Effects of Urbanization and Long-Term Rainfall on the Occurrence of Organic Compounds and Trace Elements in Reservoir Sediment Cores, Streambed Sediment, and Fish Tissue from the Santa Ana River Basin, California, 1998

Water Resources Investigations Report 02-4175
Photography: USGS banner photograph: Canyon Lake, by Scott W.T. Hamlin;
Lower left: Collecting fish, Santa Ana River below Prado Dam, by Author;
Lower right: Visual inspection of Lake Hemet sediment core, by Rudolph R. Contreras
Effects of Urbanization and Long-Term Rainfall on the Occurrence of Organic Compounds and Trace Elements in Reservoir Sediment Cores, Streambed Sediment, and Fish Tissue from the Santa Ana River Basin, California, 1998

By Carmen A. Burton

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 02-4175

Prepared in cooperation with the NATIONAL WATER-QUALITY ASSESSMENT PROGRAM)

Sacramento, California
2002
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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS AND ACRONYMS

CONVERSION FACTORS

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

\[ °F = (1.8 \times °C) + 32 \]

VERTICAL DATUM

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

NOTE TO USGS USERS: Use of hectare (ha) as an alternative name for square hectometer (hm²) is restricted to the measurement of small land or water areas. Use of liter (L) as a special name for cubic decimeter (dm³) is restricted to the measurement of liquids and gases. No prefix other than milli should be used with liter. Metric ton (t) as a name for megagram (Mg) should be restricted to commercial usage, and no prefixes should be used with it.

ABBREVIATIONS AND ACRONYMS

ft  feet
in.  inch
mi  mile
mi²  square miles
mm  millimeter
pCi/g  picocuries per gram
µg/g  microgram per gram
µg/kg  microgram per kilogram

EPA  U.S. Environmental Protection Agency
NAE  National Academy of Engineering
NAS  National Academy of Science
NAWQA  National Water-Quality Assessment Program
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<td>National Water Quality Laboratory</td>
</tr>
<tr>
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<td>polychlorinated biphenyls</td>
</tr>
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Effects of Urbanization and Long-Term Rainfall on the Occurrence of Organic Compounds and Trace Elements in Reservoir Sediment Cores, Streambed Sediment, and Fish Tissue from the Santa Ana River Basin, California, 1998

By Carmen A. Burton

ABSTRACT

Organochlorine compounds, semivolatile-organic compounds (SVOC), and trace elements were analyzed in reservoir sediment cores, streambed sediment, and fish tissue in the Santa Ana River Basin as part of the U.S. Geological Survey’s National Water-Quality Assessment Program. Three reservoirs were sampled in areas that have different degrees of urbanization. Streambed sediment and fish tissue collected at 12 sites were divided into two groups, urban and nonurban. More organochlorine compounds were detected in reservoir sediment cores, streambed sediment, and fish tissue, and at higher concentrations at urban sites than at nonurban sites. At all sites, except West Street Basin, concentrations of organochlorine compounds were lower than the probable-effect concentration (PEC). At the highly urbanized West Street Basin, chlordane and p,p′-DDE exceeded the PEC throughout the historical record. The less stringent threshold-effect concentration (TEC) was exceeded for six compounds at eight sites. Most of the organochlorine compounds detected in streambed sediment and fish tissue were at urban sites on the Santa Ana River as opposed to its tributaries, suggesting accumulation and persistence in the river.

More SVOCs were detected in reservoir sediment cores and streambed sediment, and at higher concentrations, at urban sites than at nonurban sites. At all the sites, except West Street Basin, concentrations of SVOCs were lower than the PEC. At West Street Basin, chrysene, pyrene, and total polycyclic-aromatic hydrocarbons exceeded the PEC throughout the historical record. The TEC was exceeded for 10 compounds at 3 sites. Most of the SVOCs were detected in streambed sediment at urban sites on tributaries to the Santa Ana River rather than the mainstem itself. The less frequent occurrence and lower concentrations in the Santa Ana River suggest that SVOCs are less persistent than organochlorine compounds, possibly as a result of volatization, gradation, or dilution.

Most trace-element detections in reservoir sediment cores and streambed sediment were at urban sites, and the concentrations were generally higher than at nonurban sites. Lead and zinc exceeded their PECs at West Street Basin throughout the historical record; copper exceeded its PEC at Canyon Lake, an area of urban growth. The TEC was exceeded for 10 compounds at 11 sites. Frequency of detection and concentration did not differ between tributary and Santa Ana River sites, which may be attributed to the fact that trace elements occur naturally. Four trace elements (arsenic, copper, mercury, and selenium) had higher concentrations in fish tissue at nonurban sites than at urban sites.
Concentrations decreased over time for organochlorine compounds at all three reservoirs, probably a result of the discontinued use of many of the compounds. Decreasing trends in SVOCs and trace elements were observed at West Street Basin, but increasing trends were observed at Canyon Lake. Concentrations of organochlorine compounds, SVOCs, and trace elements were higher during periods of above average rainfall at both West Street Basin and Canyon Lake.

INTRODUCTION

The Santa Ana River Basin (fig. 1) is one of many river basins in the U.S. Geological Survey’s (USGS) National Water-Quality Assessment (NAWQA) Program. The design of the NAWQA Program is to determine current water-quality conditions and water-quality trends over time (Gilliom and others, 1995). The surface-water component of the NAWQA Program integrates physical, chemical and biological data to aid in the interpretation and assessment of changes in stream quality (Gurtz, 1994). The assessment of organic compound and trace-element concentrations in reservoir sediment cores, recently deposited streambed sediment, and fish tissue is one component of the integrated approach. Sediment and fish tissue are analyzed because many hydrophobic compounds tend to concentrate in these media relative to water. The process of sediment movement and deposition may also influence the environmental transport and fate of many toxic and bioaccumulative compounds in aquatic ecosystems. As a result, sediment and tissue concentrations may better represent distribution of many hydrophobic compounds in the environment than do water samples.

Streambed sediment and fish tissue were used to assess the status of hydrophobic contaminants in the Santa Ana River Basin. However, the data record to assess changes over time is often inadequate. The data record for trend analysis may be limited by low sampling frequencies, a short period of data collection, and changing sampling and analytical methods. The use of sediment cores is one way in which a missing historical record may be partly reconstructed (Van Metre and Callender, 1996).

Purpose and Scope

This report describes the occurrence and distribution of organochlorine compounds, semivolatile-organic compounds (SVOC), and trace elements in streambed sediment and fish tissue in the Santa Ana River Basin. Trends in concentrations of detected compounds in reservoir sediment cores from three reservoirs are evaluated by parametric and nonparametric statistical tests. Detected compounds and their concentrations also are evaluated in relation to general land uses and rainfall patterns, and compared with guidelines for the protection of aquatic biota.

Acknowledgments

The author thanks the many individuals within the USGS who contributed to this study. Special thanks are extended to Robert Kent, Jason May, Terry Short, Steve Goodbred, and Larry Shelton for help with collecting the streambed-sediment and fish-tissue samples; and Peter Van Metre, Jennifer Wilson, and Scott Hamlin for doing the reservoir site selection and sediment coring. Editing was by Jerry Woodcox; illustrations by Callie Mack; and layout by James Baker.

STUDY DESIGN

Background Information

The Santa Ana River Basin occupies about 2,670 mi² of the densely populated coastal area of southern California, near Los Angeles (fig. 1). The Santa Ana River is the largest stream system in southern California, beginning in the San Bernardino Mountains (which reach altitudes exceeding 10,000 ft) and flowing more than 100 mi to the Pacific Ocean. The watershed is home to over 4.5 million people, and the population is expected to reach almost 8 million people by the year 2020 (Southern California Association of Governments, 1997).
Figure 1. Map showing Location of study area, ecoregions, reservoir sediment core sites, and streambed-sediment and fish-tissue sites, Santa Ana River Basin, California.
Urban and agricultural land uses occur primarily in the alluvial-filled valleys and coastal plain, which are located in the Southern and Central California Plains and Hills Ecoregion. The uplands, which include the San Gabriel, San Bernardino, and San Jacinto Mountains, lie within the Southern California Mountains Ecoregion and are generally steep and undeveloped (fig. 1). Land use in the basin is about 35 percent urban, 10 percent agricultural, and 55 percent open space (fig. 2), primarily steep mountain slopes. The Coastal Basin is the most urbanized subbasin; more than 50 percent of the total area is developed. If one discounts the steep slopes, about 80 percent of the coastal plain is developed. The Inland Basin is also heavily urbanized; about one-third of the total area and more than one-half of the valley floor is developed. The San Jacinto Basin is the most agricultural of the three subbasins; agricultural and urban uses each occupy less than 20 percent of the total area and nearly one-half of the valley floor. However, the San Jacinto Basin is rapidly urbanizing. Population density for the entire study area is about 1,500 people per square mile: not including the land area that is steep, the population density is about 3,000 people per square mile. In some areas, especially the coastal plain, population density is over 5,000 people per square mile (fig. 3).

