POTENTIAL FOR CHEMICAL TRANSPORT BENEATH A STORM-RUNOFF RECHARGE (RETENTION) BASIN FOR AN INDUSTRIAL CATCHMENT IN FRESNO, CALIFORNIA

By Roy A. Schroeder

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Conversion Factors

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
cubic centimeter (cm^3)	0.06102	cubic inch
centimeter per day (cm/d)	0.3937	inch per day
square centimeter (cm^2)	0.155	square inch
gram (g)	0.03527	ounce (avoirdupois)
gram per cubic centimeter (g/cm^3)	0.57808	ounce per cubic inch
hectare (ha)	2.471	acre
kilogram (kg)	2.205	pound (avoirdupois)
kilogram per year (kg/yr)	2.205	pound per year
kilometer (km)	0.6214	mile
square kilometer (km^2)	0.3861	square mile
meter (m)	3.281	foot
meter per kilometer (m/km)	5.2800	foot per mile
meter per year (m/yr)	3.281	foot per year
millimeter (mm)	0.03937	inch
square millimeter (mm^2)	0.00155	square inch

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$°F=1.8(°C)+32.$$

Vertical Datum

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

Abbreviations

°C/min	degrees Celsius per minute
dpm	disintegrations per minute (radioisotope activity)
GC-FID	gas chromatography with flame-ionization detection
GC-MS	gas chromatography with mass spectrometric identification
keV	thousand electron volt
M	molar
meq/L	milliequivalents per liter
mBq	millibecquerels
MWL	global meteoric water line
NURP	Nationwide Urban Runoff Program (established in 1978 by U.S. Environmental Protection Agency)
permil	parts per thousand
pCi/L	picocuries per liter
TU	tritium unit (1 tritium atom per 10^{18} hydrogen-1 atoms [approximately equal to 3.2 picocuries per liter])
µm	micrometer (3.937×10^{-5} in.)

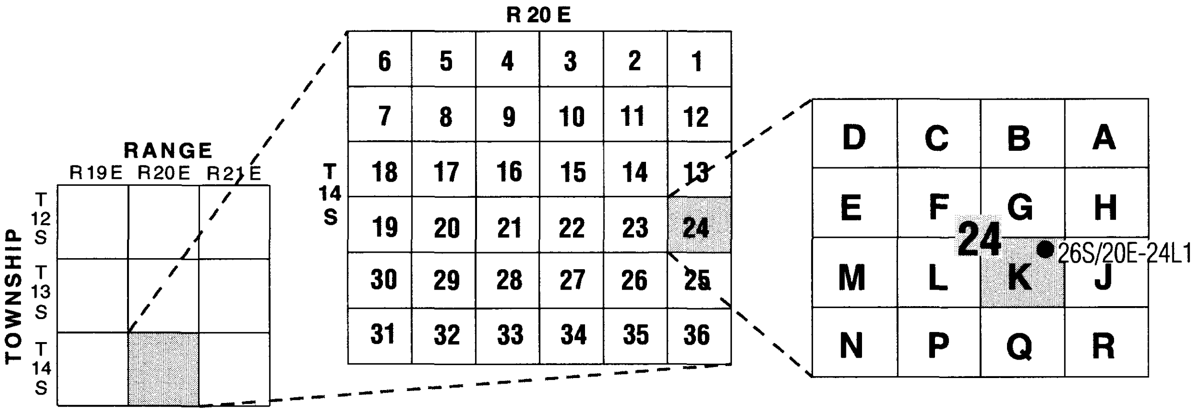
Water-Quality Information

Electrical conductivity is expressed as specific conductance, in microsiemens per centimeter at 25°C (µS/cm).

Trace-element and pesticide concentrations in water samples are given in micrograms per liter (µg/L). One thousand micrograms per liter is equivalent to 1 milligram per liter (mg/L). Micrograms per liter is approximately equivalent to "parts per billion" (ppb). Trace-element concentrations in sediment are given in micrograms per gram (µg/g). Micrograms per gram is equivalent to "parts per million" (ppm). Pesticide concentrations in sediment are given in micrograms per kilogram (µg/kg). One thousand micrograms per kilogram is equivalent to 1 microgram per gram (µg/g). Micrograms per kilogram is equivalent to "parts per billion" (ppb).

Well-Numbering System

Wells are identified and numbered according to their location in the rectangular system for the subdivision of public lands. Identification consists of the township number, north or south; the range number, east or west; and the section number. Each section is divided into sixteen 40-acre tracts lettered consecutively (except I and O), beginning with "A" in the northeast corner of the section and progressing in a sinusoidal manner to "R" in the southeast corner. Within the 40-acre tract, wells are sequentially numbered in the order they are inventoried. The final letter refers to the base line and meridian. In California, there are three base lines and meridians; Humboldt (H), Mount Diablo (M), and San Bernardino (S). All wells in the study area are referenced to the Mount Diablo base line and meridian (M) Well numbers consist of 15 characters and follow the format 014S020E24L001M. In this report, well numbers are abbreviated and written 14S/20E-24L1. Wells in the same township and range are referred to only by their section designation, 24L1. The following diagram shows how the number for well 14S/20E-24L1 is derived.



POTENTIAL FOR CHEMICAL TRANSPORT BENEATH A STORM-RUNOFF RECHARGE (RETENTION) BASIN FOR AN INDUSTRIAL CATCHMENT IN FRESNO, CALIFORNIA

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Abstract

A wide variety of chemicals from urban runoff were found at elevated concentrations in sediment that accumulated in a storm-runoff recharge basin in an industrial part of the city of Fresno. The chemicals include as many as 20 inorganic elements and about the same number of organic compounds, primarily organochlorine pesticides and polycyclic aromatic hydrocarbons. Most of these contaminants were found to be sorbed to the upper 4 centimeters of sediment, which also is the maximum depth to which atmospheric lead-210 penetrated. None of the contaminants were detected above back-background concentrations in the sediment at depths greater than 16 centimeters. In shallow sediment, zinc is the inorganic element that was most enriched; its concentration was 38 times higher in surface sediment (0–1 centimeter) than in deeper strata (below 16 centimeters). Similarly, organic carbon enrichment was nearly 1,000 times higher in the surface sediment.

Although batch-elutriation experiments demonstrated the potential for leaching of contaminants attached to sediments, a sharp decrease in concentrations with increasing sediment depth, and the extremely low level of contaminants in two monitor wells adjacent to the basin, confirmed the absence of contaminant transport to the water table. Continued long-term protection for ground water is afforded by an approximately 8-meter-thick unsaturated zone beneath the basin. Zinc, on the basis of its hundredfold-higher concentration in water from the recharge basin than in ground water, is indicated as the most sensitive surrogate for monitoring possible ground-water degradation by inorganic cations.

Results from this study were compared with previously published results from comprehensive monitoring of urban runoff to the basin during 1981-83. The comparison revealed remarkably similar patterns of chemical contamination, although estimates of sediment quantity delivered to the basin differed by a factor of 1.8. The higher estimate of sediment quantity delivered obtained by this study likely reflects imprecision in the determination of sediment depths and an unusual open texture of the thin veneer that accumulated during the 4-year period the basin had been in existence. A technique using lead-210 is illustrated that could, with adequate data collection, provide estimates of sediment and contaminant quantity delivered to recharge basins without the numerous analyses and sample-collection effort necessary to monitor runoff.

INTRODUCTION

URBAN HYDROLOGY STUDIES

In response to concerns that urban runoff may be a significant nonpoint source of contaminants, the U.S. Environmental Protection Agency (EPA) established the Nationwide Urban Runoff Program (NURP) in 1978 to characterize the quality of urban runoff and to determine the extent to which urban runoff might contribute to impairment of water quality in receiving water bodies (U.S. Environmental Protection Agency, 1983). Studies were done at 28 urban areas throughout the Nation, and the U.S. Geological Survey (USGS) participated in 11 of the studies (Driver and others, 1985). At two study areas—in Fresno, California (Oltmann and Shulters, 1989), and Long Island, New York (Ku and Simmons, 1986)—urban stormwater runoff is routed to constructed retention/recharge basins where it then percolates through the soil and recharges the aquifer.

In the studies at Fresno and Long Island, it was concluded that properties of the soil beneath the basins are highly effective in retaining urban runoff contaminants, although the ability of the soil to continue to retain contaminants was said to be unknown (U.S. Environmental Protection Agency, 1983).

