

## Xenobiotic Organic Compounds in Runoff from Fields Irrigated with Treated Wastewater

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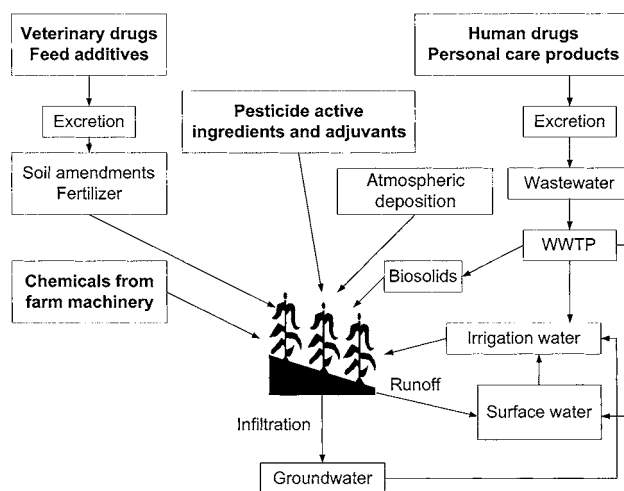
Investigations of agricultural nonpoint source pollution typically focus on a relatively narrow range of targeted toxic and biostimulatory compounds (e.g., specific pesticides, nutrients). Regular application of numerous other organic compounds to agricultural fields in pesticide formulations, irrigation water, soil amendments, and fertilizers may result in their transport into surface waters via runoff. We examined whether potentially toxic dissolved and particle-associated “nontarget” organic compounds were present in surface runoff from agricultural fields irrigated with disinfected tertiary recycled water or wastewater effluent-dominated streamwater. Gas chromatographic–mass spectrometric analyses of filtered runoff samples revealed the presence of numerous nontarget compounds of potential toxicological significance including pesticide transformation products, pesticide adjuvant chemicals, plasticizers, flame retardants, pharmaceuticals, and personal care product ingredients. Although the toxicity of many of these compounds is poorly characterized, some may elicit subtle but profound toxicological effects. Agricultural runoff also represented a source of allochthonous natural organic matter to the stream system.

**KEYWORDS:** Effluent irrigation; pharmaceuticals; personal care product ingredients; pesticide; broad-spectrum analysis; GC-MS; nonpoint source pollution

### INTRODUCTION

Investigations of nonpoint source pollution from agricultural lands typically focus on a relatively small number of regulated “target” analytes. Targeted analysis does not allow the identification of other compounds that may be present and thus provides an incomplete picture of the toxic potential of agricultural runoff. Commonly selected analytes include nutrients, specific pesticide active ingredients, eroded soil, and, less frequently, metals and metalloids. In addition to pesticides, agricultural runoff may contain numerous other “nontarget” organic contaminants derived from formulation and spray adjuvants, irrigation water, fertilizers, soil amendments, and atmospheric deposition. Runoff from agricultural fields also represents a source of allochthonous dissolved and particle-associated terrestrial natural organic matter to aquatic systems.

Xenobiotic organic compounds may be applied or transported to agricultural fields through several routes (**Figure 1**). Pesticide active ingredients are intentionally applied to combat arthropod and nematode pests, as well as to control weeds and fungal pathogens. Pesticides are rarely applied alone, but are mixed with other substances to enhance their performance and safety. These formulation and spray adjuvants may comprise up to



**Figure 1.** Routes of xenobiotic organic chemical (bold) introduction into agricultural systems. WWTP, wastewater treatment plant.

99.5% of the applied pesticide product and include organic solvents, surfactants, and polymers.

Soil amendments and fertilizers containing domestic animal wastes represent a route of introduction for veterinary therapeutics and feed additives to agricultural systems. When administered to livestock, the bioactive ingredients are subject to metabolism in the dosed animal. Parent compounds, conjugates, and other metabolites pass through the digestive tract and

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are excreted. When animal waste is used as a soil amendment or fertilizer, the potential exists for these compounds to be transported into aquatic ecosystems with surface runoff.

Human pharmaceuticals and personal care product ingredients are introduced into agricultural systems via irrigation water and sewage biosolids. In this paper, personal care product ingredients refer to chemicals in consumer products used primarily on the human body (e.g., cosmetics, toiletries, fragrances) (1). Pharmaceuticals and personal care product ingredients enter wastewater treatment plants when they are excreted, improperly disposed of, or washed from skin surfaces and fabrics. As is the case with veterinary drugs, human pharmaceuticals may be excreted as unaltered parent compounds, conjugates, or other metabolites. After entering sewage treatment plants, these substances are subject to further transformations. However, many pharmaceuticals and personal care product ingredients are inefficiently removed by conventional wastewater treatment processes and remain in treated effluent. Some of the pharmaceuticals removed from wastewater remain in an unaltered state or are reactivated in sewage sludge. The irrigation of crops with treated effluent and the use of sewage sludge or biosolids as soil amendments thus have the potential to introduce human pharmaceuticals and personal care product ingredients into surface runoff and, ultimately, receiving waters. Recent research in Europe and North America has highlighted the occurrence of numerous pharmaceuticals and personal care product ingredients in treated effluent, including analgesics, antibiotics, antiepileptics, antineoplastics, beta-blockers, blood lipid regulators, diagnostic contrast media, disinfectants, hormones and hormone mimics, psychiatric drugs, and synthetic fragrances (1).

Farm equipment may also introduce organic contaminants into agricultural soils by the leakage of fuels and other fluids and the emission of combustion byproducts. Atmospheric deposition represents an additional route of introduction of organic xenobiotics to agricultural fields. Such deposition may result from regional or long-range transport or spray drift from adjacent agricultural fields. Although not depicted in **Figure 1**, soil amendments derived from food-processing byproducts and pulp fiber residue represent further routes of introduction of organic xenobiotics into agricultural systems.

The objective of this study was to determine whether any potentially toxic dissolved and particle-associated "nontarget" organic chemicals were present in surface runoff from agricultural fields irrigated with treated wastewater. Surface runoff was collected from six fields planted in row and vegetable crops in southern California. Sampled fields were irrigated with disinfected tertiary recycled water or wastewater effluent-dominated streamwater. Surface runoff samples were analyzed for a broad spectrum of organic compounds using gas chromatographic methods with various detectors. A preliminary report of a subset of the data reported here was presented by Pedersen et al. (2).

## MATERIALS AND METHODS

**Site Description.** Sampled fields were located in the Calleguas Creek watershed in coastal Ventura County, California. The Calleguas Creek watershed is a highly productive region, with each field yielding three or four crops annually. Over 250 different crops are grown in the watershed, including celery, lettuce, strawberries, peppers, cilantro, spinach, and sweet corn. The intense agricultural practices in the watershed necessitate the application of a wide variety of pesticides, as well as large quantities of chemical fertilizers and irrigation water. Most of the cropland is irrigated throughout the dry season, as well as between storms in the rainy season.

A growing trend exists in this region to use treated wastewater for irrigation rather than discharging effluent into the stream systems (3).

**Table 1.** Site Characteristics

site	nominal area (ha)	crop	irrigation water source
A	1.3	green onion ( <i>Allium cepa</i> )	tertiary treated wastewater
B	9.9	strawberry ( <i>Fragaria ananassa</i> )	tertiary treated wastewater
C	32.1	corn ( <i>Zea mays</i> )	streamwater <sup>a</sup>
D	4.7	cilantro ( <i>Coriandrum sativum</i> )	streamwater <sup>a</sup>
E	2.4	bell pepper ( <i>Capsicum annuum</i> )	tertiary treated wastewater
F	7.4	celery ( <i>Apium graveolens</i> var. <i>Dulce</i> )	variable <sup>b</sup>

<sup>a</sup> Effluent-dominated streamwater. <sup>b</sup> Irrigation source varied between groundwater and imported effluent-dominated streamwater.