The climate is mediterranean and is characterized by hot, dry summers, and cool, wet winters. Average annual precipitation ranges from about 10 to 24 in. in the coastal plain and inland valleys, and from 24 to 48 in. in the San Gabriel and San Bernardino Mountains (U.S. Army Corps of Engineers, 1994).

Site Selection

Reservoir Sites

One purpose of this study was to assess temporal trends of hydrophobic compounds, which was accomplished by analyzing reservoir sediment cores. Three reservoir sites were selected covering a range of urban land use. West Street Basin (site A, fig. 2) is a small stormwater-retention basin in the Coastal Santa Ana Basin. It has been fully urbanized since about 1965 and has the highest population density (table 1). Canyon Lake is in the San Jacinto Basin and has mixed land use (site B, fig. 2; table 1). The area immediately surrounding Canyon Lake and within 10 mi upstream is an area of continuous urban growth. Housing development started in the mid 1960s and has continued to the present time. Periods of heavy construction occurred around 1964, 1979–80, and 1989–91.

Hemet Lake is in the San Jacinto Mountains and is mostly undeveloped (site C, fig. 2; table 1). As a result, Hemet Lake has minimal urban influence or other anthropogenic effects.

Streambed-Sediment and Fish-Tissue Sites

The second purpose of this study was to assess the current status of hydrophobic contaminants in streambed sediment and fish tissue (Gilliom and others, 1995). Stream sites were selected to cover as much of the Santa Ana River Basin as possible. However, site selection was limited by the ephemeral nature of many of the streams in the basin as a result of the hot, dry summers and concrete-lined channels with little or no sediment. Sediment was collected at 12 sites in the basin. Fish tissue was collected at 10 of these sites. The other two sites had insufficient streamflow to support a population of large fish.

Eight of the streambed sites were classified as urban on the basis of percentage urban land use (more than 25 percent) in the drainage basin or the proximity of urban land use to the site (fig. 2 and table 1). Four of the urban sites are on tributaries to the Santa Ana River; three are in the Inland Basin, and one is in the San Jacinto Basin. Warm Creek (site 7), a small urban catchment, is near San Bernardino. Mill Creek at Chino–Corona Road (site 4) and Chino Creek below Central Avenue (site 3) are northwest of Riverside. The land use upstream from these sites is primarily urban, although undeveloped lands and agriculture are present. No fish tissue was collected at Warm Creek. The fourth site is on the San Jacinto River near Elsinore (site 11). The land uses upstream from this site are urban and undeveloped. Much of the land use is agricultural, but the upstream Canyon Lake is a sink for sediment and, therefore, for most of the hydrophobic compounds from agricultural practices.
Figure 2. Map showing 1993 land use in the Santa Ana River Basin, California.
Figure 3. Map showing Population density in the Santa Ana River Basin, California.
Table 1. Population density and land use for reservoir sediment core, streambed-sediment, and fish-tissue sampling sites, in the Santa Ana River Basin, California, 1998

[USGS, U.S. Geological Survey; SAR, Santa Ana River; MWD, Metropolitan Water District; Cr, Creek; mi², square miles; population density is in people per square mile]

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<th>Map No. (figs. 1,2,3)</th>
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The other four urban sites are on the Santa Ana River: two are located in the Inland Basin and two in the Coastal Basin. Santa Ana River at MWD Crossing (site 6) and the Santa Ana River at Hamner Road (site 5) are located between the confluences of Warm Creek and Chino Creek with the Santa Ana River near Riverside, California. Santa Ana River below Prado Dam (site 2) is an integrator of water quality in the Inland Basin. Santa Ana River at Imperial Highway (site 1) is the most downstream site and integrates urban runoff downstream of Prado Dam.

Four of the streambed sites were classified as nonurban on the basis of percentage undeveloped land use (more than 80 percent, fig. 2 and table 1). The land use upstream from these sites is mainly undeveloped forest. South Fork of the Santa Ana River (site 10) and Bear Creek near Bear Creek Campground (site 9) are tributaries to the Santa Ana River that originate in the San Bernardino Mountains. The Santa Ana River at the upper powerhouse (site 8) is located at the foot of the San Bernardino Mountains upstream from its entry to the valley floor. Bear Creek and the Santa Ana River at the upper powerhouse may show some effects of urbanization from the Big Bear Lake area. San Jacinto River near San Jacinto (site 12) is located at the foot of the San Jacinto Mountains. Fish tissue was not collected at this site.

**Description of Analytes**

The occurrence and distribution of three groups of hydrophobic compounds are assessed in the NAWQA Program: organochlorine compounds, semivolatile-organic compounds (SVOC), and trace elements. Organochlorine compounds are a group of polychlorinated hydrocarbons that are persistent environmental contaminants (Amur and others, 1991). All but one of the compounds analyzed belong to a class of pesticides known as organochlorines. Most organochlorine pesticides were banned for agricultural use in the 1970s (Nowell and others, 1999), but urban use of some organochlorines (for example, chlordane and dieldrin) was allowed into the 1980s. In this report, polychlorinated byphenyls (PCB) are included in the group of organochlorines as it is also a persistent polychlorinated hydrocarbon. PCBs were widely used as coolants and lubricants for transformers and appliances. Manufacturing of PCBs was stopped in 1977 (USEPA, accessed Oct. 3, 2001). Appendix 1 shows the organochlorine compounds analyzed, along with their laboratory reporting limits, 17 analyzed in reservoir cores, 32 analyzed in streambed sediment, and 33 analyzed in fish tissue.

SVOCs consist of a variety of classes of compounds. The three classes detected most often in the Santa Ana River Basin are polycyclic-aromatic hydrocarbons (PAH), phthalates, and phenols. PAHs are a ubiquitous class of organic compounds produced during the combustion of fossil fuels (Amur and others, 1991) and other hydrocarbon-rich materials. Sources include vehicle exhaust, burning coal, forest fires, tar, and asphalt roads and roofs. Eliminating PAHs from urban runoff is difficult because of their common and varied sources. They are an environmental concern because they are toxic to aquatic life, and are probable endocrine disruptors; several are suspected human carcinogens (Bjorseth and Ramdalh, 1985; Long and Morgan, 1990; Amur and others, 1991). Phthalates are aromatic esters widely used as solvents, plasticizers and insect repellants (Budavari and others, 1989). The larger molecular weight phthalates tend to be environmentally persistent and have become widespread contaminants (Manahan, 1992). Phenols are aromatic alcohols derived from coal tar; sources include vehicle exhaust and petroleum refining. They also have been used as disinfectants (Budavari and others, 1989; Peterson and Boughton, 2000). Phenols can be absorbed through the skin and damage most types of cells (Manahan, 1992). Many SVOCs occur together in the environment and their effects can be additive (Lopes and Furlong, 2001). Appendix 2 shows the 31 SVOCs analyzed in reservoir cores and the 77 SVOCs analyzed in streambed sediment, along with their laboratory reporting limits. SVOCs were not analyzed in fish tissue because they do not bioaccumulate in organisms.
Trace elements in the aquatic environment occur naturally from weathering of rocks and mineral soils and from human sources such as burning of fossil fuels, industrial discharges, automobile emissions, pesticides and fertilizers, and discharges from wastewater-treatment facilities (Long and others, 2000). Many trace elements, such as copper (Cu), selenium (Se), and zinc (Zn), are essential to animal and plant nutrition but can be toxic at high concentrations (U.S. Department of the Interior, 1998). Trace elements at naturally occurring concentrations generally are not harmful to aquatic life (Rheaume and others, 2000), but additional inputs from human activities often increase concentrations into the range of various sediment-quality criteria for the protection of aquatic life. The slow elimination rate of some trace elements from many aquatic organisms can lead to bioaccumulation and biomagnification in aquatic food chains (Maret and Skinner, 2000). Appendix 3 shows the 46 trace elements analyzed in reservoir cores, 39 analyzed in streambed sediment, and 22 analyzed in fish tissue, along with their laboratory reporting limits.

**METHODS OF SAMPLE COLLECTION, SAMPLE PROCESSING AND DATA ANALYSIS**

Sample Collection and Processing

Reservoir-sediment cores were collected using a Benthos gravity corer, a Benthos piston corer, and a Wildco box corer, according to methods previously employed by Van Metre and coworkers (Van Metre and Callender, 1996; Van Metre and others, 1996, 1997). Replicate cores were collected from each site: one of these was split lengthwise, examined visually, and described. The other cores were sliced into 1- to 2-cm segments and sent to the National Water Quality Laboratory (NWQL) to be analyzed for organochlorine compounds, SVOCs, trace elements and cesium-137.