Nightingale (1975; 1987a,b,c; 1989) showed that concentrations of several trace elements and synthetic organic compounds from urban runoff were elevated above background levels in near-surface sediments in recharge basins in residential and commercial parts of the city of Fresno, but that the concentrations decreased rapidly with increasing sediment depth and also generally were very low in interstitial water from the unsaturated zone and in ground water beneath the basins. The study reported here extends these previous investigations to a recharge basin in an industrial catchment where the Fresno NURP study found most contaminant concentrations to be several times higher than in runoff from residential and commercial catchments (Oltmann and Shulters, 1989). This study thereby completes the evaluation of these recharge basins in each of the major urban land-use categories (industrial, commercial, and residential). This investigation included analyses of numerous synthetic organic compounds, a broad suite of more than 40 elements, and some stable and radiogenic isotopes. This study was done by the USGS in cooperation with the Fresno Metropolitan Flood Control District.

PURPOSE AND SCOPE

This report presents the results of a study during 1986–87 whose purpose was to determine whether stormwater runoff to a recharge basin in an industrial part of the city of Fresno has caused, or has the potential to cause, degradation of the ground-water quality. The study included three approaches:

1. Comparison of chemical concentrations in water from the recharge basin to concentrations in water from an aquifer beneath the recharge basin,

2. Determination of chemical-concentration profiles in sediment beneath the recharge basin, and

3. Laboratory elutriation tests in which water was mixed with contaminated basin sediment or clean aquifer soil and reanalyzed.

This study builds on previous results of the Fresno NURP study for which contaminants in urban runoff were monitored during 1981-83. Results of the NURP study were published by Brown and Caldwell Consulting Engineers (1984), Fresno Metropolitan Flood Control District (1987), Nightingale (1987a,b,c; 1989), Nightingale and others (1985), Oltmann and Shulters (1989), and Oltmann and others (1987).

ACKNOWLEDGMENTS

The author thanks Harry Nightingale of the U.S. Department of Agriculture in Fresno and Doug Harrison and Gerald Lakeman of the Fresno Metropolitan Flood Control District for helpful suggestions before and during the study. Removal of water from the recharge basin by the Fresno Metropolitan Flood Control District prior to sampling greatly facilitated the collection of sediment samples.

DESCRIPTION OF THE STUDY AREA

The city of Fresno is about 260 km southeast of San Francisco (about 180 km east of the Pacific coastline at Monterey Bay), in the San Joaquin Valley and between the San Joaquin River to the north and the Kings River to the south (fig. 1). Average annual rainfall in Fresno is about 25 cm, nearly all of which falls between October and April (Page and LeBlanc, 1969). Topographic relief is low with an average gradient of only about 1.6 m/km. Because of the flat terrain and the lack of adequate water courses through the city, almost 100 stormwater retention/recharge basins (hereinafter referred to as "recharge basins") have been constructed to dispose of surface runoff and to recharge an aquifer that has been designated as a sole-source aquifer by the U.S. Environmental Protection Agency. The average size of the basins is 4 to 6 ha, and the average size of the urban catchments served by the basins is about 2.6 km^2.

The industrial-catchment basin that was the subject of this study is in the southeast part of the Fresno metropolitan area (fig. 1). The area of the catchment is 113 ha, of which 34.2 percent is idle or vacant and 65.8 percent is used for industrial purposes. Impervious surface covers 52.5 percent of the catchment (Oltmann and Shulters, 1989). Industries present in the catchment include cotton mills, food processing, petroleum operations, chemical storage, carpet manufacturing, and light trucking (Brown and Caldwell Consulting Engineers, 1984).

Figure 1. Location of study area.

Runoff is routed to a basin (approximately one-half hectare) on the south side of the catchment. A detailed diagram of the basin and its immediate surroundings as they existed at the time of this study (1986) is shown in figure 2. Prior to this study, the basin was last dredged (scraped) in 1982, when it was deepened and rechannelized to its present form to facilitate sample collection for the NURP study (G.E. Lakeman, Fresno Metropolitan Flood Control District, oral commun., 1992). Although excavation of the basin exposed a highly permeable coarse sand, the very fine texture of muds that soon accumulate on the basin's floor may considerably reduce the effective area through which percolation takes place by restricting it to the sloping sides of the basin at high-water stages. Over a period of time, the structure increasingly functions as an evaporation (retention) pond as opposed to a recharge basin and must be scraped to again expose a more permeable bottom.

Vegetation on the rim of the basin is sparse and the water itself contains algae but no macrophytes. The area surrounding the basin is disked periodically to maintain a generally barren environment so as not to attract wildlife. The basin normally contains water to a depth of a meter or more, even during the dry summer months; however, it was pumped dry in July 1986 to permit subbottom sampling on August 4, 1986.

GEOLOGY, HYDROLOGY, AND GROUND-WATER QUALITY NEAR THE STUDY AREA

A general description of the geology, hydrology, and ground-water quality at the study area is inferred from Page and LeBlanc's (1969) summary for Fresno and its surrounding area. Their summary, in turn, was based on data and interpretations resulting from several regional studies in the Central Valley of California (Lippincott, 1902; Mendenhall and others, 1916; Davis and Poland, 1957; Davis and others, 1959, 1964; Olmsted and Davis, 1961; Meade, 1967; and Croft and Gordon, 1968).

The study area is in the Kings River high alluvial fan geomorphic unit. The water-bearing unconsolidated deposits of this unit (and of the adjacent units) are underlain by a basement complex of consolidated rocks of pre-Tertiary age. Depth to bedrock at the study area is about 1,200 m. The unconsolidated fine-grained continental deposits of Tertiary and Quaternary age, derived from weathering of crystalline rocks in the Sierra Nevada to the east, are overlain by coarser oxidized granitic alluvium of Quaternary age. Thickness of the alluvium is about 150 m at the study area, where it is capped by a veneer (a few meters thick, or less) of heavily reworked fine-grained soil.

Prior to development of the ground-water resources, the direction of ground-water movement in the Fresno area was toward the southwest; however, pumping has created a permanent cone of depression beneath the city of Fresno that now deflects ground-water movement toward the north in the vicinity of the study area (Mitten, 1984). A hydraulic gradient of 2 m/km toward the west-northwest is inferred at the study site from water-level contours for 1963 and regional maps that show similar conditions prevailing in 1975 (Page, 1975). Although ground water is unconfined on a regional scale, local areas of confinement or partial confinement may exist beneath intercalated clay and silt lenses.

A trend toward higher dissolved-solids concentration, and dominance of sodium and chloride ions, with increasing depth probably exists throughout the Fresno area, particularly in the older, fine-grained continental deposits. The base of the freshwater (defined as water in which ionic concentration is less than 2,000 mg/L in NaCl equivalents) is estimated to be 400 m below sea level (about 500 m below land surface) at the study area. However, nearly all wells in the area penetrate only the younger alluvium, in which the alkaline earths (calcium or magnesium) and bicarbonate are the predominant ions. Ground water from a 65-m-deep (perforated to only 51 m) agricultural production well, 14S/20E-24K1, about 0.4 km east of the study area probably is representative of regional ground-water quality; data from a 1957 analysis of water from this well are reproduced in table 1. Predominant ions are calcium, magnesium, and bicarbonate, and the dissolved-solids concentration of 226 mg/L is equivalent to a specific conductance of about 350 µS/cm (microsiemens per centimeter).