Irrigation water used on the sampled fields was piped directly from wastewater treatment plants or pumped from effluent-dominated streams. The effluent conveyed directly to the sampled fields met the California Tertiary Recycled Water Criteria definition of "disinfected tertiary recycled water" (4). The effluent had undergone treatment consisting of activated sludge treatment with extended aeration, sedimentation, nitrification/denitrification, sand filtration, and chlorination. The purpose of the extended aeration is to enhance the reduction of biological oxygen demand (BOD<sub>5</sub>). No animal manure fertilizers or sewage biosolids were known to be used on the fields sampled. Seabird and bat guano find some use in the watershed and so may have been applied to the fields sampled.

**Sample Collection.** Six irrigated fields adjacent to streams were sampled during both dry and wet weather over the course of two crop seasons (July 1999–April 2000). Site characteristics are displayed in **Table 1**. Sampled fields ranged in size from 5 to 10 ha and were irrigated by furrow and sprinkler techniques. Two-liter runoff samples were collected at roughly half-hour intervals over the course of selected runoff-producing irrigation and storm events using an Isco 3700 portable sampler (Isco, Lincoln, NE) or by taking grab samples. Samples were stored on ice during transport and refrigerated at 4 °C until processed.

**Sample Preparation and Extraction.** Runoff samples were filtered through 0.7- $\mu$ m glass fiber filters (PreSep TCLP, MSI, Westboro, MA) in a Teflon-lined hazardous waste pressure filtration unit (Millipore Corp., Bedford, MA). Dissolved and particle-associated compounds were thus operationally defined as those passing through or retained by the 0.7- $\mu$ m filter. The aqueous phase was liquid–liquid extracted with dichloromethane following U.S. EPA Method 3510C (5). Suspended solids were dried (6) and extracted with supercritical CO<sub>2</sub> at 36.0 MPa and 120 °C using an Isco SFX 2-10 supercritical fluid extractor. Prior to extraction, 250  $\mu$ L each of water, methanol, and dichloromethane were added as polarity modifiers (7). Five-minute static extraction was followed by a 20-min dynamic extraction. The supercritical fluid extraction method employed was originally developed for polycyclic aromatic hydrocarbons.

**Gas Chromatography–Mass Spectrometry (GC-MS).** Gas chromatographic and mass spectrometric conditions are presented in **Table 2**. A Galaxy 2000 data system (version 10.4.03) was used for mass spectral data acquisition, integration, and spectral matching against the NIST/EPA/NIH 98 mass spectral library. Library search purity (SI) values of 700 or greater were accepted for tentative identifications (8). Manual interpretation was used for some identifications, and standards were analyzed for some compounds. For structural assignments not confirmed by a second GC method or by comparison of the mass spectrum and/or retention time to that of a standard, our level of confidence in tentative identifications was based on the following factors: (1) magnitude of the SI value; (2) identities and SI values of other closely matching compounds (if any); and (3) reasonableness of the assigned identity. Such tentative structural assignments were necessarily constrained by the spectra contained in the library employed. Unknown spectra with comparable SI values (i.e., within 50 units) for several dissimilar structures were not reported. **Tables 3** and **4** indicate the level of confidence associated with compound identifications and

**Table 2.** Gas Chromatographic Conditions<sup>a</sup>

	GC-MS	GC-FPD	GC-ECD	GC-FID
GC system	Varian 3400 GC	Hewlett-Packard 6890 GC	Varian 3500 GC	Hewlett-Packard 5890 series II GC
column	30 m × 0.25 mm i.d. DB-5MS, $d_f = 0.25 \mu\text{m}$	column 1: 30 m × 0.53 mm i.d. DB-1701, $d_f = 1.0 \mu\text{m}$ column 2: 60 m × 0.32 mm i.d. DB-1, $d_f = 1.0 \mu\text{m}$	column 1: 30 m × 0.25 mm i.d. DB-1701, $d_f = 0.25 \mu\text{m}$ column 2: 30 m × 0.25 mm i.d. DB-5, $d_f = 0.25 \mu\text{m}$	60 m × 0.32 mm i.d. DB-5, $d_f = 0.25 \mu\text{m}$
temperature program	35 °C hold for 6 min; 4 °C/min to 280 °C; 2 °C/min to 310 °C; 20-min hold at 310 °C	column 1: 110 °C hold for 0.5 min; 3 °C/min to 250 °C; 30-min hold at 250 °C column 2: 110 °C hold for 0.5 min; 2.5 °C/min to 206 °C; 4 °C/min to 250 °C; 30-min hold at 250 °C	60 °C for 1 min; 15 °C/min to 150 °C; 0.1-min hold at 150 °C; 2 °C/min to 200 °C; 10-min hold at 200 °C; 5 °C/min to 280 °C; 10- or 20-min hold at 280 °C	30 °C hold for 4 min; 6 °C/min to 275 °C; 30-min hold at 275 °C
injection port	1 $\mu\text{L}$ splitless, 280 °C	1 or 2 $\mu\text{L}$ on-column, 113 °C	1 $\mu\text{L}$ splitless, 260 °C	2 $\mu\text{L}$ on column, room temperature
carrier gas	He; 0.35 m/s	He; 0.6 m/s	H <sub>2</sub> ; 0.27 m/s for column 1, 0.28 m/s for column 2	He; 0.41 m/s
detector	Finnigan 4000 quadrupole mass spectrometer; electron impact ionization; 270 °C; ion source, 70 eV; 50–550 $m/z$ scan at 1 scan/s	flame photometric detector for HP 6890 GC; 250 °C; 15:11 H <sub>2</sub> :air ratio, 7 mL/min	two Varian 2400 electron capture detectors; 330 °C	flame ionization detector for HP 5890 series II GC; 300 °C; 420 mL air/min; 30 mL H <sub>2</sub> /min

<sup>a</sup>  $d_f$ , film thickness; ECD, electron capture detector; FID, flame ionization detector; FPD, flame photometric detector; GC, gas chromatography; MS, mass spectrometry.

the criteria applied. Compound concentrations were estimated relative to the response of the acenaphthene- $d_{10}$  internal standard and must therefore be considered semiquantitative.

The U.S. EPA Region 5 Central Regional Laboratory analyzed a subset of samples for selected alkylphenols, alkylphenol ethoxylates, and bisphenol A using a large-volume injection method (9).

**Gas Chromatography—Flame Photometric Detection (GC-FPD).** The presence of organophosphorus compounds in surface runoff samples was determined using U.S. EPA Method 1657 (10). Chromatographic conditions are presented in **Table 2**. Data were quantified against seven standards by determining peak area response relative to the internal standard, triphenyl phosphate. Compound identities were confirmed by GC-FPD using a second column and/or by GC-MS.

**Gas Chromatography—Electron Capture Detection (GC-ECD).** A subset of samples was exchanged into hexane and analyzed for organochlorine compounds using dual-column GC-ECD. Chromatographic conditions are given in **Table 2**. Data were quantified using 43 standards by determining peak area response relative to an internal standard, pentachloronitrobenzene. Two surrogate standards, tetrachloro-*m*-xylene and decachlorobiphenyl, were used for the determination of relative retention times. Compound identities were confirmed by comparison of retention times on both columns as per U.S. EPA Method 608 (10).

**Gas Chromatography—Flame Ionization Detection (GC-FID).** To assess temporal variation in the levels and identities of extracted compounds, all samples were analyzed by GC-FID. Chromatographic conditions are displayed in **Table 2**. Compound concentrations were estimated relative to the response of the *n*-octacosane internal standard and therefore must be considered semiquantitative. Chromatogram profiling (11–13) was used to examine concentration changes during runoff events. The Kováts retention index was modified for programmed temperature runs (14), and data from the linear portion of the temperature program were evaluated (i.e., isothermal conditions were not included). Compound identities were assigned on the basis of total ion chromatograms (TICs) from GC-MS analyses obtained under similar column conditions using the temperature-modified retention index. Comparisons between TICs and FID chromatograms were made only for prominent peaks (i.e., signal-to-noise ratio, S/N > 10). For the compounds reported, TIC and FID responses were similar.