Organochlorine compound concentrations were analyzed in organic solvent extracts using a dual-column capillary gas chromatograph with dual electron capture detectors (Wershaw and others, 1987). SVOCs were analyzed by the same method used for reservoir-core samples. Phenol and bis(2-ethylhexyl) phthalate were corrected for laboratory contamination by subtracting the 95th-percentile concentration in laboratory blanks (27 and 100 µg/kg, respectively) from the measured concentration in the environmental sample as recommended by Gilliom and others (1998). Most trace-element concentrations were determined in acid digestions by inductively coupled plasma with mass spectrometry. Mercury concentrations were determined by cold-vapor atomic adsorption. Selenium concentrations were determined by hydride-generation atomic absorption (Briggs and Mason, 1999).
Fish tissue was collected according to guidelines established by Crawford and Luoma (1994). A backpack electrofishing unit was used to collect fish. Common carp (*Cyprinus carpio*) and brown trout (*Salmo trutta*) were the target taxa. Yellow bullhead (*Ameiurus natalis*), largemouth bass (*Micropterus salmoides*), and rainbow trout (*Oncorhynchus mykiss*) were alternate taxa collected. Fish-tissue samples were frozen and sent to the NWQL for analysis. Composite samples of four to eight whole fish of the same species were analyzed with a custom method for organochlorine compounds in solvent extracts by gas chromatography with electron-capture negative-ion mass spectrometry (Thomas Leiker, U.S. Geological Survey, written commun., 1999). Fish liver from 5 to 20 fish were composited for trace element analysis. Whole fish were used at some sites because of the small size of the fish. Trace-element concentrations in fish tissue were analyzed in acid digestions by inductively coupled plasma mass spectrometry, inductively coupled plasma atomic emission spectroscopy, and cold-vapor atomic absorption (Hoffman, 1996).

**Data Analysis**

T-tests and Wilcoxon rank sum tests (significant at *p* < 0.05, unless otherwise noted) were used to compare groups of sites (urban sites versus nonurban sites, tributary sites versus Santa Ana River sites, wet periods versus dry periods, and reservoir to reservoir). Censored values (concentrations designated as less than values) were given the concentration of one-half of the long term-method detection level (usually one-quarter of the laboratory reporting limit). If more than 25 percent of the concentrations in a group of data were censored, then statistical tests were not performed. Sites for this study were designated as urban on the basis of percentage urban land use (usually more than 25 percent) or the proximity of urban influence on a site. Nonurban sites were mostly forested and undeveloped (more than 80 percent undeveloped). Relationships with the long-term rainfall record were evaluated by comparing concentrations of analytes during wet periods with concentrations during dry periods. A relationship was accepted as correlated if statistically significant (*p* < 0.05). Wet periods, as defined herein after, are periods when most of the years had greater than mean annual precipitation; dry periods are when most of the years had equal or less than mean annual precipitation (Burton and others, 1998).

Tributary sites in this study are those sites that are located in the basin and discharge to the Santa Ana River.

Linear regression was used to analyze trends over time in reservoir sediment-core data using estimated dates of deposition. Significance (*p* < 0.05) of trends was determined by t-tests and F-tests. Estimated dates of deposition were determined by the concentration profile of cesium-137 (a radioactive byproduct of nuclear weapons testing with a half-life of about 30 years), peaks in lead and DDT, and core lithology—an approach similar to that used by Van Metre and others (1997). Estimated dates of deposition were assigned to samples from the urban West Street Basin and the urbanizing Canyon Lake. Estimated dates could not be assigned to samples from the nonurban Hemet Lake because peaks were not detected for cesium-137, lead, or DDT; therefore, the presence or absence of trends was determined using the midpoint depth of the sample segment.
Concentrations of the three classes of compounds (organochlorine compounds, SVOCs, and trace elements) at urban and nonurban sites were compared with concentrations at other sites sampled in the nation, and with various criteria guidelines. NAWQA medians for urban sites used for comparison were derived from streambed sediment and fish tissue samples collected by NAWQA study units initiated in 1991 and 1994 (Lisa Nowell, U.S. Geological Survey, written commun., 2001). Concentrations of the three classes of compounds in reservoir and streambed sediment are compared with “consensus-based” sediment quality guidelines (SQG) devised by MacDonald and others (2000). Two SQGs—probable effect concentration (PEC) and threshold effect concentration (TEC)—were developed for 10 organochlorines, 10 SVOCs and total PAH, and 8 trace elements. Most PEC and TEC values provide an accurate basis for predicting sediment toxicity or the absence of sediment toxicity, respectively, to sediment-dwelling organisms (MacDonald and others, 2000). PEC is the concentration above which adverse effects are expected to occur more often than not; TEC is the concentration below which adverse effects are not expected. Because streambed-sediment samples analyzed for trace elements in this study are from sediments finer than 0.063 mm where concentrations tend to be greatest, comparisons with the “consensus-based” sediment quality guidelines may overestimate the effects on aquatic organisms, especially if the amount of fine material is less than 60 percent of the bulk sample. The amount of fine material for each streambed sediment sample is included in appendix 11 at the back end of this report. Trace-element concentrations also may be overestimated because of the strong acid digestion used for the analysis samples.

Concentrations of organochlorines in fish tissue are compared with criteria for the protection of fish-eating wildlife for the State of New York (Newell and others, 1987), and with the recommended tissue concentrations set by the National Academy of Sciences (NAS) and National Academy of Engineering (NAE) (1973). The criteria of the State of New York are for noncancerous effects. The NAS/NAE guidelines were established to protect organisms from accumulating high concentrations of potentially toxic compounds from direct exposure, as well as from consumption of contaminated prey (Rasmussen, 1993). In some cases, guidelines were based on total DDT, total chlordane, and total PCB. Total DDT is the sum of o,p’- and p,p’-DDD, o,p’- and p,p’-DDE, and o,p’- and p,p’-DDT. Total chlordane is the sum of cis- and trans-nonachlor, cis- and trans-chlordane and oxychlordane. Total PCB is the sum of all PCB cogeners.

Concentrations of trace elements in fish tissue are compared with toxicity information compiled by the National Irrigation Water Quality Program (U.S. Department of the Interior, 1998) for toxic effects observed in aquatic organisms.

Concentrations of organochlorines and trace elements in fish tissue also are compared with concentrations from two other studies in the Santa Ana River Basin. California’s Toxic Substance Monitoring Program has collected fish tissue data at or near six of the urban sites from 1976 to the 1990s (Rasmussen, 1997). In addition, a Use-Attainability Analysis study, carried out in 1991 (Chadwick and Associates, 1992), collected fish-tissue data at or near five of the urban sites. Because the Toxic Substance Monitoring Program and the Use-Attainability Analysis studies presented trace-element concentrations in wet weight, concentrations from this study were adjusted to approximate wet weights by multiplying the dry weight concentration by the percentage dry weight of the sample. Direct comparison of the data was also complicated by the collection of different fish species as well as different tissue (fillets, liver, and whole body).
EFFECTS OF URBANIZATION AND LONG-TERM RAINFALL ON OCCURRENCE AND TRENDS

Organochlorine Compounds

Reservoir Sediment Cores

Organochlorines in sediment cores collected from three reservoirs were used to compare historical trends with current conditions. Of the 17 organochlorines analyzed in the cores, the number detected above laboratory reporting limits ranged from eight in the West Street Basin, the most urbanized site, to three in the Hemet Lake, the reference site. Also, organochlorine concentrations were highest in West Street Basin and lowest in Hemet Lake. Concentrations of most of the organochlorines detected generally decrease from the late 1960s to the 1990s at West Street Basin and Canyon Lake (fig. 4, and app. 4). Concentrations of the organochlorines detected at Hemet Lake generally decrease from the oldest sediment to the most recent sediment (app. 4).

Concentrations and trends of selected organochlorine compounds found in reservoir cores from the two urban sites (West Street Basin and Canyon Lake) are compared with data and trends reported in studies from other urban reservoirs sampled nationwide. These studies include reservoirs from the southeastern United States, Iowa, New Mexico, and California (Ging and others, 1999; Majewski, 2001; Van Metre and others, 1996, 1997; Van Metre and Mahler, 1999).

West Street Basin. Total chlordane, total PCBs and DDT and its metabolites were detected in samples from the urban West Street Basin from the oldest sediment (about 1952) to the youngest sediment (1998). Heptachlor epoxide was detected in older sediments (1950s to early 1980s). Dieldrin and methoxychlor were detected mainly in the late 1980s to 1998 (app. 4).