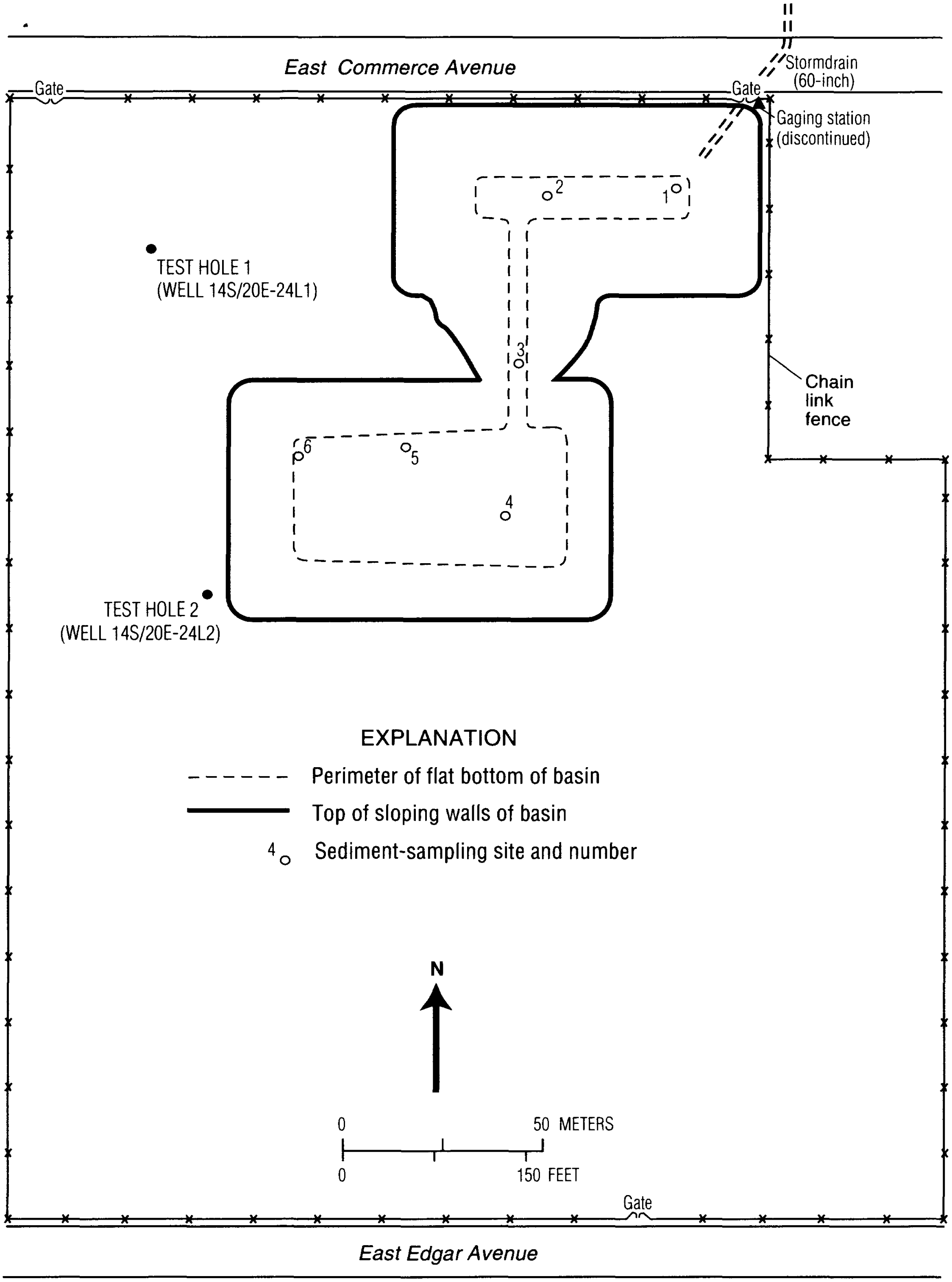

Figure 2. Recharge basin and location of test holes/monitor wells and sediment-sampling sites in the recharge basin.

Table 1. Historical ground-water-quality data from well 14S/20E-24K1 near the study site

[Sample collected September 6, 1957, by the California Department of Public Health (Page and LeBlanc, 1969, tables 14 and 20). mg/L, milligram per liter; meq/L, milliequivalent per liter; --, no data]

Constituent	Concentration (mg/L)	Concentration (meq/L)
Calcium (Ca)	23	1.15
Magnesium (Mg)	12	.99
Sodium (Na)	18	.78
Potassium (K)	4	.10
Iron (Fe)	.08	--
Bicarbonate (HCO_3)	140	2.29
Sulfate (SO_4)	7.2	.15
Chloride (Cl)	14	.39
Fluoride (F)	.1	.01
Nitrate (NO_3)	14	.23
Dissolved solids	226	--
pH=8.2 (standard units)		

FIELD AND ANALYTICAL METHODS

SITE SELECTION, WELL INSTALLATION, AND SOIL CORING

Two test holes (fig. 2) were drilled: at latitude 36°41′54"N, longitude 119°44′57"W; and at 36°41′51"N, 119°44′56"W (about 100 m south of the first test hole). The holes were drilled with a 6-inch-diameter (15 cm) hollow-stem auger, and 2-inch-diameter (5 cm) PVC monitor wells, 14S/20E-24L1 and 14S/20E-24L2, were installed in the holes.

As auger flights were pulled up and removed following insertion of the well casing in the hollow stem, the annulus between the walls of the test hole and the casing quickly was filled with a slurry of native material from the saturated zone. During this procedure the casing sank, exposing a much longer perforated interval (6 m) to the saturated zone than was intended (1–2 m). The wet, cohesionless sand (Durnford and others, 1991) below the water table rose several meters above the water table in the annulus. The remaining annulus above this sand was backfilled with a layer of bentonite pellets, then with drill cuttings from the unsaturated zone, and finally with a 1.5-m cement seal to land surface. Altitude of land surface is 86.5 m at well 14S/20E-24L1 (test hole 1) and 85.5 m at well 14S/20E-24L2 (test hole 2). Both monitor wells are perforated (slotted) from 12 to 18 m below land surface. Because the casing sank during installation, the top of the perforated interval was only about 0.6 m above the water table at well 14S/20E-24L1 and was actually about 0.3 m below the water table at well 14S/20E-24L2 when samples for water-quality analysis were collected during summer and autumn 1986.

Both monitor wells are adjacent to the recharge basin (fig. 2) and, on the basis of regional ground-water-flow patterns discussed in the previous section, the first well installed (14S/120E-24L1) is believed to be downgradient of the basin. Irregular topography at this location precluded drilling the first test hole closer than about 50 m from the recharge basin. Flatter terrain to the south permitted drilling of the second test hole within a few meters of the edge of the recharge basin, thereby increasing the probability of intercepting any small ground-water mound should one extend only a short distance beyond the basin area. The second well also decreases the chance that a contaminant plume would be missed if the local hydraulic gradient were toward the southwest (the direction of the regional gradient prior to pumping in Fresno) for any reason, including pumping from any wells near the study area itself (see Mitten and Guay, 1986, for a summary of municipal pumpage and location of wells). Although a monitor well upgradient of the basin would have provided information about the local hydraulic gradient and confirmation that water from the basin is reaching the water table and producing a ground-water mound, this study did not have sufficient resources to install a third well. Installation of lysimeters beneath the recharge basin itself, as in a previous study, would have been especially valuable but was precluded by concern that they would provide a pathway for enhanced transport of contaminants through the unsaturated zone.

Soil cores were recovered from selected depths during drilling of the test holes by lowering a 2-ft (0.6 m), split-spoon steel corer through the hollow drill stem. The depths selected for coring in test hole 1 were based on field observations of change in texture as determined from drill cuttings brought to the surface by the auger and from the drill operator's perception of changes in drilling characteristics. Depths for coring in test hole 2 were chosen to confirm the presence of low-permeability zones found in test hole 1. Particle-size distribution in the core soils was determined using sieves for the sand-size fraction and hydrometers for the fine fraction using methods described by Guy (1969). The data are given in table 2.

Table 2. Particle-size distribution in soil cores from two test holes adjacent to the recharge basin

[m, meter; --, no data]

Depth interval (m)	Percent finer than size, in millimeters, indicated										
	Gravel	Coarse sand		Medium sand	Fine sand		Silt				Clay	
	4	2	1	0.5	0.25	0.125	0.062	0.031	0.016	0.008	0.004	0.002
Test Hole 1 (Monitor Well 14S/20E-24L1)												
1.2-1.8	95	94	81	79	59	46	35	26	18	10	6	5
3.1-3.7	--	100	98	74	31	16	10	7	5	3	2	1
4.9-5.5	--	100	95	52	22	12	9	6	4	3	2	2
5.8-6.2	--	--	100	99	98	95	80	50	25	9	8	7
6.2-6.4	--	--	100	85	46	30	21	14	9	6	5	4
6.4-6.7	--	100	98	83	72	60	36	26	19	13	8	8
6.7-7.2	--	--	100	99	92	72	34	20	12	5	4	4
7.2-7.3	--	--	--	100	99	95	87	73	51	35	20	12
9.1-9.8	--	--	100	99	92	59	13	6	5	3	3	3
10.7-10.9	--	--	100	99	95	90	82	73	56	36	19	12
10.9-11.3	--	--	100	96	83	67	48	39	32	25	20	16
11.6-12.2	--	100	99	93	71	53	38	28	21	17	15	12
13.4-14.0	--	--	100	89	70	53	37	29	23	16	12	9
15.5-15.8	--	--	100	92	74	61	51	42	33	23	16	13
16.5-17.1	--	100	99	76	36	21	14	10	6	4	3	2
Test Hole 2 (Monitor Well 14S/20E-24L2)												
6.4-6.5	--	--	100	98	93	86	71	51	31	14	9	9
9.7-9.8	--	--	100	98	93	85	65	50	42	34	22	12
10.1-10.4	--	100	99	91	70	51	35	25	20	15	12	9
10.4-10.7	--	--	100	95	79	66	58	49	40	30	21	16
14.4-14.6	--	100	99	95	84	78	72	64	50	30	13	7

Particle-size data were used in conjunction with field observations to compile the lithologic logs given in table 3. Depths were recorded with a precision of 0.03 m during drilling; however, they were measured relative to land surface that was highly irregular because soil excavated to form the recharge basin had been deposited near the test holes. Therefore, accuracy of the logs relative to a fixed benchmark probably is no better than 0.3 m.

