovery surrogates to assess the efficiency of sample extraction. The average percentage recoveries were 100.9 ± 9.1 for $^{13}C_3$-atrazine and 105.5 ± 7.0 for diethyl-d_{10} diazinon. Dissolved pesticide MDLs were validated in a previous study (Hladik and others, 2008).

Sediment method blanks, replicate samples, matrix spikes, and surrogate recoveries were also processed for quality-control purposes. Matrix spikes were analyzed with 200 ng of each pesticide (table 3) spiked into three sediment samples. Matrix spike recoveries ranged from 70 to 115 percent for all of the pesticides analyzed. Replicate samples constituted 10 percent of the total samples analyzed, and the differences between replicates were less than 25 percent for all pesticides detected. No pesticides were detected in either of the two blank samples (sodium sulfate was used as the blank matrix). Recovery of the sediment surrogate mixture was used to monitor the efficiency of each extraction. The average percentage recoveries of the surrogates di-*N*-propyl-d_{14} trifluralin, dimethyl-d_6 chlorpyrifos, ring-$^{13}C_{12}$ *p,p′*-DDE, and phenoxy-$^{13}C_6$ *cis*-permethrin were 91.1 ± 8.1, 91.8 ± 6.7, 90.5 ± 8.4, and 96.9 ± 4.2, respectively. Sediment MDLs were validated in a previous study (Smalling and others, 2005).

Sediment Organic Carbon Analysis

All bed sediments were analyzed for organic carbon content using a Perkin Elmer CHNS/O analyzer (Perkin Elmer Corporation, Norwalk, Connecticut). Before analysis, sediments were dried to a constant weight at 110°C for 3 hours. Sediments were combusted at 925°C in silver boats after being exposed to concentrated hydrochloric acid (HCl) fumes in a desiccator for 24 hours to remove inorganic carbon. Acetanilide was used for instrument calibration of elemental carbon.

Results

Dissolved Pesticide Concentrations

In this study, the pesticides bifenthrin, cyproconazole, DCPA, fipronil, myclobutanil, prometryn, tetraconazole, and trifluralin were detected in water samples (table 4, table 5). The pesticide degradates fipronil sulfone and DDE were also detected. Concentrations of most compounds detected were below their MDL, and most concentrations were low, below 7 ng/L. Three fungicides, cyproconazole, myclobutanil, and tetraconazole, had concentrations that were slightly higher, 20–30 ng/L, at several sites. Pesticide detections were most frequent during the winter sampling event (February).

Table 4. Pesticide and pesticide degradate concentrations in surface-water samples collected from the Golden Gate National Recreation Area, California.

[Concentrations are in nanaogram per liter (ng/L). Samples were analyzed for the following pesticides (and pesticide degradates) that were not detected: 3,4-dichloroaniline, alachlor, allethrin, atrazine, azoxystrobin, butylate, carbaryl, carbofuran, chlorothalonil, chlorpyrifos, cycloate, cyfluthrin, λ-cyhalothrin, cypermethrin, *p,p′*-DDD, *p,p′*-DDT, deltamethrin, diazinon, EPTC, esfenvalerate, ethalfluralin, fenpropathrin, fipronil desulfinyl, fipronil sulfide, τ-fluvalinate, hexazinone, iprodione, malathion, methidathion, methoprene, methylparathion, metolachlor, molinate, napropamide, oxyflurofen, pentachloroanisole, pentachloronitrobenzene, pebulate, pendimethalin, permethrin, phosmet, piperonyl butoxide, propiconazole, resmethrin, simazine, sumithrin, tebuconazole, terbuthylazine, tetramethrin, thiobencarb, trifloxystrobin. hh:mm, hour:minute; mm/dd/yy, month/day/year; nd, not detected; ( ), concentrations less than MDL and are estimated values]