Throughout the historical record, total chlordane concentrations peaked in the late 1960s and then declined: the decline coincides with the banning of chlordane for agricultural use (USEPA, accessed Oct. 3, 2001). Urban use of chlordanes for termite control, however, continued until at least 1990 (Whitmore and others, 1992). This could explain the continued high concentrations found through 1998 in this stormwater-retention basin. Two other peaks in chlordane concentration occurred: a large one in the early 1980s and a smaller one in the mid 1990s (fig. 4). These peaks correspond to periods of above average rainfall (Burton and others, 1998), which may have mobilized sediment that had several years to accumulate chlordane residues. Despite these peaks and unlike the increasing trend observed in two urban lakes in Texas (Ging and others, 1999; Van Metre and others, 1997), a decreasing trend in total chlordane concentrations is observed (table 2). This decreasing trend may be a reflection of the fully urbanized state of the drainage area, as well as the discontinued use of chlordane.

PCB concentrations exceed the TEC (59.8 µg/kg) but not the PEC (676 µg/kg) throughout the historical record; however, PCB concentration has declined through time and the most recent sample was below the TEC (fig. 4). Concentrations are higher than concentrations found in other urban reservoirs. The highest peak occurred about 1967 followed by a sharp decline. This coincides with the discontinued use of PCBs (USEPA, accessed Oct. 3, 2001). Two other peaks in PCBs, similar to the peaks in chlordane concentrations, were observed. These peaks also corresponded to periods of above average rainfall (fig. 4) (Burton and others, 1998).

Throughout the historical record, total DDT concentrations exceeded the TEC (5.28 µg/kg) but not the PEC (572 µg/kg) (fig. 4). In a manner similar to chlordane and PCBs, total DDT concentrations decreased after organochlorines were banned in the U.S. in the early 1970s (USEPA, accessed Oct. 3, 2001). The total DDT concentrations exceeded those found in most other urban reservoirs sampled nationwide, except Town Lake in Austin, Texas, which had a peak in 1961 due to a spill; Town Lake has a total DDT concentration similar to West Street Basin. Two additional peaks in West Street Basin correlate (p < 0.1) to periods of above average rainfall (table 2) (Burton and others, 1998).
Figure 4. Graphs showing selected organochlorine-compound concentrations in reservoir sediment cores from Canyon Lake, Riverside County, and West Street Basin, Orange County, California, 1998. (Open symbol (o) denotes value is less than laboratory reporting limit; sediment-quality guidelines from McDonald and others, 2000.)
Table 2. Correlation of selected organochlorine compounds in reservoir sediment cores with rainfall and time or decreasing depth, in the Santa Ana River Basin, California

[significant at $p < 0.05$; nd, not enough detections to determine correlation with rainfall or trend; ---, no data]

<table>
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<tr>
<th>Constituent</th>
<th>Correlation with rainfall</th>
<th>Trend with time or decreasing depth</th>
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<tr>
<td></td>
<td>West Street Basin&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Canyon Lake</td>
</tr>
<tr>
<td></td>
<td>$p$-value</td>
<td>Direction of trend; $p$-value; $R^2$-value</td>
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<td>Dieldrin</td>
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<td>nd</td>
</tr>
<tr>
<td>Methoxychlor</td>
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<td>nd</td>
</tr>
<tr>
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</tr>
<tr>
<td>$p,p'$-DDT</td>
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<td>.134</td>
</tr>
<tr>
<td>Total DDT</td>
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<td>.860</td>
</tr>
<tr>
<td>PCB</td>
<td>.438</td>
<td>.340</td>
</tr>
</tbody>
</table>

<sup>1</sup>Correlation with rainfall based on data with the estimated date of deposition 1965–98.
Dieldrin concentrations exceed the TEC (1.90 µg/kg) periodically throughout the historical record (fig. 4). Concentrations are below the TEC from the 1950s through the 1970s except for peaks that correlate ($p < 0.1$) to periods of above average rainfall. However, an increasing trend is observed through the 1980s and 1990s. This trend continued even after dieldrin was banned for all uses in 1987, which suggests the possibility of continued use.

Methoxychlor concentrations are below laboratory reporting limit for the early part of the historical record but increased in the late 1980s (fig. 4). Methoxychlor is used as a substitute for DDT (Manahan, 1992), and the increase in concentration may be due to the banning of DDT. Methoxychlor is used for home and garden applications more than for agricultural crops (Nowell and others, 1999), and this may be the case at West Street Basin as the reported use of methoxychlor in the county is very low (California EPA, accessed Oct. 16, 2001).

Canyon Lake. DDT or its metabolites were detected in samples from the recently urbanized Canyon Lake Basin from the oldest sediment (about 1950) to the youngest sediment (1998) (fig. 4 and app. 4). Chlordane and PCBs were detected in most of the samples. Dieldrin was detected in a few samples from the late 1980s to 1990s.

Total DDT concentrations exceed the TEC throughout the historical record, except around the late 1980s (fig. 4). In a manner similar to West Street Basin and other urban reservoirs sampled nationwide, total DDT concentrations peaked in the 1960s and decreased after this organochlorine was banned in the 1970s. Concentrations are usually lower than in West Street Basin and are similar to those of urban reservoirs sampled in Texas (Ging and others, 1999; Van Metre and others, 1997) but higher than in other urban reservoirs sampled nationwide.

Chlordane detections are above the TEC (3.24 µg/kg), but below the PEC (17.6 µg/kg) throughout the historical record. Concentrations at Canyon Lake are much lower than at West Street Basin, as well as in other urban reservoirs sampled nationwide. Unlike concentrations in other urban reservoirs, chlordane concentrations did not peak in the 1960s. However, there were peaks in the concentration that correlate ($p < 0.1$) to periods of above average rainfall (table 2, and fig. 4).

Throughout the historical record, PCB concentration was below the TEC. Concentrations were much lower than in the West Street Basin, as well as other urban reservoirs nationwide. The peaks in PCB concentrations correspond to periods of above average rainfall similar to that found in West Street Basin but at much lower concentrations.

Hemet Lake. In the oldest sediment in nonurban Hemet Lake, sample depth 32 to 35 cm, total chlordane, $p,p'$-DDE, and $p,p'$-DDT were detected close to their laboratory reporting limits (app. 1 and 4). In the youngest sediment, sample depth 0 to 2 cm, only $p,p'$-DDE was detected at a concentration just above the laboratory reporting limit (app. 1 and 4). These results indicate that concentrations of $p,p'$-DDE have significantly decreased with time (table 2). Because Hemet Lake is minimally impacted by urban or agricultural use, the most likely source of the organochlorines is atmospheric deposition (Larson and others, 1997).

Streambed Sediment

Of the 32 organochlorine compounds analyzed for, 12 were detected in streambed sediment above laboratory reporting limits. The most frequently detected were total chlordane, DDT, and DDT metabolites (app. 5). More organochlorines were detected in streambed sediment at the eight urban sites than at the four nonurban sites (figs. 5A and 6); 12 different compounds were detected at the urban sites with an average of 4 compounds per site, whereas, 3 were detected at the nonurban sites with an average of 1 compound per site (fig. 6). The higher frequency of detections at urban sites is also observed nationwide (Wong and others, 2000).

Of the most frequently detected compounds, only total chlordane and $p,p'$-DDE had statistically-significant higher concentrations ($p < 0.05$) at urban sites than at nonurban sites (fig. 7A). Other organochlorines, however, follow this pattern; the lack of statistical significance probably arises because of the relatively large variance in the sample set and small sample size.
Figure 5. Graphs showing number of organic compounds detected at each site, Santa Ana River Basin, California, 1998: (A) organochlorine compounds in streambed sediment and fish tissue and (B) semivolatile-organic compounds in streambed sediment.
At the urban sites, there were more detections of organochlorine compounds in the Santa Ana River than in its tributaries (fig. 5A). Also, most of the compounds detected in the tributaries were detected in samples from at least one Santa Ana River site (app. 5). Within the Santa Ana River, the concentration of some compounds increased at downstream sites; whereas, for others, concentrations decreased (fig. 8). These observations suggest that the compounds with increasing concentrations may have additional sources along the Santa Ana River such as tributaries or storm drains not sampled in this study. Presumably, sediment from the tributaries is transported from the tributary drainage and deposited in the Santa Ana River. For compounds with decreasing concentrations, these observations suggest the compounds originate from tributaries and are diluted in the Santa Ana River.

The median concentrations of $p,p'$-DDE, $p,p'$-DDT, and total DDT from the Santa Ana River urban sites in the Santa Ana River Basin tend to be higher than the median from other NAWQA urban sites, although the difference is not statistically significant (fig. 7A); other organochlorines detected were about the same as or below NAWQA urban medians.