Although changes in color and texture commonly are gradual and subtle, three distinct zones of silty clay were found and correlated between the test holes: at 7.2-7.3 m, 10.7-10.9 m, and 15.5-15.8 m in test

Table 3. Geologic log for test hole 1 adjacent to the recharge basin

[Rock-color terms are from Goddard and others, 1948. m, meter; mm, millimeter]

Depth (m)	Thickness (m)	Description
0.6	0.6	Fine sand, silt, and clay in about equal proportions, moderate-yellowish-brown (10 YR 5/4). Surface soil heavily reworked and mixed with soil excavated in construction of recharge pond.
2.5	1.9	Sand, fine to coarse, silty, moderate-yellowish-brown (10 YR 5/4) tending to dark-yellowish-orange (10 YR 6/6). Numerous small concrete chips decreasing in abundance with depth, thin (1 mm) calcareous stringers and bands.
5.8	3.3	Sand, fine to coarse, pale-yellowish-brown (10 YR 6/2) with some moderate-yellowish-brown (10 YR 5/4) marbling. Biotite, quartz, and mica grains abundant. Measured 10-percent silt and 90-percent sand. Becoming finer below 5.6 m.
6.2	.4	Silt, fine sand, pale-yellowish-brown (10 YR 6/2) with numerous small (1-3 mm) light-brown (5 YR 5/6) blebs. Measured 70-percent silt.
6.4	.2	Sand, fine to medium, silt, pale-yellowish-brown (10 YR 6/2). Measured 15-percent silt.
7.2	.8	Sand, fine, silty, moderate-yellowish-brown (10 YR 5/4). Measured 30-percent silt.
[1]7.3	.1	Silt, clayey, moderate-yellowish-brown (10 YR 5/4) tending to dark-yellowish-brown (10 YR 4/2). Measured 70-percent silt and 20-percent clay.
10.7	3.4	Fine sand, some silt, color fluctuating between moderate-yellowish-brown (10 YR 5/4) and light-brown (5 YR 5/6) throughout interval. Measured 80-percent fine sand and 10-percent silt.
[1]10.9	.2	Silt, clayey, pale-yellowish-brown (10 YR 6/2) to dark-yellowish-brown (10 YR 4/2). Measured 60-percent silt and 20-percent clay.
13.0	2.1	Sand, fine to medium, with silt and clay, poorly sorted, light-brown (5 YR 5/6) blebs at top of interval blending entirely into moderate-brown (5 YR 4/4) matrix below 11.6 m. Clay and silt decreasing and fine sand increasing slightly with depth. Measured 15-percent clay and 20- to 30-percent silt. Bottom of interval in saturated zone.
15.5	2.5	Sand, fine to coarse, with silt and clay, (slightly coarser than interval above), changing gradually from moderate-yellowish-brown (10 YR 5/4) at top of interval to light-brown (5 YR 5/6) at botton of interval.
[1]15.9	.4	Sand, silty with greyish clay blebs, moderate-yellowish-brown (10 YR 5/4). Measured 35-percent silt and 15-percent clay.
18.3	2.4	Sand, fine to coarse, becoming coarser with increasing depth, moderate-yellowish-brown (10 YR 5/4) tending to light-brown (5 YR 5/6). Biotite, quartz, and mica grains abundant (similar to 2.5-5.8 m interval). Measured 10-percent silt.

[1] Finer, less-permeable zones visually identified during coring.

hole 1; and at 6.4-6.5 m, 9.7-9.8 m, and 14.4-14.6 m in test hole 2 (table 4). Difference in the depth below land surface of these three zones matches closely the difference in land-surface altitude at the test holes. The water table was between the middle and deepest of these zones in each test hole.

SAMPLING OF SEDIMENT FROM THE RECHARGE BASIN

To facilitate sampling of accumulated sediment in the recharge basin, all water was pumped from the basin in mid-July 1986, and the exposed sediment was allowed to dry for about 3 weeks prior to sampling. As the fine-grained sediment covering the floor of the basin dried, shrinkage cracks formed thin polygonal plates. The plates were about 1 cm thick (although actual thickness is somewhat imprecise because the bottom surface of the plates was irregular) and represent the most recently deposited sediment that accumulated in the recharge basin.

Removal of the plates (the 0- to 1-cm depth samples) exposed an unusual geometric surface that bore a striking resemblance to a honeycomb, the individual cells of which were several millimeters across and deep. The sediment was strongly reduced, as indicated by its black color, except for a thin veneer of brown (oxidized) clay rimming the edge of each cell wall. It is suggested that the cells were formed by escape of gas bubbles as the mud was drying. Gas bubbles, accompanied by a small oil sheen, commonly were seen breaking the water's surface when the basin was flooded. This gas is presumed to be hydrogen sulfide, carbon dioxide, methane, and (or) nitrogen generated by microbial activity within the sediments. After the basin's water had been removed, the underlying sediment was exposed to air entering through cracks at the sediment surface, and oxidation produced the thin brown rind on the cells.

The 1-cm-thick surface-sediment plates were removed for analysis from six sites on the basin floor. The basin floor slopes gently downward from the

Table 4. Sand, silt, and clay content of soil cores from two test holes adjacent to the recharge basin

[Contents, in weight-percent, calculated from data in table 2. m, meter]

Depth interval (m)	Coarse sand	Medium sand	Fine sand	Silt	Clay
Test Hole 1 (Monitor Well 14S/20E-24L1)					
1.2-1.8	15	20	24	29	6
3.1-3.7	26	43	21	8	2
4.9-5.5	48	30	13	7	2
5.8-6.2	1	1	18	72	8
6.2-6.4	15	39	25	16	5
6.4-6.7	17	11	36	28	8
6.7-7.2	1	7	58	30	4
[1]7.2-7.3	0	1	12	67	20
9.1-9.8	1	7	79	10	3
[1]10.7-10.9	1	4	13	63	19
10.9-11.3	4	13	35	28	20
11.6-12.2	7	22	33	23	15
13.4-14.0	11	19	33	25	12
[1]15.5-15.8	8	18	23	35	16
16.5-17.1	24	40	22	11	3
Test Hole 2 (Monitor Well 14S/20E-24L2)					
[1]6.4-6.5	2	5	22	62	9
[1]9.7-9.8	2	5	28	43	22
10.1-10.4	9	21	35	23	12
10.4-10.7	5	16	21	37	21
[1]14.4-14.6	5	11	12	59	13

[1] Finer, less-permeable zones visually identified during coring.

northeast corner, where the storm runoff enters the basin, toward the south (fig. 2); therefore, a spatial gradation of increasing fines toward the south was anticipated. The particle-size data from the six sites that are presented in table 5 provide some evidence for such a trend, although the difference in percentage of fine fraction is small. Clay-plus-silt content ranges from 67 percent at sediment-sampling site 2 to 77 percent at site 4; however, clay contents are about 10 percent greater at sites 5 and 6 in comparison with the other four sites. In addition to the 0-1 cm (surface-sediment plate) samples, two successive thin layers, estimated to each be only about 1 mm thick, were scaped from the surface near site 5. Both were found to contain approximately equal proportions of clay and silt and virtually no sand (table 5). Accordingly, the small differences in the percentage of fine fraction between surface samples at the six sites could simply be due to varying proportions from the very thin layer of fine sediment at the surface (top few millimeters) and the coarser sediment immediately below the surface (to a depth of 1 cm).

In addition to surface samples from the five sites, sediment and native soil to a depth of 1.5 m were collected at site 5 in the recharge basin. This site, which seemed to be the deepest part of the basin, was 4.9 m below the top of the cement seal at well 14S/20E-24L1 (test hole 1). Successive layers of sediment were exposed and collected at site 5 by excavating a rectangular pit with a small hand trowel. The pit was "telescoped" inward in a staircase arrangement to eliminate sloughing of overlying sediment as successive layers were uncovered. Excavation continued in this manner to a depth of 64 cm; the deepest sample, from 120 to 150 cm, then was obtained with a manually operated 2-inch-diameter (5 cm) steel auger. Although the color of sediment samples lightened considerably with increasing depth, even the deepest sample had a grayish-tan color indicative of an anaerobic environment.

The particle-size-distribution data (table 5) for the subbottom-deposit samples collected at site 5 show the existence of a shallow zone, from the sediment surface to a depth of 8 cm, in which silt and clay predominate, and a deeper zone, below 16 cm, in which sand predominates (with little silt and clay present). The interval between 8 and 16 cm is a transition zone between the overlying sediment derived from outside the basin, presumably brought in by runoff from the catchment, and the underlying natural alluvium referred to throughout this report as "soils" or "substrata."