Site	Date	Time	Bifenthrin	Cyproconazole	DCPA	*p,p′*-DDE	Fipronil	Fipronil Sulfone	Myclobutanil	Prometryn	Tetraconazole	Trifluralin
	(mm/dd/yy)	(hh:mm)										
Coyote Creek	2/15/2006	10:30	nd	nd	nd	nd	nd	nd	nd	nd	18.8	nd
	4/19/2006	14:50	nd	nd	nd	nd	nd	nd	(2.6)	nd	nd	nd
	7/12/2006	15:20	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Milagra Creek	2/15/2006	14:40	nd	28.1	(0.8)	nd	nd	(1.4)	25.7	3.4	28.9	nd
	4/19/2006	10:10	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	7/12/2006	10:30	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Nyhan Creek	2/15/2006	10:50	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	4/19/2006	14:40	nd	nd	nd	nd	(0.8)	nd	nd	nd	nd	nd
	7/12/2006	15:05	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Redwood Creek	2/15/2006	10:00	nd	nd	nd	nd	nd	nd	nd	nd	18.8	nd
	4/19/2006	15:15	nd	nd	nd	nd	nd	nd	(3.8)	nd	nd	nd
	7/12/2006	15:45	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Rodeo Creek	2/15/2006	11:30	nd	nd	nd	nd	nd	nd	21.2	nd	22.3	nd
	4/19/2006	14:05	(1.6)	nd	nd	4.4	nd	nd	(4.4)	nd	nd	(1.4)
	7/12/2006	14:20	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sanchez Creek	2/15/2006	15:00	nd	nd	nd	nd	nd	nd	nd	nd	20.0	nd
	4/19/2006	9:50	nd	(5.6)	nd	nd	nd	nd	(6.6)	nd	nd	nd
	7/12/2006	10:00	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table 5. Pesticide concentrations in surface-water samples collected from the Presidio of San Francisco, California.

[Concentrations are in nanogram per liter (ng/L). Samples were analyzed for the following pesticides that were not detected: allethrin, cyfluthrin, λ-cyhalothrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, τ-fluvalinate, permethrin, resmethrin, sumithrin, tetramethrin. hh:mm, hour:minute; mm/dd/yy, month/day/year; nd, not detected; ( ), concentrations less than MDL and are estimated values]

Site	Date (mm/dd/yy)	Time (hh:mm)	Bifenthrin
Dragonfly Creek	2/15/2006	13:10	nd
	4/19/2006	12:15	nd
	7/12/2006	12:50	nd
Lobos Creek	2/15/2006	13:30	nd
	4/19/2006	12:45	nd
	7/12/2006	11:50	(1.2)
Tennessee Hollow Creek	2/15/2006	12:20	nd
	4/19/2006	11:30	nd
	7/12/2006	13:20	nd

None of the pesticides detected had drinking-water-quality levels set by the state of California (either for regulatory limits for drinking-water quality, or nonregulatory thresholds for drinking-water quality) or by the U.S. Environmental Protection Agency (USEPA); therefore, no comparisons can be made. The USEPA has set aquatic-life benchmark levels (U.S. Environmental Protection Agency, 2007) for two of the pesticides detected, DCPA and trifluralin. The aquatic-life benchmarks for DCPA have been set at acute levels for fish, invertebrates and plants; they range from 11,000 to 15,000 µg/L. Trifluralin has acute- and chronic-level benchmarks; the chronic levels for fish and invertebrates are 1.14 and 2.4 µg/L, respectively, and the acute levels are between 8 and 280 µg/L for fish, invertebrates, and plants. DCPA was detected in Milagra Creek at an estimated concentration of 0.8 ng/L, and trifluralin was detected in Rodeo Creek at an estimated concentration of 1.4 ng/L (table 4), both of which are well below the USEPA benchmarks for aquatic life.

Sediment-Associated Pesticide Concentrations

The only two pesticides detected in sediment samples were the historically used insecticide DDT and its degradate DDE (table 6). Most detections were below the MDL, and all were below 3 ng/g. No pyrethroids (bifenthrin, cyfluthrin, λ-cyhalothrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, τ-fluvalinate, permethrin, resmethrin, or sumithrin) were detected in sediment samples.

Table 6. Concentrations of sediment-associated total organic carbon, pesticides, and pesticide degradates collected from the Golden Gate National Recreation Area, California.