Concentrations of the compounds detected were more than an order of magnitude below their respective PEC; however, some organochlorines detected at urban sites were above the TEC (fig. 7A). Total DDT and $p,p'$-DDE at six of the eight urban sites had concentrations greater than their respective TECs. Two urban sites had $p,p'$-DDT concentrations greater than its TEC. One urban site had the total chlordane concentration greater than its TEC. Another site had PCB concentrations equivalent to the TEC. Most of these sites were located on the Santa Ana River or on Warm Creek (app. 5).
Figure 7. Graphs showing Selected organochlorine concentrations, criteria standards, and NAWQA medians in (A) streambed sediment and (B) fish tissue in the Santa Ana River Basin, California, 1998. (LRL is laboratory reporting limit; sediment quality guidelines from McDonald and others, 2000; NAS/NAE, criteria for the protection of fish-eating wildlife from National Academy of Science/National Academy of Engineering, 1973; NYSDEC criteria for the protection of fish-eating wildlife from New York State Department of Environmental Conservation (Newell and others, 1987).)
Figure 8. Diagram showing Distribution of organochlorine compounds in streambed sediment between urban tributary sites and Santa Ana River sites, California, 1998. Numbers in parentheses are concentrations in microgram per kilogram.
Fish Tissue

Of the 33 organochlorine compounds analyzed, 9 were detected in fish tissue above laboratory reporting limits. The most frequently detected were \( p,p' \)-DDE, PCBs, and total chlordane (app. 5). Nine different compounds were detected in fish tissue at urban sites with an average of almost four compounds per site (fig. 6); two were detected at the nonurban sites, with an average of about one per site. The higher frequency of detections at urban sites is also observed nationwide (Wong and others, 2000). Concentration of \( p,p' \)-DDE at urban sites was significantly higher \((p < 0.05)\) than at nonurban sites (fig. 7B). Other organochlorine compounds that were detected tended to have higher concentrations at urban sites than at nonurban sites; however, tests of significance could not be performed because of the high number of censored values.

More organochlorines were detected in fish tissue at the four urban sites on the Santa Ana River than at either the urban tributary sites or the nonurban sites (fig. 5A). The concentrations also were usually higher in the Santa Ana River than in its tributaries (app. 5). This observation is in agreement with observations in streambed sediment. This suggests that sources for some of the compounds may be along the Santa Ana River or in other unsampled tributaries or storm drains feeding into the Santa Ana River.

Only the median concentration for \( p,p' \)-DDE at urban sites in the Santa Ana River Basin is above the median for NAWQA urban sites. The medians for all other organochlorines are at or below the NAWQA urban medians (fig. 7B).

Concentrations of the detected organochlorines were below the guidelines set by the State of New York (Newell and others, 1987) and the NAS/NAE (1973) for the protection of fish-eating wildlife for both urban and nonurban sites (fig. 7B).

PCB and \( p,p' \)-DDE were the most commonly detected contaminants in this study, similar to the California Toxic Substance Monitoring Program (Rasmussen, 1993, 1995, 1997; Rasmussen and Blethrow, 1990) and the Use-Attainability Analysis study (Chadwick and Associates, 1992). Based on these studies, concentrations seem to fluctuate over time, but overall, concentrations of organochlorines in fish tissue seem to decrease in the Santa Ana River Basin. Differences in concentrations of organochlorines observed in this study from concentrations observed in the Toxic Substance Monitoring Program and Use-Attainability Analysis study probably result from differences in fish species, the tissue type analyzed, or natural variability.

Semivolatile-Organic Compounds

Reservoir Sediment Cores

Sediment cores also were used to determine historical trends in SVOC concentrations and to compare trends with current conditions. The cores provide a historical record of almost 50 years. Of the 31 SVOCs analyzed in reservoir cores, 29 were PAHs and 2 were phenols (app. 6).

Concentrations and trends of the selected SVOCs found in reservoir cores from the two urban sites (West Street Basin and Canyon Lake) were compared with data and trends reported in studies from other urban reservoirs sampled nationwide. These studies include reservoirs from Texas, California, Virginia, New York, Minnesota, and Washington (Ging and others, 1999; Majewski, 2001; Van Metre and Callender, 1999; Van Metre and Mahler, 1999; Van Metre and others, 2000).

West Street Basin. All 31 SVOCs were detected throughout the historical record. For 9 of the 10 PAHs and total PAH with sediment quality guidelines, the PEC was exceeded at least once during the historical record; the one exception is naphthalene (fig. 9 and app. 6). Chrysene, pyrene, and total PAH were detected above their PECs throughout the historical record, except for the most recently deposited sediment. The TEC was exceeded throughout the historical record for almost all PAHs except for naphthalene (fig. 9 and app. 6).

The total PAH concentration (21,000 µg/kg) observed at the top of the core (most recent sediment) at the West Street Basin (app. 6) is within the range of values observed in reservoir cores nationwide (2,790 to 224,000 µg/kg). Recent sediment in 7 of the 12 urban reservoirs and lakes sampled nationwide had values greater than that observed at West Street Basin; 5 had lower values. However, the peak concentration of total PAH (125,000 µg/kg) is greater in West Street Basin than in all but one site sampled nationwide. The one urban site where the peak concentration (224,000 µg/kg) is higher than West Street Basin is a stormwater-retention basin in Long Island, New York.
Figure 9. Graphs showing selected polycyclic-aromatic-hydrocarbon concentrations in reservoir sediment cores from Canyon Lake, Riverside County, and West Street Basin, Orange County, California, 1998. (Open symbol (o) denotes value is less than laboratory reporting limit; sediment-quality guidelines from McDonald and others, 2000.)
Since 1965, the concentration of the SVOCs shows some relationship with the long-term rainfall record (fig. 9). The concentrations are typically higher during wet periods and lower during dry periods. Prior to 1965, the concentrations do not correlate with rainfall. The period of correlation corresponds to a period when the basin was almost completely urbanized and there was little disturbance of soils as a result of construction. The period of no correlation corresponds to the period of widespread urbanization.

Prior to 1965, the concentrations do not correlate with rainfall. The period of correlation corresponds to a period when the basin was almost completely urbanized and there was little disturbance of soils as a result of construction. The period of no correlation corresponds to the period of widespread urbanization.

The high concentrations observed around 1960 may correlate with the onset of urbanization and hence, increased mobilization of sediment. Housing construction near the West Street Basin was largely from 1955 to 1958, with a lesser number of houses built in 1962. The cores were dated in 2-cm sections that cover a short range of years. The estimated dates of deposition for core samples at 30 to 32 cm and 34 to 36 cm are about 1964 and 1956, respectively (app. 6). Therefore, the “peak core” at about 1960 would represent 1960 ± 4 year, which would include the effects of construction from both 1955–58 and 1962.

Linear regression shows that there is a decreasing trend in concentrations from older to younger sediment for 28 of the 29 PAHs (table 3). Coronene shows no trend. This decrease with respect to time contrasts with the increasing trends observed in the nationwide sampling at other urban sites for PAHs. The decreasing trends in PAHs could be attributed to lack of further urbanization in this basin, cleaner car exhaust, and air pollution regulations. Linear regression for the two phenols, phenol and p-cresol, showed no significant trend over time, although concentrations appear to be increasing (table 3 and app 6).

Canyon Lake. Nineteen of the 31 SVOCs analyzed were detected at least once during the historical record; 12 were detected at least half of the time; and 7 were detected at least two-thirds of the time (app. 6). Perylene, 2,6-dimethylnaphthalene, and pyrene were detected most frequently. Unlike West Street Basin, neither the PEC nor the TEC in Canyon Lake were exceeded at anytime for any PAH that has sediment quality guidelines (fig. 9 and app. 6). Concentrations of PAHs in Canyon Lake in the most recent sediment are lower than concentrations found in other urban sites sampled nationally.

The concentrations of 7 of the 12 SVOCs detected at least half of the time throughout the historical record at Canyon Lake show a significant correlation with long-term rainfall (table 3). The concentrations are higher during wet periods and lower during dry periods. The other five SVOCs (detected at least half of the time) showed a similar trend, although it is not statistically significant. The data from West Street Basin and Canyon Lake suggest that there is a correlation with rainfall if the drainage basin is not urbanized and when the basin is fully urbanized; however, the relation is affected by landscape changes such as extensive construction.

Linear regression shows a decreasing trend in concentrations from older to younger sediment for PAHs in Canyon Lake, unlike that observed for West Street Basin (table 3). This increasing trend is in agreement with other urban sites nationwide. The increase in PAHs at Canyon Lake probably is due to urbanization as well as other anthropogenic effects, such as increased automobile use (Van Metre and others, 2000). The increase did not occur at the West Street Basin, which has been fully urbanized since about 1965. Phenol showed a decreasing trend with time, and p-cresol did not have a trend although there was a high peak in the late 1990s whose cause is not known at this time (app. 6).