## RESULTS AND DISCUSSION

Broad-spectrum chromatographic profiles from GC-FID analyses were reconstructed to qualitatively assess temporal variation in the levels and identities of extracted compounds. **Figure 2** displays an exemplary series of five reconstructed FID chromatograms from the 16 September 1999 irrigation event at site F. Only peaks with retention indices between 900 and 1900 are shown. The peak at approximately 1655 corresponds to the tributyl phosphate surrogate standard added for organophosphorus insecticide analysis. Two points can be illustrated with this figure. First, the FID chromatograms demonstrate the presence of a number of dissolved organic compounds in surface runoff. Most traditionally targeted pollutants (e.g., regulated U.S. EPA priority pollutants, specific pesticides) were present at only low levels (i.e., <0.05  $\mu\text{g/L}$ ), so low that the peaks are not visible on the reconstructed chromatograms in **Figure 2**. These target compounds included chlorpyrifos, diazinon, xylene, naphthalene, and 1- and 2-methylnaphthalene. Xylene was present at higher levels (ca.  $\sim 0.17 \mu\text{g/L}$ ) but had a retention index below 900; the corresponding peak is therefore not displayed in **Figure 2**. The FID chromatograms contain numerous other peaks corresponding to nontarget compounds, some of which may represent toxicologically relevant chemicals. For example, the peaks labeled HHCb and AHTN correspond to the synthetic polycyclic musk fragrances Galaxolide and Tonalide. The peaks labeled TCPP represent the trialkyl phosphate flame-retardant chemical tris(chloropropyl) phosphate, and those labeled carisoprodol correspond to a skeletal muscle relaxant drug. A second point that can be made from the reconstructed chromatograms is that concentrations of some nontarget compounds exhibit substantial temporal variation. Therefore, quantification of the mass flux of these compounds in runoff requires sampling over the course of runoff events.

Analysis of water and suspended particle extracts by GC-MS revealed the presence of a variety of compounds, some

Table 3. Dissolved Organic Compounds Present or Suspected To Be Present in Agricultural Runoff<sup>a</sup>

compound	<i>M<sub>r</sub></i> <sup>b</sup>	notes <sup>c</sup>	compound	<i>M<sub>r</sub></i> <sup>b</sup>	notes <sup>c</sup>
Organochlorine Insecticides and Transformation Products					
$\gamma$ -hexachlorocyclohexane	291	A <sub>3</sub>	<i>p,p'</i> -DDT	355	A <sub>3</sub>
<i>o,p'</i> -DDE	316	D			
Organophosphorus Insecticides and Transformation Products					
dichlorvos	221	A <sub>2</sub>	diazinon	304	A <sub>1,2</sub>
dimethoate	229	A <sub>1,2</sub>	hydroxydiazinon	321	C
methyl parathion	263	A <sub>2</sub>	malathion	330	A <sub>2,2</sub>
disulfoton	274	A <sub>2</sub>	chlorpyrifos	351	A <sub>2,2</sub>
Other Pesticides					
cycloate	215	E	myclobutanil	288	C
metalaxyl	279	C	iprodione	329	C
Pharmaceuticals and Personal Care Product Ingredients					
<i>p</i> -toluenesulfonamide	171	A <sub>1</sub>	HHCB	258	C,3
benzophenone	182	3	AHTN	258	E,3
<i>N,N</i> -diethyltoluamide	191	D	carisoprodol	260	A <sub>1</sub>
Flame Retardants and Plasticizers					
<i>N</i> -butyl benzenesulfonamide	213	A <sub>1</sub>	tris(2-butoxyethyl) phosphate	399	B
tris(2-chloroethyl) phosphate	285	B	diisononyl phthalate	418	E
tris(chloropropyl) phosphate	328	B	tris(1,3-dichloro-2-propyl) phosphate	431	B
diisooctyl phthalate	390	A <sub>1,1</sub>			
Other Organophosphorus Compounds					
triphenylphosphine oxide	278	B	formylmethylenetriphenylphosphorane	304	C
Polychlorinated Biphenyls					
2,4'-DCB (BZ 8)	223	A <sub>3</sub>	2,3',4,4',5-PeCB (BZ 118)	326	A <sub>3</sub>
2,2',5-TrCB (BZ 18)	258	A <sub>3</sub>	2,2',3,3',4,4',5-HeCB (BZ 170)	395	A <sub>3</sub>
2,2',4,4'-TeCB (BZ 52)	292	A <sub>3</sub>	2,2',3,4,4',5,5'-HeCB (BZ 180)	395	A <sub>3</sub>
2,3',4,4'-TeCB (BZ 66)	292	A <sub>3</sub>			
Halides/Related					
chloroform	118	D	1-iodo-2-methylnonane	268	D
benzyl chloride	126	D			
Isocyanate Compounds					
2,3-dimethylphenyl isocyanate	147	E			
Heterocyclics					
1,2-benzisothiazole	132	D	1,2-benzisothiazole-3-carboxylic acid	179	E
5-methyl-1 <i>H</i> -benzotriazole	133		2-(methylthio)benzothiazole	181	B
octahydro-(4- <i>all-trans</i> )-3(2 <i>H</i> )-isoquinolinone	153	C	16-hexadecanolide	254	D,3
<i>N</i> -cyclohexyl-2-pyrrolidone	167	C	2(5 <i>H</i> )-furanone, 4-methyl-3,5,5-tris(2-methyl-2-propenyl)-	260	
isosorbide dimethyl ether	174	C			
Terpenoids					
limonene	136	D,3	iridomyrmecin	168	E,2
verbenone	150	E,3	di- <i>epi</i> - $\alpha$ -cedrene epoxide	220	E
camphor	152	E,3	farnesol	222	E
Carboxylic Acids					
<i>n</i> -dodecanoic acid	200	C	8-methyl-9-tetradecenoic acid	240	D
diethylene glycol monobutyl ether acetate	204	B	<i>n</i> -pentadecanoic acid	242	D
<i>n</i> -tridecanoic acid	214	D	<i>n</i> -hexadec-11-enoic acid	254	D
2-methyl-2,2-dimethyl-1-(2-hydroxy-1-methylethyl)-propylpropanoic acid	216	C	<i>n</i> -hexadecanoic acid	256	A <sub>1</sub>
<i>n</i> -tetradec-9-enoic acid	226	D	<i>n</i> -heptadecanoic acid	270	C
<i>n</i> -tetradecanoic acid	228	B	<i>n</i> -octadec-9-enoic acid	282	D
			<i>n</i> -octadecanoic acid	284	D
Esters					
butyl methacrylate	142	B,1	acetic acid, 3,7,11,15-tetramethylhexadecyl ester	340	
hexanedioic acid, mono(2-ethylhexyl) ester	258	E	octadecanoic acid, butyl ester	340	D
triethyl citrate	276	E	9-hexadecenoic acid, icosyl ester	534	E
hexadecanoic acid, butyl ester	312	B			
Phenols/Related					
<i>tert</i> -butylphenol	150	D	2,4-bis(1-methyl-1-phenylethyl)phenol	330	C
2,6-bis(1,1-dimethylethyl)-4-(1-methyl-1-phenylethyl)phenol	324	C	2,4-bis(dimethylbenzyl)-6- <i>tert</i> -butylphenol	386	C
Alcohols/Related					
2-nonen-1-ol	142	E	3,7,11-trimethyl-2,6,10-dodecatrien-1-ol	222	D
2-decen-1-ol	156	D	tetraethylene glycol dimethyl ether	222	D
diethylene glycol monobutyl ether	162	D	globulol	222	E
1-tridecanol	200	D	2,4,7,9-tetramethyl-5-decyne-4,7-diol	226	C
1-[2-(2-methoxy-1-methylethoxy)-1-methylethoxy]-2-propanol	206	C	9-hexadecen-1-ol	240	D
3-isopropyl-4-methyl-dec-1-en-4-ol	212	E	1-heptadecanol	256	D