[Concentrations are in nanogram per gram (ng/g). Samples were analyzed for the following pesticides that were not detected: alachlor, atrazine, bifenthrin, butylate, carbaryl, carbofuran, chlorpyrifos, cycloate, cyfluthrin, λ-cyhalothrin, cypermethrin, DCPA, *p,p′*-DDD, deltamethrin, diazinon, EPTC, esfenvalerate, ethalfluralin, fenpropathrin, τ-fluvalinate, hexazinone, malathion, methidathion, methylparathion, metolachlor, molinate, napropamide, oxyflurofen, pebulate, pendimethalin, permethrin, phosmet, piperonyl butoxide, prometryn, resmethrin, simazine, sumithrin, thiobencarb, trifluralin. hh:mm, hour:minute; mm/dd/yy, month/day/year; nd, not detected; ( ), concentrations less than MDL and are estimated values; %, percent]

Site	Date (mm/dd/yy)	Time (hh:mm)	Organic carbon (%)	*p,p′*-DDE	*p,p′*-DDT
Coyote Creek	2/15/2006	10:30	0.4	(0.1)	nd
	4/19/2006	14:50	0.3	nd	nd
	7/12/2006	15:20	0.4	nd	(0.6)
Milagra Creek	2/15/2006	14:40	0.7	nd	nd
	4/19/2006	10:10	1.7	nd	2.0
	7/12/2006	10:30	0.6	nd	nd
Nyhan Creek	2/15/2006	10:50	0.4	nd	nd
	4/19/2006	14:40	0.8	nd	nd
	7/12/2006	15:05	1.9	nd	(0.2)
Redwood Creek	2/15/2006	10:00	0.8	nd	(0.4)
	4/19/2006	15:15	0.4	(0.1)	(0.4)
	7/12/2006	15:45	0.6	nd	nd
Rodeo Creek	2/15/2006	11:30	5.6	nd	(1.1)
	4/19/2006	14:05	4.5	nd	2.8
	7/12/2006	14:20	5.4	nd	nd
Sanchez Creek	2/15/2006	15:00	2.8	nd	nd
	4/19/2006	9:50	0.9	nd	nd
	7/12/2006	10:00	3.5	nd	nd

References Cited

Cooprider, M., 2004, San Francisco area network preliminary water quality status report: National Park Service, 45 p.

California Department of Pesticide Regulation, 2005, Pesticide use data for 2005 [digital data]: Sacramento, California, Department of Pesticide Regulation.

Hladik, M.L., Smalling, K.L., and Kuivila, K.M., 2008, A multi-residue method for the analysis of pesticides and pesticide degradates in water using HLB solid-phase extraction and gas chromatography-ion trap mass spectrometry: Bulletin of Environmental Contamination and Toxicology, v. 80, p. 139–144.

Johnson, B., 2004, Diazinon and pesticide-related toxicity in bay area urban creeks water quality attainment strategy and total maximum daily load (TMDL) final project report, California Regional Water Quality Control Board, San Francisco Bay Region: San Francisco, Calif., 110 p.

Smalling, K.L., Orlando, J.L., and Kuivila, K.M., 2005, Analysis of pesticides in surface water and sediment from Yolo Bypass, California, 2004–2005: U.S. Geological Survey Scientific Investigations Report 2005-5220, 20 p.

State Water Resources Control Board, 2006, 2006 Clean Water Act Section 303(d) List of Water Quality Limited Segments, accessed May 30, 2007, at http://www.swrcb.ca.gov/water_issues/programs/tmdl/303d_lists2006.shtml

TDC Environmental, 2005, Pesticides in urban surface water: urban pesticides use trends annual report 2005, 29 p.

U.S. Environmental Protection Agency, 2002, Total maximum daily loads, accessed January 31, 2007, at http://www.epa.gov/owow/tmdl/

U.S. Environmental Protection Agency, 2004, Diazinon: phase out of all residential uses of the insecticide, accessed January 31, 2007, at http://www.epa.gov/pesticides/factsheets/chemicals/diazinon-factsheet.htm

U.S. Environmental Protection Agency, 2007, Technical overview of ecological risk assessment aquatic life benchmark table, accessed March 7, 2007, at http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm

U.S. Fish and Wildlife Service, 2007, Species information: threatened and endangered animals and plants, accessed January 31, 2007, at http://www.fws.gov/endangered/wildlife.html

Wilde, F.D., and Radtke, D.B., eds., 1998, chapter sections variously dated, Field measurements: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps A4, A6.