Hemet Lake. Of the 31 SVOCs analyzed, 10 were detected at least once during the historical record; 4 PAHs and 2 phenols were detected throughout most if not all of the record (app. 6). Perylene, 2,6-dimethylnaphthalene, p-cresol, and phenol were most frequently detected. TECs were not exceeded at any time. Although the number of compounds detected in Hemet Lake was fewer than that detected in Canyon Lake, the peak total PAH concentration in Hemet Lake (741 µg/kg) was similar to that in Canyon Lake (758 µg/kg).
Table 3. Correlation of selected semivolatile-organic compounds in reservoir sediment cores with rainfall and time or decreasing depth, in the Santa Ana River Basin, California

[PAH, polycyclic-aromatic hydrocarbon; significant at $p < 0.05$; nd, not enough detections to determine correlation with rainfall or trend;—, no data]

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<th>Constituent</th>
<th>Correlation with rainfall</th>
<th>Trend with time or decreasing depth</th>
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<td></td>
<td>West Street Basin</td>
<td>Canyon Lake</td>
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<tr>
<td></td>
<td>p-value</td>
<td>Direction of trend; p-value; $R^2$-value</td>
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<td>Pyrene</td>
<td>.020</td>
<td>Decreasing; 0.015; 0.462</td>
</tr>
<tr>
<td>Total PAH</td>
<td>.092</td>
<td>Decreasing; 0.025; 0.410</td>
</tr>
</tbody>
</table>

*Correlation with rainfall based on data with the estimated date of deposition 1965–98.
The concentration of PAHs at Hemet Lake can be compared to only one site sampled nationally, Dillon Reservoir, a mountain site in Colorado. Concentrations of PAHs in Hemet Lake are equivalent or lower than PAH concentrations found in Dillon Reservoir (Greve and others, 2001). This is probably a result of the heavy automobile traffic near Dillon Reservoir, which is immediately adjacent to an interstate highway and has four ski areas within its watershed, and the lack of development near Hemet Lake.

Linear regression shows that the trend of PAH concentrations are decreasing from deeper (older) to shallow (younger) sediment (table 3, and app.6); however, the trends for p-cresol and 2,6-dimethylnaphthalene are increasing. The reasons for these divergent trends are unknown.

Streambed Sediment

Of the 77 SVOCs analyzed in streambed sediment, 20 were detected above the laboratory reporting limit; most of the detections were PAHs. More SVOCs were detected at the eight urban sites than at the four nonurban sites (figs. 5B and 6); 20 different compounds were detected at urban sites with an average of 8 compounds per site (fig. 6) whereas 3 were detected in nonurban sites with an average of 1 per site. Of the detected compounds, p-cresol was the only compound that did not have a statistically-significant higher concentration at urban sites. Four SVOCs were detected more than half of the time at urban sites; p-cresol, bis-(2-ethylhexy)phthalate, 2,6-dimethyl phthalate, and anthraquinone. The three compounds detected at nonurban sites were phenols and phthalates.

Most of the SVOCs detected at urban sites were located on tributaries to the Santa Ana River (fig. 5B). The concentrations of most SVOCs were also statistically higher ($p < 0.05$) at tributary sites. At the three tributary sites that had the highest frequency of detections, the land use was over 50-percent urban; the frequency at all other sites was less than 50-percent urban. Two of the tributary sites, Chino Creek and Warm Creek, that had a high frequency of detections have a major freeway nearby. These sites also had the highest population density within their drainage areas (fig. 3 and table 1).

The four Santa Ana River sites are downstream from the tributary sites; therefore, the decrease in concentration may result from volatization of the compounds, degradation, dilution, or a combination of these. SVOCs not detected at the downstream sites may be present but at concentrations below detection limits.

Median concentrations for all PAHs are at or below NAWQA medians for urban sites except for 2,6-dimethylnaphthalene. Medians for phenol, p-cresol, and two phthalates are also above the NAWQA median (fig. 10).

For the 10 PAHs that have sediment quality guidelines, the concentration in streambed sediment was at least an order of magnitude lower than their PEC. However, 7 of the 10 PAHs had detections above the TEC (fig. 10, and app. 7); all of these exceedences were on Warm Creek and Chino Creek, the two sites that have the highest urban land use and population density (table 1).

Trace Elements

Reservoir Sediment Cores

Sediment cores also were used to determine historical trends in trace-element concentrations and for comparison with current conditions. The cores provide a historical record of almost 50 years. Of the 46 trace elements analyzed, 13 are on the EPA list of 126 priority toxic pollutants (USEPA, 1994). Eight of the 13 [arsenic (As), cadmium (Cd), Cr, Cu, Pb, Hg, nickel (Ni), and zinc (Zn)] have sediment quality guidelines for the preservation of aquatic life derived by MacDonald and others (2000); guidelines for selenium have been derived by Van Derveer and Canton (1997).

Concentrations and trends of the nine selected trace elements found in reservoir cores from the two urban sites (West Street Basin and Canyon Lake) are compared with data and trends reported in studies from other urban reservoirs sampled nationwide. These studies include reservoirs from the southeastern United States (Callender and Van Metre, 1997; Callender and Rice, 2000), Utah (Naftz and others, 2000,) and Texas (Van Metre and others, 1997; Ging and others, 1999; and Van Metre and Mahler, 1999).
Figure 10. Graph showing Selected semivolatile-organic compounds in streambed sediment at urban sites, Santa Ana River Basin, California, 1998. (Sediment-quality guidelines from McDonald and others, 2000.) NAWQA, National Water-Quality Assessment.
West Street Basin. All 46 trace elements were detected at least once. All but silver were detected throughout the historical record (app. 8). For seven of the nine trace elements that have sediment quality guidelines, the PEC was exceeded at least once during the historical record, usually during the early part of the record; arsenic and mercury did not exceed their respective PEC (fig. 11). The TEC was exceeded throughout the historical record for lead and zinc. The TEC was exceeded throughout the historical record for seven of the nine trace elements; arsenic and selenium were the exceptions (fig. 11).

For five of the nine selected trace elements (Cr, Cu, Pb, Ni and Zn), higher concentrations were at the top of the core (most recent sediment) at West Street Basin than in the nationwide sampling. In contrast, arsenic and mercury concentrations were at or lower than at nationwide sites. The two remaining trace elements (Se and Cd) did not have nationwide concentrations available for comparison.

Since 1965, the concentration of arsenic showed significant correlation with the rainfall record (table 4). The other trace elements show some relationship with rainfall (fig. 11), but these are not statistically significant. The lack of significance may be due to the impervious area preventing access to natural sources of trace elements in the drainage area. The concentrations are typically higher during wet periods and lower during dry periods. The correlation with rainfall is similar to that observed for the SVOCs in West Street Basin.

Linear regression shows that there is a decreasing trend in the nine selected trace-element concentrations from older to younger sediment (table 4). The decreasing trend for lead agrees with trends observed in nine urban reservoirs sampled nationwide. The decreasing trend for zinc is in contrast to increasing or no trends observed at six reservoirs sampled nationwide. The decreasing trends for five of the nine trace elements (As, Cr, Cu, Hg, and Ni) agree with one reservoir in Texas (Van Metre and others, 1997), but the decreasing trends for arsenic and mercury are in contrast to another reservoir in Texas (Ging and others, 1999). Selenium and cadmium had no reported trends for comparison.

Canyon Lake. Of the 46 trace elements analyzed, all were detected throughout the historical record except silver (app. 9). For the nine trace elements with sediment quality guidelines, the PEC was not exceeded. However, seven of the trace elements exceeded the TEC at least once during the historical record (fig. 11); four of these (Cr, Cu, Ni, and Zn) exceeded the TEC throughout the historical record; and three (As, Pb, and Se) intermittently exceeded the TEC.

The four trace elements that exceed the TEC (Cr, Cu, Ni, and Zn) had higher concentrations in the most recently deposited sediment at Canyon Lake than was found in the nationwide sampling. Arsenic and mercury had concentrations that are about the same as concentrations found in reservoir cores from urban sites nationwide. Only lead was lower than most nationwide urban sites. Concentrations of most trace elements were lower at Canyon Lake than at West Street Basin (fig. 11); arsenic, copper, and selenium were generally higher in the more recently deposited sediment.

Of the selected trace elements, six (As, Cd, Cu, Pb, Se, and Zn) had concentrations significantly correlated with rainfall (table 4 and fig. 11). The concentrations are typically higher during wet periods and lower during dry periods. The correlation with rainfall was stronger for Canyon Lake than for West Street Basin—possibly because the drainage area for Canyon Lake is larger.