Table 3 (Continued)

compound	$M_r^b$	notes <sup>c</sup>	compound	$M_r^b$	notes <sup>c</sup>
		Aldehydes			
octanal	128	E	2-dodecanal	182	C
nonanal	142	D	tetradecanal	212	D
decanal	156		11-hexadecanal	238	D
undecanal	170	E			
		Ketones			
<i>p</i> -methylacetophenone	134	E	6,10-dimethyl-5,9-undecadien-2-one	194	D
<i>o</i> -methoxyacetophenone	150	D	geranyl acetone	240	D,3
4,4-dimethyl-2-propenylcyclopentanone	152	E			
		Amines/Amides			
<i>N,N</i> -dibutylformamide	157	B	<i>N,N</i> -dimethyl-1-pentadecanamine	255	
<i>N,N</i> -diethyl-4-methylbenzamide	191	D			
		Aliphatic/Aromatic Hydrocarbons			
<i>o</i> -xylene	106	D,1	nonadecane	268	E
2,6-dimethyl-2,6-octadiene	138	D	2,6,10,15-tetramethylheptadecane	296	D
1-dodecene	168	D	2,6,10,14,18-pentamethyl-2,6,10,14,18-icosapentaene	342	D
dodecane	170	A <sub>1</sub>	octacosane	394	B
2,5,6,11,14-pentaopentadecane	222	D	nonacosane	408	C
2,4-diphenyl-4-methyl-2-pentene	236	C			
		Polycyclic Aromatic Hydrocarbons			
naphthalene	128	A <sub>1,1</sub>	fluoranthene	202	A <sub>1</sub>
1-methylnaphthalene	142	A <sub>1,1</sub>	benzo[ <i>e</i> ]pyrene	252	A <sub>1</sub>
2-methylnaphthalene	142	A <sub>1,1</sub>	benzo[ <i>a</i> ]pyrene	252	A <sub>1</sub>
pyrene	202	A <sub>1</sub>			
		Compounds Present in Background/Blank Analyses <sup>d</sup>			
propanoic acid, 2-methyl-3-hydroxy-2,4,4-trimethyl-pentyl ester	216	C	heptasiloxane, hexadecamethyl-octasiloxane, hexadecamethyl-cyclooctasiloxane, hexadecamethyl-cyclononasiloxane, octadecamethyl-	532	E
dibutyl phthalate	278	B,1		578	E
benzyl butyl phthalate	312	B,1		592	E,1
cyclopentasiloxane, decamethyl-	370	C,1		666	E,1

<sup>a</sup>List derived from analyses of water-phase extracts of agricultural runoff from four fields by GC-MS with EI ionization. An EI library search purity (SI) value of 700 or greater was accepted as tentative identification. <sup>b</sup>Relative molecular mass. <sup>c</sup>Explanation of notes: (A) Compound identity confirmed by (A<sub>1</sub>) comparison of mass spectrum and/or retention time to that of an authentic standard, (A<sub>2</sub>) GC-FPD (27), or (A<sub>3</sub>) GC-ECD. (B) Confidence in structure high. Excellent match between mass spectrum and that of EI library (SI ≥ 900); no other close matches. (C) Confidence in structure moderately high. Good match between mass spectrum and that of EI library (SI = 750–899); no other close matches. (D) Structure known to a reasonable degree of certainty, but location of substituted functional group and/or double bond uncertain. (E) Compound identity questionable. Most reasonable identity listed. EI search purity value low (700–749). This represented 25 of 133 tentatively identified compounds. Further investigation of the identities of these peaks may be warranted. <sup>d</sup>Siloxanes may have originated from column bleed or vial septa. Phthalates were laboratory contaminants. The propanoic acid ester probably derived from plastic materials used in the laboratory. (1) Used as pesticide formulation or spray adjuvant. (2) Insect pheromone. (3) Fragrance compound.

having potential toxicological significance (Tables 3 and 4). Identified compounds included agricultural chemicals, wastewater effluent-derived contaminants, and soil organic matter components. Mass spectral identifications were made following the approach of Bernier et al. (16). Tables 3 and 4 list the level of confidence associated with each identification and describe the criteria applied. The level of uncertainty is highest for compounds assigned to class E. These compounds had low library search purity values (SI value = 700–749). Tentative identifications reflect the most reasonable match in the NIST/EPA/NIH 98 mass spectral library. Nearly 19% and 11% of tentatively identified compounds in water and suspended particle extracts were assigned to class E. A number of compounds had SI values exceeding 749, but did not fulfill the criteria outlined in Tables 3 and 4. These tentative identifications should also be regarded with caution. Further investigation of the identities of unassigned peaks and those assigned to class E may be warranted.

GC-FPD analysis revealed the presence of organophosphorus insecticides in all water and some suspended particle extracts. GC-ECD analysis of selected water-phase extracts demonstrated the occurrence of organochlorine pesticides and polychlorinated biphenyls (PCBs). Specific compound classes are discussed in the following sections.

**Agricultural Chemicals.** Water-phase extracts contained a number of currently used and legacy pesticides representing several classes, as well as possible pesticide formulation and spray adjuvants (Table 3). The number of identified agricultural chemicals associated with suspended particles was substantially lower (Table 4), possibly because the supercritical fluid extraction procedure used had been optimized for polycyclic aromatic hydrocarbons.

**Organochlorine Pesticides.** GC-ECD and GC-MS analyses of irrigation and storm runoff samples revealed detectable concentrations of *p,p'*-DDT [1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane; 20–120 ng/L]. Dissolved concentrations of *p,p'*-DDT were below the U.S. EPA acute water quality criterion of 1100 ng/L but above the chronic criterion of 1 ng/L. The use of DDT was banned in the United States in 1973 (15). The presence of DDT and a major metabolite (see below) in runoff 27 years after discontinuation reflects the stability of the parent molecule and its transformation product. A potential contemporary source of DDT in the watershed is the insecticide dicofol [2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol], which may contain up to 0.1% DDT and related compounds as contaminants (17). However, none of the fields containing DDT and its metabolites in runoff had been treated with dicofol during the past decade (18).

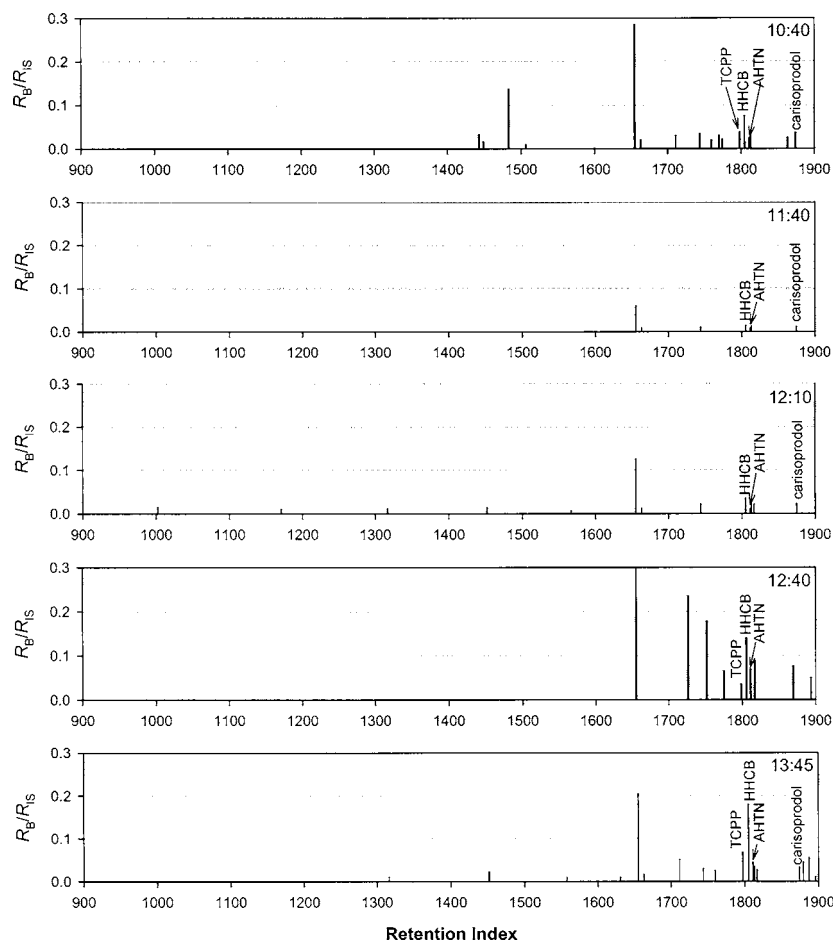
Table 4. Sorbed Organic Compounds Present or Suspected to Be Present in Agricultural Runoff<sup>a</sup>