On the basis of the difference in altitude between test hole 1 and basin sediment-sampling site 5, one would expect the lithology of the basin deposits immediately below 16 cm to be similar to that of the test hole between 4.9 and 5.5 m. However, minor differences in particle-size distribution and in element concentrations suggest that the basin deposits below 16 cm more closely resemble those from 5.5 to 5.8 m in test hole 1 (for which chemical data exist but particle-size data do not). Specifically, the basin deposits below 16 cm consist predominantly of a fine-to-medium sand, whereas the soil from 4.9 to 5.5 m in test hole 1 consists predominantly of a coarse-to-medium sand (compare data in tables 2 and 5). In addition, comparison of selected element (Fe, Mg, Mn, Th, Ti, and V) concentrations (data given in tables 7 and 9 and discussed in later sections of this report) shows that basin deposits below 16 cm are closer in chemical composition to soils between 5.5 and 5.8 m than to soils between 4.9 and 5.5 m in test hole 1. It should be noted, however, that chemical differences between the two soil samples are small and that the element arsenic presents a pattern opposite to that of the aforementioned six elements.

CHEMICAL ANALYSIS OF WATER, SOIL, AND SEDIMENT

A Teflon bailer with Teflon ball-check valve was used to collect ground-water samples from the two monitor wells installed for this study. Aliquots for analysis of inorganic constituents and nutrients were filtered through a membrane with 0.45-µm pores. Aliquots for analysis of gross organic indicators (such as methylene blue active detergents, tannin plus lignin, and oil and grease) and specific organic compounds were not filtered. Samples for analysis of organic compounds were stored at temperatures near 0°C and analyzed within a few days of their collection. Samples for analysis of cations and trace elements were stabilized by addition of nitric acid to pH approximately 2 and nutrients were preserved by addition of mercuric chloride and storage at temperatures near 0°C. Samples for trace-element analysis in the low-concentration (sub-ppb) range were acidified with ultrapure nitric acid and stored in Teflon bottles.

Grab samples of water from the recharge basin, and samples from the laboratory elutriation study (discussed in detail later in the "Laboratory Elutriation Experiments" section) were processed and analyzed in a manner similar to that used for the ground-water samples, except that collection and sample-preservation techniques for low-level (sub-ppb) trace-

Table 5. Particle-size distribution in sediment beneath the recharge basin

[cm, centimeter; ~, interval is approximate. --, no data]

	Percent finer than size, in millimeters, indicated											
	Gravel	Coarse sand		Medium sand	Fine sand		Silt				Clay	
	4	2	1	0.5	0.25	0.125	0.062	0.031	0.016	0.008	0.004	0.002
Site No.	**Surficial (0-1 cm) Sediment from Recharge Basin**											
1	--	--	100	97	92	84	70	51	35	21	19	17
2	--	--	100	98	92	84	67	49	30	16	14	13
3	--	--	100	97	86	79	70	65	46	26	16	14
4	--	--	--	--	100	90	77	68	53	33	19	11
5	--	--	--	100	95	80	71	68	58	44	27	17
6	--	--	--	100	87	75	69	66	58	42	25	14
Depth interval (cm)	**Subbottom Sediment from Site 5 in Recharge Basin**											
~-0.1	--	--	--	--	100	99	98	96	88	71	50	34
~.1-.2	--	--	--	100	99	99	97	91	81	68	51	35
0-1	--	--	--	100	95	80	71	68	58	44	27	17
1-2	--	--	--	100	84	72	65	61	51	37	20	15
2-4	--	--	--	100	94	87	70	56	39	21	13	13
4-8	--	--	--	100	93	87	80	72	48	25	15	12
8-16	--	100	99	97	89	80	53	40	20	7	5	5
16-32	--	--	100	96	75	42	9	3	1	1	1	1
32-64	--	--	100	96	60	29	7	3	1	1	1	1
120-150	--	--	100	96	69	23	5	2	1	1	1	1

element samples described above were used for only some of the samples (readily recognized in data tables 6, 12, and 13 by the reporting of significant digits to the tenths microgram-per-liter (sub-ppb) level for several trace elements). Solutions from the elutriation test were centrifuged rather than filtered.

Aqueous chemical constituents were analyzed by the USGS National Water Quality Laboratory in Arvada, Colorado, using methods described by Wershaw and others (1987) and Fishman and Friedman (1989). Tritium initially was analyzed at the University of California, San Diego, and these analyses later were confirmed at the USGS Isotope Laboratory in Reston, Virginia, using a liquid-scintillation counting method. Stable isotopes of hydrogen and oxygen also were analyzed in the Reston laboratory.

Sediment and soil samples for determination of organic constituents were stored in glass jars at temperatures near 0°C until their analysis a few days after collection, or they were frozen for later use in the laboratory elutriation tests. Organic constituents and nutrients were analyzed by the USGS National Water Quality Laboratory using methods described by Wershaw and others (1987) and Fishman and Friedman (1989). Groups of organic compounds that were analyzed include the organochlorines, organophosphorous insecticides, chlorophenoxy-acid herbicides, and extractable priority pollutants. In addition to these specific compounds, extractable nonspecific organic compounds were analyzed by gas chromatography with flame ionization detection (GC-FID).

The GC-FID scans provide only a general indication of organic contaminant concentrations because total concentrations determined by GC-FID amount to only about 1 percent of total organic carbon (analyzed by combustion) in near-surface sediments from the basin. For GC-FID analysis, a 25-g (approximate dry weight) subsample of sediment was extracted with a methanol plus methylene chloride solvent mixture for 12 hours using continuous Soxhlet extraction. The extract then was concentrated using a Kuderna-Danish apparatus. Surrogate compounds were added prior to extraction to check recovery, and perdeuteronaphthalene ($C_{10}D_8$) was added as an internal standard to the extract just prior to GC-FID analysis. Chromatographic separation was done using a 25-m by 0.21-mm SE-54 fused silica capillary column held initially at 50°C for 5 minutes then increased to 300°C at 6°C/min. Concentrations were calculated relative to the response of the internal standard (as "$C_{10}D_8$ equivalents").

For the gas chromatography-electron impact mass spectrometric (GC-MS) analysis of two sediment samples (0-1 cm and 8-16 cm depths) from site 5, approximately 25 g (dry weight) of sediment was processed and chromatographed in the same way as for GC-FID analysis. However, the chromatography column was coupled directly to a mass spectrometer, which was set to analyze from 45-450 atomic mass units with a scan time of 0.25 second. Compound identifications were based on comparison of the gas chromatographic peak retention time and mass spectrum with similar data for standard compounds. In addition to priority pollutants, a computerized library search for nontarget compounds was done. Although many compounds were detected, especially in the surface sample, only a few could even be identified by the compound class to which they belong.

Analysis of soil and sediment samples for element concentrations was done in the USGS Analytical Facility in Denver using methods (Severson and others, 1987) identical to those also used for a multisite reconnaissance of irrigation drainage effects that was done concurrently with this study (see, also, Schroeder and others, 1988, and Arbogast, 1990, for details on analytical methods). The samples were prepared for analysis by drying at about 30°C and grinding to pass an 80-mesh (180 µm) sieve. Virtually complete mineral digestion was effected with a combination of strong acids. Inductively coupled argon-plasma atomic emission spectrometry (ICP) was used to analyze a broad suite of about 40 elements. Arsenic and selenium were analyzed using hydride-generation atomic absorption. Mercury was analyzed using flameless cold-vapor atomic absorption. Boron was analyzed on a hot-water extract. Uranium and thorium were analyzed using delayed-neutron activation.

Lead-210 (^{210}Pb) and radium-226 (^{226}Ra) were analyzed in 13 sediment samples from the recharge basin and in 2 soil samples from test hole 1. J.K. Cochran, at the State University of New York, Stony Brook, analyzed these samples using a nondestructive gamma-counting technique. About 90 to 150 g dried sediment (or soil) was sealed in 100 cm^3 aluminum cans and stored for 2 weeks to allow gaseous radon-222 (^{222}Rn) to reach decay equilibrium with ^{226}Ra. Gamma emissions were counted on a 1,000 mm^2, 10-mm-thick, Canberra Electronics planar germanium detector. The 46.5 keV (thousand electron volt) ^{210}Pb peak and the 352 keV ^{214}Pb peak were used to measure ^{210}Pb and ^{226}Ra activity, respectively. Counting time was about 24 hours. Detector efficiencies were determined using laboratory as well as National Bureau of Standards sediment standards.

Corrections for sample self-absorption of gamma rays were made by measuring the attenuation of ^{210}Pb and ^{226}Ra sources placed on the sample cans. Concentrations are reported in disintegrations per minute per gram dry sediment (dpm/g) with precision based on counting statistics.