Linear regression shows an increasing trend for three trace-element (As, Cu, and Zn) concentrations from older to younger sediment (table 4). This agrees with the trends in two reservoirs in Texas (Van Metre and others, 1997; Ging and others, 1999). The six other trace elements (Cd, Cr, Pb, Hg, Ni, and Se) showed no trend. The lack of trend for lead is in contrast with decreasing trends found in nine reservoirs sampled nationwide.

Hemet Lake. All 46 trace elements were detected at least once. All but silver were detected throughout the historical record (app. 10). For five of the nine trace elements that have sediment-quality guidelines (As, Cu, Cr, Ni, and Zn), the TEC was exceeded at least once during the historical record; copper, nickel and zinc exceeded the TEC throughout the core.
Figure 11. Graphs showing Selected trace-element concentrations in reservoir sediment cores from Canyon Lake, Riverside County, and West Street Basin, Orange County, California, 1998. (Sediment-quality guidelines from McDonald and others, 2000.)
Table 4. Correlation of selected trace elements in reservoir sediment cores with rainfall and time or decreasing depth, in the Santa Ana River Basin, California

[Significant at \( p < 0.05; —, \) no data]

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Correlation with rainfall</th>
<th>TREND WITH TIME OR DECREASING DEPTH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>West Street Basin</td>
<td>Canyon Lake</td>
</tr>
<tr>
<td></td>
<td>( p )-value</td>
<td>Direction of trend; ( p )-value; ( R^2 )-value</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.014</td>
<td>0.003</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.732</td>
<td>0.034</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.751</td>
<td>0.613</td>
</tr>
<tr>
<td>Copper</td>
<td>0.536</td>
<td>0.004</td>
</tr>
<tr>
<td>Lead</td>
<td>0.764</td>
<td>0.145</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.567</td>
<td>0.442</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.616</td>
<td>0.709</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.168</td>
<td>0.069</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.450</td>
<td>0.045</td>
</tr>
</tbody>
</table>

*Correlation with rainfall based on data with the estimated date of deposition 1965–98.
The concentrations of trace elements in the most recently deposited sediment at Hemet Lake were at or lower than concentrations at the two comparable reservoirs sampled as part of the nationwide studies: Lake Sidney Lanier, a rural lake in Georgia; and Dillon Reservoir, a mountain reservoir in Colorado (Callender and Rice, 2000; Greve and others, 2001). Concentrations of seven of the nine trace elements are statistically lower \((p < 0.05)\) at Hemet Lake than at Canyon Lake. Mercury concentrations are statistically higher at Hemet Lake than at Canyon Lake; arsenic concentrations are similar to those at Canyon Lake.

Linear regression shows a decreasing trend in lead and nickel from older to younger sediment. The decrease in lead concentrations agrees with trends in other reservoirs nationwide and probably reflects the decreased use of leaded gasoline. Arsenic, copper, mercury, and selenium have increasing trends. The increase in arsenic and copper concentrations with time is also observed at Canyon Lake but not at Dillon Reservoir. The remaining three trace elements (Cd, Cr, and Zn) showed no significant trends (table 4).

**Streambed Sediment**

Of the 39 trace elements analyzed for in streambed sediment, 36 were detected above the laboratory reporting limit. Of the 36 trace elements detected, 30 were detected at all 12 sites (app. 11). Of the 36 trace elements detected, 12 are on the EPA list of 126 priority pollutants (USEPA, 1994); nine of these have SQGs (McDonald and others, 2000; Van Derveer and Canton, 1997).

Of the nine trace elements that have SQGs, eight (As, Cd, Cr, Cu, Pb, Hg, Ni, and Zn) had concentrations that were significantly higher \((p < 0.05)\) at urban sites than at nonurban sites; selenium was the exception (fig. 12A).

At urban sites, the concentration of chromium was significantly higher \((p < 0.05)\) in the Santa Ana River sites than in the tributary sites; however, the remaining trace elements showed no difference in concentration between tributary sites and the Santa Ana River. This lack of difference is in contrast with organochlorine compounds and SVOCs and may be attributed to the fact that trace elements occur naturally.

The median concentrations of the selected trace elements from the urban sites in the Santa Ana River Basin are at or lower than the medians from other NAWQA urban sites nationwide (fig. 12A).

The PEC for arsenic was exceeded at San Jacinto River near Elsinore, an urban site in the San Jacinto Basin; and the PEC for zinc was exceeded at Chino and Warm Creek, two urban sites in the Inland Basin (app. 11). The TEC for all nine trace elements (fig. 12A) was exceeded at least once at urban sites. The TEC for chromium and zinc was exceeded at all eight urban sites; the TEC for copper and nickel was exceeded at more than half of the urban sites. Four trace elements (Cr, Cu, Ni, and Zn) exceeded the TEC at least once at nonurban sites.

**Fish Tissue**

Of the 22 trace elements analyzed in fish tissue, all but antimony and beryllium were detected above laboratory reporting limits (apps. 3 and 11). Of the 20 trace elements detected, 10 are on the EPA list of 126 priority pollutants; 4 of the 10 (Cu, Hg, Se, and Zn) were detected at all sites sampled. Copper, selenium, and zinc are essential nutrients for aquatic life (U.S. Department of the Interior, 1998).

For the 10 detected trace elements that are on the EPA list, 4 \([\text{Hg, Se, Ag (} p < 0.05\text{), and As (} p < 0.1\text{)}\)] were detected at statistically-significant higher concentrations at nonurban sites than at urban sites (fig. 12B and app. 11). This is in contrast with streambed sediment. Copper concentrations were also very high at two of the nonurban sites, Bear Creek and Santa Ana River at the upper powerhouse, compared with the other nonurban and urban sites in this study. Mercury and copper concentrations exceeded water-quality criteria in Big Bear Lake and in some of its tributaries upstream from the sites that had high copper concentrations in fish tissue (California Regional Water Quality Control Board, 1995). The water high in copper from Big Bear Lake may have flowed downstream and bioaccumulated in fish at the two downstream sites.
Figure 12. Graph showing selected trace-element concentrations and sediment-quality guidelines in (A) streambed sediment and (B) fish tissue in the Santa Ana River Basin, California, 1998. (LRL, laboratory reporting limit; NAWQA, National Water-Quality Assessment) (Sediment quality guidelines from McDonald and others, 2000; selenium guidelines from Van Derveer and Canton, 2001.)
In general, trace-element concentrations in fish-liver tissue from urban sites on tributaries were not significantly different from concentrations in fish-liver tissue from urban sites on the Santa Ana River. The same trend was observed in streambed sediment. Copper, selenium, and zinc concentrations in samples from Chino Creek and Mill Creek were higher than in samples from other tributaries; and also were higher than at sites on the Santa Ana River upstream from the confluence of Chino and Mill Creeks (app. 11). However, this difference may owe to comparing concentrations in fish liver collected from Chino and Mill Creeks, which tends to have higher concentrations of many trace elements, to concentrations in whole fish collected at sites upstream of the confluence with these two creeks. The Chino and Mill Creek sites are in areas with some of the most intensive urban and agricultural land use in the study area (fig. 2). The two sites on the Santa Ana River below its confluence with these two creeks had concentrations of copper, selenium, and zinc higher than at the Santa Ana River sites above the confluence. Concentrations below Prado Dam were lower than concentrations at Chino and Mill Creek, indicating dilution of these contaminants. Increased concentrations of selenium and zinc at Imperial Highway (site farthest downstream) indicate additional sources for these two trace elements below Prado Dam.

The median concentration for zinc at urban sites in the Santa Ana River Basin is above the NAWQA median for urban sites. The medians for the other trace elements are at or below the NAWQA urban medians (fig. 12B).

Copper is the only trace element that may exceed potentially toxic concentrations on the basis of toxicity information compiled by the National Irrigation Water Quality Program (U.S. Department of the Interior, 1998). Elevated levels were observed at two nonurban sites, Santa Ana River at upper powerhouse (300 and 160 µg/g) and Bear Creek (230 µg/g). Toxicity effects were observed in fish with copper concentrations in liver tissue as low as 83 µg/g. Comparison with toxicity information is limited owing to differences in tissue type and fish species.

Concentrations of trace elements from the current study were compared with previously collected data from California’s Toxic Substance Monitoring Program at six sites (Rasmussen, 1993; 1995; 1997; Rasmussen and Blethrow, 1990), and to the Use-Attainability Analysis study at five sites (Chadwick and Associates, 1992). These studies provide a time-series record of concentrations. Based on these prior studies, copper and zinc concentrations are increasing at Chino Creek, Mill Creek, and Santa Ana River at Imperial Highway. The significance of the increase cannot be determined because many of the differences in concentrations between and within studies may owe to differences in fish species and tissue type as well as natural variability. Concentrations of trace elements at other sites show no trends.