compound	<i>M<sub>r</sub></i> <sup>b</sup>	notes <sup>c</sup>	compound	<i>M<sub>r</sub></i> <sup>b</sup>	notes <sup>c</sup>
Organochlorine Insecticides and Transformation Products					
<i>o,p'</i> -DDE	316	D			
Organophosphorus Insecticides and Transformation Products					
disulfoton	274	A <sub>2</sub>	chlorpyrifos	351	A <sub>2</sub>
diazinon	304	A <sub>2</sub>			
Other Pesticides					
permethrin	390	B			
Plasticizers					
diisooctyl phthalate	390	D,1			
Other Organophosphorus Compounds					
phosphonic acid, dioctadecyl ester	586				
Sulfones					
diphenyl sulfone	218	C			
Heterocyclics					
3-ethyl-4-methyl-1 <i>H</i> -pyrrole-2,5-dione	139	C	10-[(tetrahydro-2 <i>H</i> -pyran-2-yl)oxy]-1-decanol	258	E
2-(4 <i>H</i> )-benzofuranone, 5,6,7,7a-tetrahydro-4,4,7a-trimethyl-4,8,12-trimethyltridecan-4-olide	180	C	4,8,12,16-tetramethylheptadecan-4-olide	324	D
	254	E			
Terpenoids					
limonene	136	E,3	epicoprostanol	386	D,2
farnesol	222	D	cholesterol	386	B,2
isophytol	296	B	γ-sitosterol	414	D
Carboxylic Acids					
dodecanoic acid	200		<i>n</i> -tetradecanoic acid	228	C
2-methyl-2,2-dimethyl-1-(2-hydroxy-1-methylethyl)propylpropanoic acid	216		<i>n</i> -hexadecanoic acid	256	B
			<i>n</i> -octadecanoic acid	284	
Esters					
butyl methacrylate	142	B,1	tridecanoic acid, methyl ester	228	
9-dodecanoic acid, methyl ester	212		7-hexadecenoic acid, methyl ester	268	D
dodecanoic acid, ethenyl ester	226	E	3,4,2-cyclopentaneundecanoic acid, methyl ester	268	E
Alcohols/Related					
2-nonen-1-ol	142	E	9-octadecen-1-ol	268	
1-undecanol	172		3,7,11,15-tetramethyl-2-hexadecen-1-ol	296	B
Aldehydes					
2-octenal	126	C	2-nonenal	140	D
octanal	128	C			
Ketones					
6,10,11-trimethyl-2-pentadecanone	268		6,10,14-trimethyl-2-pentadecanone	268	C
Aliphatic/Aromatic Hydrocarbons					
5,5-dimethyl-1-ethyl-1,3-cyclopentadiene	122		2-methyl-1-pentadecene	224	
1,2,3,4-tetramethylbenzene	134		hexadecane	226	A <sub>1</sub>
1,1-dimethylheptane	160	E	heptadecane	240	A <sub>1</sub>
4-tetradecene	196	D	9-octadecene	252	D
6-tetradecene	196	D	3,7,11,15-tetramethyl-2-hexadecene	280	
7-tetradecene	196	D	5-icosene	280	D
2,3,5,8-tetramethyldecane	198		pentacosane	352	C
pentadecane	212	A <sub>1</sub>	heptacosane	380	C
<i>trans</i> -2,9- <i>transoid</i> -9,10- <i>trans</i> -tricyclo[8.6.0.0(2,9)]hexadeca-3,15-diene	216		nonacosane	408	C
Polycyclic Aromatic Hydrocarbons					
naphthalene	128	A <sub>1</sub> ,1	2-methylnaphthalene	142	A <sub>1</sub> ,1
1-methylnaphthalene	142	A <sub>1</sub> ,1	pyrene	202	A <sub>1</sub>
Compounds Present in Background/Blank Analyses <sup>d</sup>					
2-chlorovinyl dimethylethoxysilane	164	C	dibutyl phthalate	278	1
propanoic acid, 2-methyl-3-hydroxy-2,4,4-trimethylpentyl ester	216	C	bis(2-ethylhexyl) phthalate	390	B
			cyclohexasiloxane, dodecamethyl-	444	C,1

<sup>a</sup> List derived from analyses of supercritical CO<sub>2</sub> extracts of suspended particles in agricultural runoff from four fields by GC-MS with EI ionization. An EI library search purity (SI) value of 700 or greater was accepted as tentative identification. <sup>b</sup> Relative molecular mass. <sup>c</sup> Explanation of notes: (A) Compound identity confirmed by (A<sub>1</sub>) comparison of mass spectrum and/or retention time to that of an authentic standard or (A<sub>2</sub>) GC-FPD (27). (B) Confidence in structure high. Excellent match between mass spectrum and that of EI library (SI ≥ 900); no other close matches. (C) Confidence in structure moderately high. Good match between mass spectrum and that of EI library (SI = 750–899); no other close matches. (D) Structure known to a reasonable degree of certainty, but location of substituted functional group and/or double bond uncertain. (E) Compound identity questionable. Most reasonable identity listed. EI search purity value low (700–749). This represented 7 of 66 tentatively identified compounds. Further investigation of the identities of these peaks may be warranted. <sup>d</sup> Siloxanes may have originated from column bleed or vial septa. Phthalates were laboratory contaminants. The propanoic acid ester probably derived from plastic materials used in the laboratory. (1) Used as pesticide formulation or spray adjuvant. (2) Fecal sterol. (3) Fragrance compound.

Some samples also contained lindane (1α,2α,3β,4α,5α,6β-hexachlorocyclohexane; 6–32 ng/L). Lindane is often applied

in mixtures with fungicides and other pesticides and continues to be used in the watershed. Observed runoff concentrations



**Figure 2.** Reconstructed FID chromatographic profiles for the 16 September 1999 irrigation runoff event at site F. The abscissa is retention index. The ordinate is detector response relative to the *n*-octacosane internal standard. AHTN, 7-acetyl-1,1,3,4,4,6-hexamethyltetrahydronaphthalene; HHCB, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran; TCPP, tris(chloropropyl) phosphate.

were significantly lower than those shown to cause lethality to the ostracod *Cypridopsis vidua* (48-h  $LC_{50} = 3.2 \mu\text{g/L}$ ) (19). Lindane is a persistent xenoestrogen that has been shown to elicit vitellogenin production in Atlantic salmon (*Salmo salar*) (20).

**Organophosphorus Insecticides.** Nearly all samples analyzed by GC-FPD contained organophosphorus insecticides, particularly chlorpyrifos [*O,O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate] and diazinon [*O,O*-diethyl *O*-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate]. An average of 45% and 14% of the mass of chlorpyrifos and diazinon, respectively, in runoff was associated with the particulate phase (21). Other organophosphorus insecticides present included dichlorvos 2,2-dichlorovinyl dimethyl phosphate, dimethoate [*O,O*-dimethyl *S*-methylcarbamoylmethyl phosphorodithioate], disulfoton *S*-methyl *O*-2-(1-methylheptyl)-4,6-dinitrophenyl thiocarbamate], malathion [*S*-1,2-bis(ethoxycarbonyl)ethyl *O,O*-dimethyl phosphorodithioate], and methyl parathion [*O,O*-dimethyl *O*-4-nitrophenyl phosphorothioate]. Organophosphorus insecticides inhibit acetylcholinesterase (AChE), an enzyme involved in neurotransmission in both vertebrates and invertebrates.

Dissolved concentrations of organophosphorus insecticides in irrigation and storm runoff are displayed in **Table 5**. For comparison purposes, corresponding acute and chronic water quality criteria and 96-h  $LC_{50}$  values are presented. The 96-h  $LC_{50}$  values are those for the most sensitive invertebrate species we found reported in the literature. Dissolved concentrations of organophosphorus insecticides exhibited significant variability within events, as well as between events and between sites.