QUALITY OF RECHARGE-BASIN WATER AND GROUND WATER

The most direct way of determining whether recharge from the study basin has impaired ground-water quality is to measure chemical concentrations in the basin sediment and concentrations in nearby ground water. Nightingale (1975, 1987a,b,c, and 1989) found that several trace elements and synthetic organic compounds were strongly sorbed by soils beneath five recharge basins in residential and commercial parts of the city of Fresno and that their concentrations were low in soil moisture from the unsaturated zone and in ground water immediately below a basin. Accordingly, although contaminant levels in sediment were expected (and found) to be higher at the recharge basin in the commercial catchment that was the subject of this study, little or no effect on ground-water quality was anticipated.

An important consideration in evaluating the potential for ground-water contamination by urban-runoff chemical constituents is establishing whether runoff in the basin actually reaches the water table below the basin in significant amounts. Measurement of soil-moisture content in the unsaturated zone and installation of several monitor wells to determine the local hydraulic gradient would provide direct evidence of recharge but were beyond the resources available for this study. Nevertheless, water-budget calculations indicate that the potential for substantial recharge exists. On the basis of mean annual rainfall of 26 cm, measured rainfall-runoff coefficient, soil-water capacity, and physical dimensions of the catchment and recharge basin (Oltmann and Schulters, 1989), mean annual runoff should be sufficient to saturate soil above the water table for a distance of about 100 m beyond the basin's boundaries. Of course, this simplified calculation assumes symmetrical spreading beneath the recharge basin. On the basis of saturated hydraulic conductivities calculated from measured soil characteristics, Nightingale (1989) concluded that subsurface silt and clay strata (lenses) would cause lateral movement of water beneath a Fresno recharge basin that had a measured infiltration rate of 16 cm/d (almost 60 m/yr). If the soil deposits in the recharge area above the lenses are assumed to be isotropic and homogeneous and the recharge rate is constant, then the radius of the area infiltrated must vary inversely with the square root of vertical hydraulic conductivity (Freeze and Cherry, 1979, p. 16). On the basis of this relation and the inferred variation in hydraulic conductivities (Nightingale, 1989), the water would be expected to spread laterally a distance of about three times the basin's diameter. The likelihood that recharge reaches the water table directly beneath and near (as opposed to some great distance from) the basin is inferred on the basis of arguments given above, along with the absence of significant lithologic discontinuities at the test holes.

Additional evidence that ground water at the water table has mixed with a substantial volume of water from the recharge basin was obtained from analysis of tritium and the stable isotopes of hydrogen and oxygen.

ISOTOPIC EVIDENCE FOR RECHARGE

Tritium, the radioactive isotope of hydrogen having a half-life of 12.43 years, is produced naturally by cosmic-ray interactions with the upper atmosphere. Atmospheric detonation of thermonuclear weapons produced large quantities of tritium with the result that tritium concentrations in precipitation began increasing above natural levels about 1950, reaching a peak that was 10^2-10^3 times natural levels in the mid-1960's, and then gradually declining following the international treaty that banned atmospheric testing by the major nuclear powers. Tritium in precipitation today remains several times higher than natural levels. It is this bomb-produced tritium transient that can be used to distinguish post-1950 water from older water.

On the basis of nationwide maps of tritium deposition (Michel, 1989), it is estimated that average annual tritium concentration in precipitation at the city of Fresno was slightly greater than 10 TU (tritium units) at the time of this study. (One tritium unit is one tritium atom per 10^{18} hydrogen-1 atoms and equals approximately 3.2 picocuries per liter.) On the basis of physical properties of the aquifer (Williamson and others, 1989, and Hugh Mitten, USGS, written commun., 1986), it is concluded that regional ground water in the city of Fresno that originates as recharge in the Sierra Nevada foothills is unlikely to contain any tritium. The measured tritium concentration of 10.2 TU in the recharge basin (table 6) is close to the estimated tritium concentration in local precipitation. It is presumed that the

Table 6. Concentrations of dissolved inorganic and total-recoverable organic constituents in water from the recharge basin and from two nearby monitor wells

[Water from recharge basin collected January 29, 1986, except sample for analysis of isotopes, mercury, and bromide collected July 11, 1986. Monitor wells sampled August 4, 1986. MBAS, methylene blue active surfactants; PCBs, polychlorinated biphenyls; µS/cm, microsiemen per centimeter at 25° Celsius; °C, degrees Celsius; mg/L, milligram per liter; µg/L, microgram per liter; permil, parts per thousand; --, no data; <, less than indicated reporting limit]

Constituent	Concentration, in indicated units		
	Recharge basin	Well 14S/20E-24L1	Well 14S/20E-24L2
Major Constituents			
Temperature (°C)	--	17	17
Specific conductance (µS/cm)	360	420	379
pH (standard units)	6.9	8.1	8.1
Calcium (mg/L)	13	22	34
Magnesium (mg/L)	5.3	11	16
Sodium (mg/L)	14	53	15
Potassium (mg/L)	18	3.2	3.4
Chloride (mg/L)	23	10	7.4
Sulfate (mg/L)	32	24	26
Fluoride (mg/L)	.1	.1	.1
Silica (mg/L as SiO_2)	5.4	49	49
Alkalinity (mg/L as $CaCO_3$)	13	171	--
Nutrients			
Nitrite + nitrate (mg/L as N)	4.0	4.0	4.8
Ammonium (mg/L as N)	7.0	.02	.02
Kjeldahl nitrogen (mg/L as N)	13	.6	.7
Orthophosphate (mg/L as P)	4.3	.04	.06
Organic carbon (mg/L as C)	--	3.9	3.9
Trace Elements (µg/L)			
Arsenic (As)	3	3	2
Barium (Ba)	--	100	100
Boron (B)	90	80	110
Bromine (Br)	<10	<10	<10
Cadmium (Cd)	1	.73	1.1
Chromium (Cr)	<1	.50	.35
Cobalt (Co)	3	1.0	1.5
Copper (Cu)	7	3.5	4.5
Iron (Fe)	210	16	48
Lead (Pb)	2	<.08	<.08
Manganese (Mn)	120	210	78
Mercury (Hg)	.1	<.1	<.1
Molybdenum (Mo)	10	15	5
Nickel (Ni)	4	6.8	11
Selenium (Se)	<1	<1	<1
Silver (Ag)	<1	<.03	<.03
Strontium (Sr)	170	170	220
Vanadium (V)	--	19	15
Zinc (Zn)	130	.5	.4
Isotopes			
δD (permil)	-16.0	-51.5	-49.5
$\delta^{18}O$ (permil)	1.19	-7.20	-7.05
^{3}H (tritium units)	10.2±.8	6.4±.7	5.8±.6

Table 6. Concentrations of dissolved inorganic and total-recoverable organic constituents in water from the recharge basin and from two nearby monitor wells--*Continued*

Constituent	Concentration, in indicated units		
	Recharge basin	Well 14S/20E-24L1	Well 14S/20E-24L2
Broad Organic Indicators			
Tannin and lignin (mg/L as tannic acid)	2.8	<1	<1
Phenols (µg/L as phenol)	5	3	--
MBAS detergents (mg/L)	.29	.11	.08
Synthetic Organic Compounds (µg/L)			
1,2-Dichloroethane	<3	<.2	.2
1,1,1-Trichloroethane	<3	.2	.2
Dichlorodifluoromethane	<3	.2	<.2
Lindane	.01	<.001	<.001
Endosulfan	<.01	.002	<.001
Malathion	.01	<.01	<.01
Parathion	.01	<.01	<.01
Diazinon	<.01	.01	<.01
Purgeable priority pollutants	<3	<.2	<.2
Base/neutral-extractable priority pollutants	([1])	--	--
Acid-extractable priority pollutants	([1])	([1])	([1])
Organochlorine insecticides + PCB's	<.01	<.001	<.001
Organophosphorus insecticides	<.01	<.01	<.01

[1] Value is less than reporting limit, which is 5 µg/L for most extractable organic priority pollutants.

basin contains a mixture of ground water used by industries in the catchment area and not discharged to a municipal treatment plant in addition to precipitation runoff, and that it is the precipitation runoff that was the principal source of tritium in the sample from the recharge basin collected January 29, 1986.

Tritium concentrations of about 6 TU in both monitor wells (table 6) seem to indicate significant recharge from the basin. However, the evidence is compromised by the recent finding of tritium in many wells throughout the San Joaquin Valley, including 46 TU in well 14S/20E-34G1, a 124-foot well about 3 km southwest of the study site (Shelton and Miller, 1991). Recharge by extensive irrigation with surface water likely is the source of tritium in ground water throughout the San Joaquin Valley; in the city of Fresno, artificial recharge also is a potential source of tritium.