**SUMMARY AND CONCLUSIONS**

Many of the constituents in the three groups of compounds (organochlorines, SVOCs, and trace elements) analyzed in this study are of anthropogenic origin. As a result, detection frequency and concentrations were generally higher at urban sites than at nonurban sites.

More organochlorine compounds were detected in reservoir sediment cores, streambed sediment, and fish tissue; and at higher concentrations, at urban sites than at nonurban sites. The trend of higher frequency of detections of organochlorines at urban sites also was observed nationwide. Total chlordane and p,p’-DDE were the two organochlorines detected most often and at statistically-significant higher concentrations ($p < 0.05$) in streambed sediment and fish tissue at urban sites than at nonurban sites. Even though the use of most organochlorines has been banned for several years, the presence of organochlorines in the different media shows the persistence of these compounds in the environment.

At the urban sites, more organochlorines were detected in streambed sediment and fish tissue at sites on the Santa Ana River than on its tributaries. Also, concentrations of most organochlorines were higher in the Santa Ana River. The more frequent occurrences and higher concentrations in the Santa Ana River suggests transport from the tributaries, and deposition in the Santa Ana River, as well as additional sources along the Santa Ana River such as tributaries and storm drains not sampled.
More SVOCs were detected in reservoir sediment cores and streambed sediment and, at higher concentrations, at urban sites than at nonurban sites. This trend is similar to that observed for organochlorine compounds. More SVOCs were detected at urban sites on tributaries, and at higher concentrations, than at urban sites on the Santa Ana River. This is in contrast to that observed for organochlorines. The less frequent occurrence and lower concentrations in the Santa Ana River suggest that SVOCs are less persistent than organochlorine compounds, possibly due to volatization, degradation, or dilution.

Trace elements, unlike organochlorines and most SVOCs, have naturally occurring sources as well as anthropogenic sources. Nevertheless, urbanization appears to have some effect on concentration. In reservoir sediment cores and streambed sediment, most of the trace elements that have sediment-quality guidelines (SQG) (As, Cd, Cr, Cu, Pb, Hg, Ni, and Zn) had significantly higher concentrations at urban sites than at nonurban sites. In contrast, four trace elements with SQGs (As, Cu, Hg, and Se) had significantly higher concentrations in fish tissue at nonurban sites. Frequency of detection and concentrations of trace elements did not differ between urban sites on tributaries and urban sites on the Santa Ana River. This is in contrast to that observed for organochlorine compounds and SVOCs. This may be because of naturally occurring sources of many trace elements.

A large number of analyses were completed for this study at each of the 3 reservoir and 12 streambed sites. Many of the analyses can be compared with various environmental guidelines. Of the 979 analyses for organochlorine compounds in sediment samples, 470 can be compared with SQGs; there were 31 exceedences of the probable-effect concentration (PEC). Almost all of these exceedences occurred in the reservoir sediment core from the highly urbanized West Street Basin, a stormwater catchment; seven exceedences occurred at Canyon Lake and none at Hemet Lake. At West Street Basin, chlordane and \(p,p'-\text{DDE}\) exceeded their PECs throughout the historical record including the most recent sediment. Chlordane, total DDT, and total PCB concentrations in West Street Basin were generally higher than concentrations observed in urban reservoirs sampled nationwide. Only the median concentrations for \(p,p'-\text{DDE}\), \(p,p'-\text{DDT}\) and total DDT in streambed sediment were greater at urban sites in the Santa Ana River Basin than NAWQA medians.

Of the 363 analyses for organochlorines in fish tissue, 55 were compared with NAS/NAE or State of New York guidelines for the protection of fish-eating wildlife; there were no exceedences. In a manner similar to sediment, only the \(p,p'-\text{DDE}\) median concentration at urban sites was greater than the NAWQA urban median.

Of the 2,009 analyses for SVOCs in sediment samples, 470 were compared with SQGs; there were 47 exceedences of PEC. All of these exceedences occurred in reservoir sediment cores from West Street Basin. Chysene, pyrene, and total PAH were detected above their PECs throughout the historical record, except for the most recently deposited sediment. Concentrations of most SVOCs from all three reservoirs were about the same as or less than concentrations observed in reservoirs sampled nationwide. Median concentrations of SVOCs in streambed sediment at urban sites were less than NAWQA urban medians, except for 2,6-dimethylnaphthalene, phenol, \(p\)-cresol, and two phthalates.

Of the 3,549 analyses for trace elements in sediment samples, 639 were compared with SQGs; there were 74 exceedences of PECs. Sixty of the exceedences were in reservoir sediment cores from West Street Basin; 11 occurred at Canyon Lake and 3 in streambed sediment. Lead and zinc were detected above their PECs throughout the historical record at West Street Basin. Copper was detected above its PEC throughout the historical record at Canyon Lake. Arsenic exceeded the PEC in streambed sediment at San Jacinto River near Elsinore and zinc exceeded its PEC at Chino Creek and Warm Creek.

Of the 242 analyses for trace elements in fish tissue, only 15 were compared to toxicity guidelines compiled by the National Irrigation Water Quality Program because of differences in tissue type analyzed; there were no exceedences. Copper may exceed potentially toxic concentrations at two nonurban sites. However, zinc was the only trace element greater than the NAWQA median for urban sites.
Analysis of reservoir sediment core provides an opportunity to identify temporal trends in concentration; however, data interpretation is complex due to changes in land use and rainfall. Decreasing temporal trends were observed for organochlorine compounds in all three reservoirs, except for methoxychlor in West Street Basin. The use of most organochlorine compounds was discontinued in the early 1970s, which resulted in the decreasing trend. The continued presence of most organochlorine compounds in the environment reflects the persistence of the compounds.

Concentrations of organochlorine compounds also are correlated with land use and rainfall. The highly urbanized West Street Basin had higher concentrations than the less urbanized Canyon Lake. Organochlorine concentrations also tended to be higher during periods of above average rainfall. However, the effect of rainfall can be offset by changes in land use. The early part of the historical record (before 1965) at West Street Basin did not reflect rainfall conditions, possibly because of the rapid urbanization within the small drainage area. After 1965, land use was relatively stable and significant effects on concentrations were correlated with rainfall.

The concentrations of organochlorine compounds observed in Canyon Lake reflect some correlation with rainfall, but the relation was not as significant as at West Street Basin. This may be because of the effects of the slow, but continuous urbanization in the drainage area coupled with the decreasing trend in organochlorine compounds.

Decreasing SVOC concentrations with time were observed at West Street Basin and Hemet Lake; this agrees with the trends observed for organochlorine compounds. In contrast, increasing trends in SVOC concentrations were observed at Canyon Lake. The diverging trends may be caused by the effects of the increasing urbanization at Canyon Lake, which has not occurred at West Street Basin or Hemet Lake.

Concentrations of SVOCs also correlated with land use and rainfall. The highly urbanized West Street Basin had higher concentrations than Canyon Lake. Correlation with rainfall was observed at both West Street Basin (after 1965) and Canyon Lake. Unlike organochlorine compounds, the relation was more significant at Canyon Lake than at West Street Basin, possibly because of increased vehicle traffic, road surface, and other urban effects near Canyon Lake. Decreasing trends in trace elements were observed at West Street Basin. Canyon Lake exhibited no trends for most trace elements with the exception of As, Cu, and Zn. Hemet Lake had either increasing or decreasing trends for most of the trace elements. The significant trends at West Street Basin and Hemet but not at Canyon Lake may be attributed to the relatively stable land use at West Street Basin (after 1965) and Hemet Lake in comparison with Canyon Lake.

Concentrations of trace elements were correlated with land use and showed some relation to rainfall. Concentrations of most trace elements were higher at West Street Basin than at Canyon Lake or Hemet Lake. There was little correlation of trace elements with rainfall at West Street Basin except for arsenic; this contrasts with that observed for SVOCs. At Canyon Lake, six of the nine trace elements correlated with rainfall.

In general, the data from this study showed that organochlorine compounds, SVOCs, and trace elements are detected more frequently and at higher concentrations at urban sites than at nonurban sites, which suggests that urbanization generally impairs sediment quality. However, when the land use is stable, as in West Street Basin and Hemet Lake, the sediment quality is improving. The data also show some relation between long-term rainfall and the concentrations of organochlorine compounds, SVOCs, and trace elements in reservoir-sediment core. This correlation is stronger when land use is relatively stable.

Comparison of the data from this study with environmental guidelines showed that organochlorine compounds, SVOCs, and trace elements in recent streambed sediment were almost always lower than the PEC and TEC; of the almost 2,000 analyses, there were 3 exceedences of PEC and 62 exceedences of TEC. Comparison of fish-tissue data with potential toxicity levels showed no exceedences for organochlorine compounds or trace elements.
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California Regional Water Quality Control Board, 1995, Water quality control plan, Santa Ana River Basin (8), variously paged.