**Table 5.** Concentrations of Dissolved Organophosphorus Insecticides in Surface Runoff from Agricultural Fields

compound	dissolved concentration (ng/L)			96-h $LC_{50}$
	irrigation runoff	storm runoff	water quality criteria, acute/chronic	
chlorpyrifos	<3–981	<3–409	20/14 <sup>a</sup>	38 <sup>e</sup>
diazinon	<3–231	<3–105000	80/50 <sup>a</sup>	200 <sup>f</sup>
dichlorvos	<3–89	<3–1340	<i>b</i>	100 <sup>g</sup>
dimethoate	<13–1550	<13–381000	<i>b</i>	43000 <sup>g</sup>
disulfoton	<5–442	<5–106	<i>b</i>	3900 <sup>h</sup>
malathion	<5–187	<5–216	<sup>b</sup> /100 <sup>c</sup>	500 <sup>f</sup>
methyl parathion	<13–9150	<13	80 <sup>d</sup>	3800 <sup>f</sup>

<sup>a</sup> Reference 50. <sup>b</sup> No current or proposed U.S. water quality criteria. <sup>c</sup> Reference 52. <sup>d</sup> Interim water quality criterion (53). <sup>e</sup> *Ceriodaphnia dubia* (water flea) (50). <sup>f</sup> *Gammarus fasciatus* (amphipod) (19). <sup>g</sup> *Pteronarcys californica* (stonefly) (19). <sup>h</sup> *Palaemonetes kadiakensis* (glass shrimp) (19).

Dissolved concentrations varied over several orders of magnitude during some runoff events, often exceeded established and draft water quality criteria, and were sometimes greater than reported  $LC_{50}$  values for sensitive aquatic invertebrates. Organophosphorus insecticides were usually present as mixtures. Because of the potential additive toxicity of these compounds, even when concentrations of individual organophosphorus insecticides were below levels of concern, their combined effect may result in toxicity to nontarget organisms (21).

**Nontarget Pesticides.** Runoff water and suspended sediment contained several additional, nontarget pesticides for which

**Table 6.** Summary of Nontarget Pesticides Present in Surface Runoff from Agricultural Fields

compound	class	medium <sup>a</sup>	approx concn	<i>Daphnia magna</i> 48-h LC <sub>50</sub> <sup>b</sup> (μg/L)	log <i>K</i> <sub>ow</sub>
cycloate	thiocarbamate herbicide	w	1.04–1.55 μg/L	5600 <sup>c</sup>	3.9 <sup>b</sup>
iprodione	dicarboximide fungicide	w	0.71–1.0 μg/L	250	3.1 <sup>b</sup>
metalaxyl	phenylamide fungicide	w	0.27 μg/L	12500	1.7 <sup>d</sup>
myclobutanil	azole fungicide	w	4.10 μg/L	11000	2.9 <sup>b</sup>
permethrin	pyrethroid insecticide	ss	0.052 μg/kg	0.6	6.1 <sup>b</sup>

<sup>a</sup> ss, suspended sediment; w, water. <sup>b</sup> Reference 54. <sup>c</sup> No data found for nontarget algae or aquatic macrophytes. <sup>d</sup> Reference 51.

water quality criteria have not been developed in the United States. Approximate concentrations and published toxicity values are given in **Table 6**. The synthetic pyrethroid insecticide permethrin [3-phenoxybenzyl (1*RS*)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] was identified on suspended sediment from a celery field (site F) to which it was applied. Permethrin exhibits a moderate propensity to bioaccumulate in fish (log BCF = 1.7–4.3) (22) and appears to act as a weak estrogen receptor agonist (23). The selective systemic herbicide cycloate [*S*-ethyl cyclohexyl(ethyl) thiocarbamate] was tentatively identified in runoff from a field planted with leafy green vegetables (site A) to which it had been applied several times during the crop season. Three fungicides were present in runoff from two fields: iprodione [3-(3,5-dichlorophenyl)-*N*-isopropyl-2,4-dioximidazolidine-1-carboxamide], myclobutanil (RS) [2-(4-chlorophenyl)-2-(1*H*-1,2,4-triazol-1-ylmethyl) hexanenitrile], and metalaxyl [methyl *N*-2-methoxyacetyl-*N*-2,6,-xylyl-DL-alaninate]. Iprodione and metalaxyl were present in wet season runoff from fields planted in spinach and cilantro. Iprodione is a contact and locally systemic fungicide that inhibits germination of spores and growth of fungal mycelium. Metalaxyl inhibits protein synthesis and finds use as a systemic soil and foliar fungicide in combination with fungicides possessing different modes of action. Metalaxyl appears to induce certain malignancies by nongenotoxic mechanisms (24). The ergosterol synthesis inhibitor myclobutanil was detected in irrigation runoff from a strawberry field (site B).

**Pesticide Transformation Products.** In addition to parent compounds, several pesticide transformation products were identified in runoff from sampled fields. The major DDT metabolite *o,p'*-DDE 1,1-dichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl) ethylene; 10–50 ng/L and ~84 μg/kg} was present in irrigation and storm runoff samples. *o,p'*-DDE has been shown to induce vitellogenesis in juvenile rainbow trout (*Oncorhynchus mykiss*) and to exhibit low affinity for hepatic cytosolic estrogen binding sites (25). Dichlorvos, a compound finding use as an insecticide itself, was not reported to have been applied to agricultural fields in the watershed during 1998–2000 (18). Its presence in agricultural runoff was likely due to the degradation of the organophosphate insecticide naled [(*RS*) 1,2-dibromo-2,2-dichloroethyl dimethyl phosphate]. Dichlorvos is highly toxic to aquatic invertebrates, with a 48-h EC<sub>50</sub> value for *Daphnia pulex* of 70 ng/L (19). Runoff concentrations sometimes exceeded this value by up to an order of magnitude. Hydroxydiazinon [*O,O*-diethyl *O*-2-(1-hydroxy-1-methylethyl)-6-methylpyrimidin-4-yl] phosphorothioate] is a diazinon photodegradation or microbial transformation product (26–28). Like the parent compound, hydroxydiazinon inhibits AChE. The

literature contains few reports of the occurrence of this compound in environmental matrices (26, 27) or its effects on aquatic organisms. In some samples, the concentration of this transformation product was 0.6% of that of the parent compound.

**Chemicals Used as Pesticide Adjuvants.** Runoff samples contained a variety of compounds that may reflect their usage as pesticide formulation and spray adjuvants. So-called “inert ingredients” often comprise the bulk of pesticide formulations and include some potentially toxic compounds. Because these compounds have other uses and may be present in treated wastewater, we cannot definitively link their occurrence in runoff with their use as pesticide adjuvants. The presence of several of them in runoff from storm events and their reported use on sampled fields, however, suggests that at least some may derive from adjuvants rather than wastewater. Information on the uses and toxicity classification of these compounds is presented in **Table 7**.

A number of aromatic petroleum distillates finding use as pesticide adjuvants were identified in runoff from irrigated fields, including xylene, naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene. Several ethylene glycol derivatives originating from nonionic surfactants were present in irrigation and storm runoff: diethylene glycol monobutyl ether (2–5 μg/L), diethylene glycol monobutyl ether acetate (24–60 μg/L), and tetraethylene glycol dimethyl ether (~2 μg/L). The presence of butyl methacrylate (~21 μg/L) in some runoff samples may derive from its use as a pesticide adjuvant.

Organosilicone compounds and phthalic acid esters are often employed as pesticide adjuvants. However, some of these compounds occurred in blanks as background contaminants, preventing us from confidently determining their presence in our samples. Previous studies in our laboratory indicated that benzyl butyl phthalate, bis(2-ethylhexyl) phthalate, and dibutyl phthalate were laboratory contaminants (29). However, our samples contained two phthalates that may find use as adjuvants and were not present as laboratory contaminants, most notably diisooctyl phthalate (DIOP; 0.2–4.1 μg/L). This compound was present in runoff from both rain and irrigation events. DIOP is also used as a plasticizer. We believe that the siloxanes originated from the column stationary phase and the septa of the vials used to store extracts, although dimethyl polysiloxane was used as a spray adjuvant on several of the fields sampled (18).