Stable-isotope ratios of hydrogen ($^2H/^1H$ or D/H) and oxygen ($^{18}O/^{16}O$) also can be used to infer recharge and possibly to place constraints on the timing of such recharge from the basin. Both isotope ratios are expressed here as permil in the commonly used δ (delta) notation relative to the Vienna-Standard Mean Ocean Water (V-SMOW) standard. The general relation between hydrogen- and oxygen-isotope ratios in precipitation is shown by the global meteoric-water line (MWL) in figure 3 (Craig, 1961). This line has a slope of 8, and the isotopic composition of waters that have undergone evaporation typically fall to the right of this line; that is, they are enriched in ^{18}O relative to deuterium. This deviation from the MWL, as well as relatively high values of δD and $\delta^{18}O$, indicates that water in the recharge basin at the time of sampling for stable isotopes on July 11, 1986, was highly evaporated.

The hydrogen-isotope ratio of precipitation in the city of Fresno can be inferred, from regional-scale data along an east-west traverse between the Pacific Coast and Nevada, to be about -80 permil (Ingraham and Taylor, 1991). Ground water from most wells in

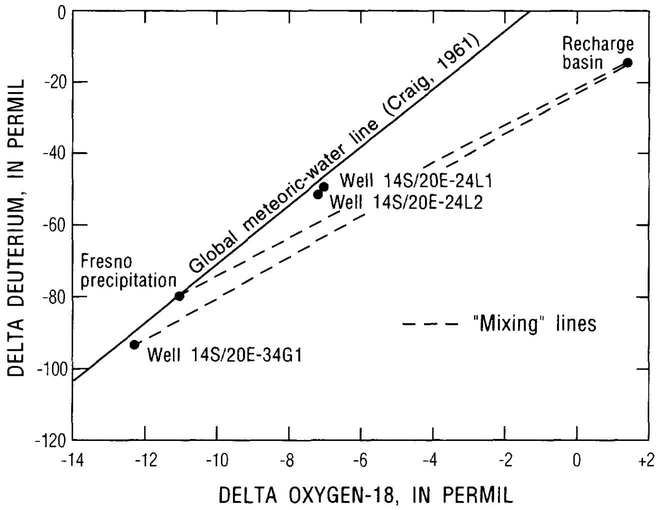

Figure 3. Relation between hydrogen and oxygen stable-isotope ratios in recharge-basin water and nearby ground water.

the vicinity of the city of Fresno has a δD slightly less than -90 permil. Even the isotopic composition of water from well 14S/20E-34G1 (alluded to in the earlier discussion on tritium), at δD=-91.5 permil and $\delta^{18}O$=-12.3 permil, does not differ greatly from the composition expected for ground water free of local recharge by surface water or irrigation—apparently because the local recharge has not undergone substantial evaporation. As can be seen in figure 3 (dashed lines), there is no way the isotopic composition measured in the two monitor wells can be obtained by mixing regional ground water or local precipitation with recharge-basin water in varying proportions. On the basis of this departure from a simple two-member mixing model, it is concluded that one or more of the following conditions are necessary to explain the isotopic composition found in the monitor wells:

1. The δD of precipitation may have been higher (less negative) at the time of this study than the inferred estimate of -80 permil.
2. The D and ^{18}O contents of regional ground water at the study site may be higher than represented by well 14S/20E-34G1. D and ^{18}O contents are reported to be higher in some wells several kilometers from the study area (Shelton and Miller, 1991).
3. Recharge in the basin might be occurring during periods when the basin's water has undergone less evaporation, such as during the winter; as a result, ^{1}H and ^{16}O concentrations ordinarily would be considerably higher (^{2}H and ^{18}O would be lower) than during summer when the basin was sampled. It is reasonable that recharge should be much greater following winter storms when the basin was observed by the author to be fuller than during the dry summer season when it contains less water.

Although the relative importance of each of the above explanations cannot be evaluated without frequent monitoring over a period of time, the fact that δD and $\delta^{18}O$ values in the monitor wells generally are less negative than in other wells in the Fresno area argues strongly that recharge from the basin is reaching the water table locally.

The stable-isotope data, together with the tritium data, suggest that basin recharge is comparable in importance at the study site to regional ground-water flow from the Sierra Nevada foothills, so that any storm-runoff contaminants not effectively removed by the soil beneath the basin should be easily detectable by means of shallow monitor wells such as those that were installed for this study. Nevertheless, the sparse isotope data presented do not support quantitatively apportioning ground water at the monitor wells between regional flow and basin recharge. Apart from the limitations discussed above, seasonal and annual isotope variations in precipitation are likely to be quite large. For example, mean annual tritium concentration in precipitation during 1980-81 is nearly double that of the near-record wet period of 1982-83 (Michel, 1989). Also, mean annual δD in precipitation was found to vary as much as 40 permil between 1981 and 1989 at some sites in a monitoring network that included 32 locations in southeastern California and adjacent parts of Nevada and Arizona (Friedman and others, 1992).

MAJOR IONS AND TRACE ELEMENTS

Comparison between water samples from the recharge basin and the monitor wells (table 6), and comparison of both with regional ground-water composition listed in table 1, reveals little difference in such broad measures of water quality as dissolved-solids concentration and specific conductance. For chloride, which is an ideal unreactive tracer (as are isotopes), differences are larger but still too small to be useful. Although differences are large for silica and bicarbonate (alkalinity), precipitation and dissolution reactions make both unsuitable as tracers. Of the major ions, potassium (K) is the most useful indicator of whether cationic contaminants in the recharge basin reach the water table. Aqueous potassium concentrations are about 5 times higher in the recharge basin than in either regional ground water (table 1) or the nearby monitor wells (table 6)—indicating that there is no discernible transport of this cation to the water table. Profiles of dissolved- and exchangeable-cation concentrations beneath a recharge basin in the city of Fresno show that removal of dissolved potassium in percolating recharge water occurs through ion-exchange reactions with clay minerals in the soil (Nightingale, 1989).

Zinc is potentially an even more sensitive surrogate than is potassium, as the concentration of zinc is more than 100 times higher in the recharge basin than in the monitor wells (table 6). Motor vehicles, and especially motor oil, have been implicated as the major source of zinc in the urban environment (Wigington and others, 1983). The reason for such a large enrichment (comparative concentration ratio) for aqueous zinc in the recharge basin is unknown; however, it may be related partly to its role as a biological micronutrient and partly to its greater solubility than other heavy metals with large anthropogenic inputs (Harter, 1983; Wigington and others, 1983). (These same reasons can be used to explain the high concentrations of potassium.) In any case, because the available data show that trace metals in urban runoff have not affected ground-water quality at this site, monitoring for zinc would be very effective in demonstrating continued absence of impairment by trace-metal cations.

ORGANIC PRIORITY POLLUTANTS AND PESTICIDES

Water from the recharge basin and from monitor wells was analyzed for three gross organic indicators: tannin and lignin, total phenols, and methylene blue active surfactant (MBAS) detergents. All were reported present in the recharge basin and some also were detected in the monitor wells (table 6). However, the baseline for colorimetic detection of these analytes in dissimilar waters is likely to be variable and is sufficiently uncertain that their reported detection at very low levels in the monitor-well samples is not conclusive evidence for their actual presence (that is, the levels detected likely represent "false positives").

Several groups of synthetic organic chemicals also were analyzed: purgeable and extractable priority pollutants, organochlorine compounds, and organophosphorous insecticides. Only a few were found and, because their reported aqueous concentrations were at the laboratory reporting limit, their presence should not be inferred without further sampling.

Organic (and trace-metal) concentrations generally are much higher in sediments than in water and, for this reason, the sediment (soils) data presented in the next section of this report provide a much more sensitive indicator of organic contaminant migration than do the aqueous-phase data.

CHEMICAL CONCENTRATIONS IN SEDIMENT AND SOIL

Chemical analysis of sediment beneath the recharge basin and of soil from test holes provides this study with the strongest evidence that sorption by the solid phase is a very effective mechanism for removal of inorganic and organic contaminants, and that only a very small fraction of the available capacity for removal is used after a few years. Results of these analyses are presented in tables 7 to 10, and in table 14 (results reported in table 14 are discussed later, in the "Laboratory Elutriation Experiments" section). The results given in these tables indicate marked attenuation in concentration of numerous elements and synthetic organic chemicals within the top few centimeters beneath the recharge basin.

INORGANIC ELEMENTS

The determination of "background levels" is more difficult for inorganic elements than for synthetic organic chemicals; whereas the former occur naturally in variable concentrations, the latter are completely absent in soil and sediment known to be free of human influence.