**Wastewater-Derived Microcontaminants.** In addition to pesticide active ingredients, insecticide transformation products, and possible adjuvants, broad spectrum analysis of agricultural runoff revealed the presence of a variety of xenobiotic com-



**Table 7.** Summary of Selected Nontarget Anthropogenic Compounds Identified in Agricultural Runoff<sup>a</sup>

compound	class	use	comments
AHTN	polycyclic musk	fragrance in perfumes, cosmetics, soaps, shampoos, laundry detergent, and fabric softeners	weak estrogen receptor agonist <sup>b</sup>
benzophenone	benzophenone	fragrance fixative, mfg of pharmaceuticals and pesticides	
<i>N</i> -butyl benzenesulfonamide butyl methacrylate	benzenesulfonamide acrylate	plasticizer, mfg of herbicides pesticide adjuvant mfg of methacrylate resins, adhesives, solvent coatings, and oil additives emulsions for paper, textiles, and leather finishing	neurotoxic to laboratory mammals <sup>c</sup> potentially toxic inert ingredient <sup>d</sup>
carisoprodol	pharmaceutical	muscle relaxant analgesic	
diethylene glycol monobutyl ether	glycol ether	pesticide adjuvant automobile antifreeze de-icing agents industrial solvent detergent	potentially toxic inert ingredient <sup>d</sup>
diethylene glycol monobutyl ether acetate	glycol ether	pesticide adjuvant degradate automobile antifreeze de-icing agents industrial solvent detergent	
diethyltoluamide HHCB	benzamide polycyclic musk	insect repellent fragrance in perfumes, cosmetics, soaps, shampoos, laundry detergent, and fabric softeners	CNS disturbances in mammals weak estrogen receptor agonist, <sup>b</sup> possible artificial pheromone <sup>e</sup>
1-methylnaphthalene	aromatic petroleum distillate	pesticide adjuvant dye and resin mfg	
2-methylnaphthalene	aromatic petroleum distillate	pesticide adjuvant dye and resin mfg	
2-(methylthio)benzothiazole	benzothiazole	fungicide degradate vulcanization accelerator degradate biocorrosion inhibitor degradate	
naphthalene	aromatic petroleum distillate	pesticide adjuvant pesticide mothballs toilet deodorant carbaryl mfg production of dyes, resins, and tanning agents	possible human carcinogen <sup>f</sup>
tetraethylene glycol dimethyl ether	glycol ether	possible pesticide adjuvant automobile antifreeze de-icing agents industrial solvent detergent	
<i>p</i> -toluenesulfonamide	benzenesulfonamide	oral hypoglycemic metabolite fish pharmaceutical degradate disinfectant metabolite plasticizer in lacquers	
tris(2-butoxyethyl) phosphate tris(2-chloroethyl) phosphate	trialkyl phosphate ester trialkyl phosphate ester	flame retardant flame retardant	AChE inhibitor <sup>g</sup> AChE inhibitor <sup>h</sup> carcinogenic to mice and rats <sup>i</sup>
tris(chloropropyl) phosphate tris(1,3-dichloro-2-propyl) phosphate phosphate xylene	trialkyl phosphate ester trialkyl phosphate ester aromatic petroleum distillate	flame retardant flame retardant pesticide adjuvant electroplating paint stripping pharmaceutical mfg floor polishes	carcinogenic to rats <sup>i</sup> potentially toxic inert ingredient, <sup>d</sup> suspected developmental and reproductive toxicant, possible immuno- and neurotoxicity

<sup>a</sup> AChE, acetylcholinesterase; AHTN, 7-acetyl-1,1,3,4,4,6-hexamethyltetrahydronaphthalene; CNS, central nervous system; HHCB, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran; mfg, manufacturing. <sup>b</sup> Reference 55. <sup>c</sup> References 56, 57. <sup>d</sup> Reference 58. <sup>e</sup> Reference 59. <sup>f</sup> Reference 60. <sup>g</sup> Reference 34. <sup>h</sup> Reference 62. <sup>i</sup> Reference 33.

pounds likely deriving from treated wastewater. These included a number of EPA priority pollutants (i.e., polychlorinated biphenyls, polycyclic aromatic hydrocarbons) as well as plasticizers, flame-retardants chemicals, pharmaceuticals, and personal care product ingredients. Information on the nonpriority contaminants is summarized in **Table 7**.

**Polychlorinated Biphenyls.** Di-, tetra-, and heptachlorinated PCB congeners (mostly noncoplanar) were detected in runoff samples at concentrations ranging from 2 to 174 ng/L. These compounds are ubiquitous environmental contaminants, and in addition to irrigation with treated wastewater, they may have originated from atmospheric deposition. These persistent hy-

drophobic compounds are classified as probable human carcinogens and are known endocrine disruptors (30). The mono-ortho-substituted PCB 2,3',4,4',5-pentachlorobiphenyl (BZ 118) is a weak aryl hydrocarbon receptor ligand (30). The di-ortho-substituted 2,2',3,4,4',5,5'-heptachlorobiphenyl (BZ 180) was shown to have pleiotropic effects on estrogen receptors (31).

**Polycyclic Aromatic Hydrocarbons.** A variety of polycyclic aromatic hydrocarbons (PAHs) were present in both the suspended solid and aqueous phase in samples from irrigation and storm events. These compounds included phenanthrene (0.001–0.020  $\mu\text{g/L}$ ;  $\sim 0.2 \mu\text{g/kg}$ ), pyrene ( $\sim 0.001 \mu\text{g/L}$ ), chrysene/triphenylene (0.001–0.008  $\mu\text{g/L}$ ), benzo[*e*]pyrene ( $\sim 0.003 \mu\text{g/L}$ ), benzo[*a*]pyrene ( $\sim 0.003 \mu\text{g/L}$ ), and perylene ( $\sim 0.004 \mu\text{g/L}$ ). Trace amounts phenanthrene, fluoranthene, and pyrene were detected in irrigation water from one field. PAHs derive from petroleum products and their combustion. PAHs are photoactivated toxicants (i.e., their toxicity to aquatic organisms increases with simultaneous exposure to UV irradiation). Several PAHs identified in agricultural runoff are known (e.g., pyrene) or probable (e.g., benzo[*a*]pyrene, chrysene) human carcinogens.

**Plasticizers and Flame-Retardant Chemicals.** The sulfonamide plasticizer *N*-butyl benzenesulfonamide ( $\sim 2 \mu\text{g/L}$ ) was identified in runoff from fields irrigated with treated wastewater, as were several alkylated phosphate ester flame-retardant plasticizers: tris(2-chloroethyl) phosphate (0.4–1.2  $\mu\text{g/L}$ ), tris(chloropropyl) phosphate (0.6–1.6  $\mu\text{g/L}$ ), tris(2-butoxyethyl) phosphate (3.3–6.2  $\mu\text{g/L}$ ), and tris(1,3-dichloro-2-propyl) phosphate (0.3–0.7  $\mu\text{g/L}$ ). *N*-Butyl benzenesulfonamide is used in polyamide and copolyamide plastics and in the manufacture of sulfonyl carbamate herbicides (32). Alkylated phosphate esters are employed as flame retardants in polyurethane foams, resins, poly(vinyl chloride) compounds, floor polishes, lacquers, plastics, synthetic rubber, synthetic fibers, and cellulose ester compounds (33–35).

**Human Pharmaceuticals.** Two pharmaceuticals and a pharmaceutical metabolite were identified in irrigation water and runoff from fields irrigated with tertiary treated wastewater and effluent-dominated streamwater. The muscle relaxant and analgesic drug carisoprodol (*N*-isopropyl-2-methyl-2-propyl-1,3-propanediol dicarbamate) was identified in runoff from a field irrigated with effluent-dominated streamwater ( $\sim 0.9 \mu\text{g/L}$ ). The oral hypoglycemic metabolite *p*-toluenesulfonamide (36) was identified in runoff from fields irrigated with treated effluent ( $\sim 10 \mu\text{g/L}$ ). Caffeine (1,3,7-trimethyl-2,6-dioxo-1,2,3,6-tetrahydropurine) was present in irrigation water at one site but was not detected in surface runoff by the broad spectrum analysis.

**Personal Care Product Ingredients.** Several consumer personal care product ingredients were identified in runoff from fields irrigated with treated wastewater or water from an effluent-dominated stream. The synthetic polycyclic musk fragrances HHCb (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[*g*]-2-benzopyran, Galaxolide; 0.4–1.3  $\mu\text{g/L}$ ) and AHTN (7-acetyl-1,1,3,4,4,6-hexamethyltetrahydronaphthalene, Tonalide; 0.8–5.7  $\mu\text{g/L}$ ) were tentatively identified in the water phase from two fields. These compounds are present in numerous consumer products (cf. **Table 7**) and are incompletely removed by conventional wastewater treatment processes (37). A number of other compounds used as fragrances in consumer products were tentatively identified in water-phase extracts: 16-hexadecanolide, limonene, verbenone, camphor, and geranyl acetone. The lactone 16-hexadecanolide is a component of the musky scent of orchids (38). Runoff from fields irrigated with tertiary effluent also contained detectable levels of the widely

used insect repellent *N,N*-diethyltoluamide (DEET;  $\sim 0.4 \mu\text{g/L}$ ) and the fragrance fixative benzophenone ( $\sim 0.8 \mu\text{g/L}$ ). *N,N*-Diethyltoluamide was among the most frequently detected compounds in a recent U.S. Geological Survey reconnaissance study of organic wastewater contaminants in U.S. streams (39).

**Biomarkers.** Two fecal sterols (viz., cholesterol and epicoprostanol) were detected sorbed to suspended particles in runoff from fields irrigated with tertiary treated wastewater or effluent-dominated streamwater. While treated wastewater appears to be the likely source of these compounds, contributions from bat and seabird guano applied as fertilizers cannot be ruled out. The  $5\beta$ -stanol, epicoprostanol, is formed by anaerobic microbial hydrogenation of cholesterol and considered indicative of mammalian fecal contamination (40).

**Soil Natural Organic Matter.** Although this study was not designed to characterize nonliving components of soil organic matter, the majority of organic carbon compounds in the water and suspended particle extracts derived from natural organic matter (NOM). The analytical procedure employed allowed evaluation of the lower molecular weight components of dissolved and particulate soil organic matter extractable by dichloromethane and supercritical  $\text{CO}_2$ , separable on a DB-5MS column, and amenable to analysis by GC-MS. Extracts of the dissolved phase contained a wide variety of relatively low molecular weight ( $M_r \leq 534$  u) NOM components (**Table 3**). Major components of dissolved NOM included saturated ( $\text{C}_{12}$ – $\text{C}_{18}$ ) and monounsaturated ( $\text{C}_{14:1}$ ,  $\text{C}_{16:1}$ ,  $\text{C}_{18:1}$ ) fatty acids; saturated, monounsaturated, and branched aliphatic alcohols ( $\text{C}_9$ – $\text{C}_{17}$ ); and the  $\text{C}_{12}$  *n*-alkane. Even-carbon-numbered fatty acids predominated and included lauric acid (*n*-dodecanoic acid), myristic acid (*n*-tetradecanoic acid), palmitic acid (*n*-hexadecanoic acid), stearic acid (*n*-octadecanoic acid), and oleic acid (*n*-octadec-9-enoic acid). The presence of palmitic and oleic acids in irrigation water indicates that soil organic matter was not the sole source of these compounds. Chefetz and co-workers (41–43) noted the presence of a homologous series of long-chain fatty acid methyl esters in tetramethylammonium hydroxide (TMAH)-treated soil and peat humic acid, including those corresponding to the dissolved unsaturated fatty acids identified in this study. These authors suggested that the prevalence of even-carbon-numbered long-chain fatty acids was due to inputs of plant biopolymers such as cutin, cutan, suberin, and suberan (41–43). The tentatively identified  $\text{C}_8$ – $\text{C}_{16}$  aldehydes may represent oxidative degradation products of unsaturated fatty acids from plant residues (44). We also tentatively identified monoterpenoids (e.g., iridomyrmecin, limonene) and sesquiterpenoids (e.g., farnesol) and their derivatives (e.g., diepi- $\alpha$ -cedrene epoxide) in water-phase extracts. Interestingly, iridomyrmecin is an insect pheromone (45, 46). The essential plant oil globulol, tentatively identified in water-phase extracts from site B, may have originated from eucalyptus trees bordering the field. These soluble organic compounds represent allochthonous components of stream-dissolved organic matter in this watershed.

The range of NOM components extracted from suspended soil particles was similarly broad, with molecular weights between 126 and 414 u. Supercritical  $\text{CO}_2$  extracts of suspended particles contained more aliphatic hydrocarbons than DCM extracts of the water phase. The saturated  $\text{C}_{16}$  fatty acid constituted the bulk of the identifiable soil organic matter extracted and, as mentioned above, was at least in part due to its presence in irrigation water. Many of the more polar compounds tentatively identified in the water phase were not detected sorbed to suspended particles. The *n*-alkanes hepta-

cosane and nonacosane and the triterpenoid phytosterol  $\gamma$ -sitosterol are components of plant waxes and were identified sorbed to suspended particles. Methyl esters of C<sub>12</sub> and C<sub>16</sub> fatty acids were also tentatively identified. Schulden and Schnitzer (47) noted the predominance of C<sub>14</sub>–C<sub>40</sub> *n*-fatty acids, dioic acids, and *n*-alkyl monoesters in supercritical CO<sub>2</sub> extracts of two soils.

**Management Implications.** Protection of aquatic ecosystems requires that the full suite of potentially toxic compounds entering surface waters be considered. Current ecotoxicity tests are insufficiently comprehensive to accommodate the large range of potential toxicants and broad spectrum of possibly subtle effects (1). Comprehensive chemical characterization of runoff contaminants will be required to assess the ecological risks associated with agricultural runoff. The ecotoxicological significance of low concentrations of xenobiotic organic chemicals, especially human pharmaceuticals and personal care product ingredients, remains to be elucidated. Some human pharmaceuticals have been shown to modulate endocrine function, act as developmental/behavioral signaling agents, or sensitize nontarget organisms to other toxicants (1). Treated wastewater used for irrigation, as well as sewage sludge-derived soil amendments and animal manures, should be further investigated as potential sources of human and veterinary pharmaceuticals and personal care product ingredients.

Food crops may take up wastewater-derived contaminants in irrigation water (and biosolids), as recent studies of antimicrobial agent toxicity to soybeans suggest (48). Chiou et al. (49) used a partition-limited model to examine organic contaminant uptake by crop plants. An inverse relationship was found between the octanol–water partition coefficient ( $K_{ow}$ ) and a quasi-equilibrium factor describing the approach to equilibrium of an organic contaminant between the plant and the soil interstitial water (49). Chiou et al. (49) concluded that concentrations of relatively water-soluble contaminants in plants would be nearly at equilibrium with soil interstitial water, while levels of less soluble compounds in plants would be further from their equilibrium values (49). In the present study, plant concentrations of more hydrophobic wastewater effluent-derived contaminants such as HHCb ( $\log K_{ow} = 5.9$ ; ref 50) would be expected to be dominated by uptake by plant lipids, while highly water-soluble contaminants such as *p*-toluenesulfonamide ( $\log K_{ow} = 0.82$ ; ref 51) would be present primarily in the water phase of high water content plants (e.g., lettuce, celery). Because this latter compound is ionizable, active transport must also be considered (50). Uptake of wastewater-derived contaminants by crop plants warrants further research.

#### ACKNOWLEDGMENT

The field and laboratory assistance of Joshua Burnam, Guadalupe Chapa, Magali Garduño, Theresa Lam, Chen-Hung Michael Lin, Xinling Ouyang, and Medhi Wangpaichitr is gratefully acknowledged. Ed Ruth and Mary E. Soliman are thanked for GC-MS analysis and assistance in MS interpretations. Ed Ruth also performed the GC-ECD analyses. Larry Zintek (U.S. EPA Region 5) is thanked for the analysis of a subset of samples. Azko Nobel generously provided the tris(1,3-dichloro-2-propyl) phosphate standard.

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Received for review September 11, 2002. Revised manuscript received November 8, 2002. Accepted November 8, 2002. This research was supported by a cooperative agreement with the U.S. Environmental Protection Agency. During the course of this research J.A.P. was supported by the U.S. Environmental Protection Agency and a Charles F. Scott Fellowship. This work has not been reviewed by USEPA, so no endorsement should be inferred.

JF025953Q