Comparisons of trace-element data show that natural variability far exceeds any differences resulting from sampling and analytical imprecision. The range in concentration for 43 elements analyzed in five soil cores from test hole 1 exceeds 10 percent for all 32 of the elements whose concentrations exceed reporting limits (table 7). This contrasts markedly with the nearly identical concentrations measured for sediment samples collected immediately adjacent to one another from depths of 0 to 1 cm (table 8) and 120 to 150 cm (tables 8 and 9) at site 5 in the recharge basin. For the highly contaminated surficial samples, measurable concentrations are identical for 20 elements and differ by more than 10 percent for only 4 elements (molybdenum, potassium, thorium, and ytterbium). For the background-level

Table 7. Concentrations of elements and radioisotopes in soil cores from test hole 1 adjacent to the recharge basin

[Element concentrations in micrograms per gram dry weight and radioisotope concentrations in disintegrations per minute per gram dry weight. --, no data; <, less than indicated reporting limit]

Element/isotope	Symbol	Concentration				
		Depth (meters below land surface)				
		4.9-5.5	5.5-5.8	5.8-6.2	6.2-6.4	10.9-11.3
Aluminum	Al	69,000	73,000	82,000	70,000	89,000
Arsenic	As	1.2	4.5	9.5	3.9	4.2
Barium	Ba	1,000	900	830	820	510
Beryllium	Be	1	1	2	1	<1
Bismuth	Bi	<10	<10	<10	<10	<10
Boron	B	<0.4	<.4	<.4	<.4	1.9
Cadmium	Cd	<2	<2	<2	<2	<2
Calcium	Ca	17,000	18,000	23,000	19,000	24,000
Cerium	Ce	35	50	63	54	37
Chromium	Cr	16	20	26	29	140
Cobalt	Co	4	7	9	6	19
Copper	Cu	4	8	12	6	26
Europium	Eu	<2	<2	<2	<2	<2
Gallium	Ga	12	14	16	13	16
Gold	Au	<8	<8	<8	<8	<8
Holmium	Ho	<4	<4	<4	<4	<4
Iron	Fe	13,000	23,000	25,000	23,000	38,000
Lanthanum	La	21	29	36	31	19
Lead	Pb	24	19	23	16	14
Lithium	Li	11	17	24	14	30
Magnesium	Mg	3,400	5,700	8,200	5,200	15,000
Manganese	Mn	230	400	560	390	590
Mercury	Hg	<.02	<.02	<.02	<.02	<.02
Molybdenum	Mo	<2	<2	<2	<2	<2
Neodymium	Nd	14	20	25	22	18
Nickel	Ni	7	10	12	10	140
Niobium	Nb	5	9	11	8	5
Phosphorus	P	300	400	800	300	300
Potassium	K	30,000	29,000	28,000	27,000	18,000
Scandium	Sc	3	5	8	4	14
Selenium	Se	<.2	<.2	<.2	<.2	<.2
Silver	Ag	<2	<2	<2	<2	<2
Sodium	Na	22,000	23,000	26,000	23,000	19,000
Strontium	Sr	360	350	380	350	280
Tantalum	Ta	<40	<40	<40	<40	<40
Thorium	Th	7.74	13.9	19.3	12.8	4.7
Tin	Sn	<10	<10	<10	<10	<10
Titanium	Ti	1,300	2,100	3,000	2,100	3,100
Uranium	U	1.57	3.10	3.52	2.53	2.24
Vanadium	V	29	54	63	56	91
Ytterbium	Yb	<1	1	2	2	2
Yttrium	Y	9	13	18	14	17
Zinc	Zn	22	38	53	33	69
Lead-210	$^{210}\mathrm{Pb}$	2.01±.24	--	--	2.95±.32	--
Radium-226	$^{226}\mathrm{Ra}$	1.43±.05	--	--	2.70±.21	--
Lead-210 excess	$^{210}\mathrm{Pb}_{xs}$	.58±.25	--	--	.25±.38	--

Table 8. Concentrations of chemical constituents and radioisotopes in surface (0-1 cm) sediment from six sites in the recharge basin

[Chemical concentrations in micrograms per gram dry weight; radioisotope concentrations in disintegrations per minute per gram dry weight. GC-FID, gas chromatography with flame-ionization detection. cm, centimeter; --, no data; <, less than indicated reporting limit]

Constituent	Symbol (where applicable)	Concentration at site:						
		1	2	3	4	5[1]	5[1]	6
Aluminum	Al	59,000	66,000	70,000	71,000	70,000	70,000	72,000
Arsenic	As	5.3	17	6.9	9.0	18	17	16
Barium	Ba	580	650	680	680	640	680	680
Beryllium	Be	1	1	1	1	1	1	<1
Bismuth	Bi	<10	<10	<10	<10	<10	<10	<10
Boron	B	7.9	5.6	5.4	3.6	3.9	3.9	4.3
Cadmium	Cd	<2	<2	<2	<2	<2	<2	<2
Calcium	Ca	28,000	27,000	22,000	19,000	17,000	17,000	17,000
Cerium	Ce	42	46	52	53	54	53	54
Chromium	Cr	44	59	61	71	83	84	86
Cobalt	Co	10	10	13	14	17	17	17
Copper	Cu	63	74	64	97	140	140	130
Europium	Eu	<2	<2	<2	<2	<2	<2	<2
Gallium	Ga	12	13	15	16	16	16	17
Gold	Au	<8	<8	<8	<8	<8	<8	<8
Holmium	Ho	<4	<4	<4	<4	<4	<4	<4
Iron	Fe	22,000	23,000	30,000	34,000	38,000	39,000	40,000
Lanthanum	La	24	26	30	31	31	31	32
Lead	Pb	91	92	110	130	170	170	160
Lithium	Li	20	24	33	37	45	45	46
Magnesium	Mg	10,000	11,000	12,000	12,000	14,000	14,000	14,000
Manganese	Mn	490	490	600	560	640	650	650
Mercury	Hg	.07	.06	.10	.11	.22	.23	.19
Molybdenum	Mo	2	<2	3	3	6	5	6
Neodymium	Nd	17	17	21	21	20	20	20
Nickel	Ni	31	33	43	51	66	68	68
Niobium	Nb	8	7	8	7	7	7	8
Phosphorus	P	1,500	1,200	1,500	1,800	2,200	2,300	2,400
Potassium	K	19,000	21,000	22,000	22,000	18,000	21,000	22,000
Scandium	Sc	6	7	9	9	10	10	10
Selenium	Se	.4	.6	.5	.7	1.0	1.0	.9
Silver	Ag	<2	<2	<2	<2	<2	<2	<2
Sodium	Na	20,000	20,000	18,000	16,000	13,000	13,000	13,000
Strontium	Sr	410	370	340	290	270	270	270
Tantalum	Ta	<40	<40	<40	<40	<40	<40	<40
Thorium	Th	12.7	12.3	19.7	21.4	20.6	30.1	25.1
Tin	Sn	<10	<10	<10	<10	<10	<10	<10
Titanium	Ti	2,300	2,500	2,900	3,000	2,900	3,100	3,200
Uranium	U	5.08	4.64	4.78	5.70	11.6	11.3	10.0
Vanadium	V	59	64	75	83	94	94	97
Ytterbium	Yb	1	1	2	2	1	2	2
Yttrium	Y	13	13	14	14	14	14	14
Zinc	Zn	590	490	510	750	1,200	1,200	1,200
Nitrite+nitrate (as N)		10	23	11	7	8	--	3
Ammonium (as N)		1,800	1,400	830	1,400	1,100	--	990
Phosphorus (as P)		2,000	1,700	1,800	1,900	87	--	2,800
Organic carbon (as C)		170,000	95,000	100,000	130,000	160,000	--	150,000

Footnote at end of table.

Table 8. Concentrations of chemical constituents and radioisotopes in surface (0-1 cm) sediment from six sites in the recharge basin--*Continued*

Constituent	Symbol (where applicable)	Concentration at site:						
		1	2	3	4	5[1]	5[1]	6
Inorganic carbon (as C)		200	100	100	100	200	--	300
Oil and grease		24,000	13,000	17,000	16,000	22,000	--	20,000
GC/FID (as $C_{10}D_8$ equivalents)		370	370	1,300	1,400	1,500	--	2,700
Aldrin		<.0005	<.001	<.001	<.001	<.0005	--	<.0005
Lindane		.001	<.0011	<.0011	.0011	.0011	--	<.0005
Chlordane		.13	.14	.64	.20	.21	--	.18
DDD		.064	.005	.060	.005	.035	--	.032
DDE		.065	.043	.070	.071	.040	--	.077
DDT		.0050	.0041	<.0011	.012	<.0005	--	<.0005
Dieldrin		.0021	.0041	.0051	.0061	<.0005	--	.0015
Endosulfan		--	--	<.001	--	--	--	<.0005
Endrin		<.0005	<.0011	<.0011	<.0011	<.0005	--	<.0005
Heptachlor		.0025	.0031	.0031	.0031	.0021	--	.0031
Heptachlor expoxide		<.0005	<.0011	<.0001	<.0011	<.0051	--	<.0005
PCB		.031	.021	.033	.030	.039	--	.040
PCN		<.005	<.010	<.010	<.010	<.005	--	<.005
Lead-210	^{210}Pb	5.18±.17	5.40±.18	6.92±.21	8.81±.29	10.1±.3	--	10.9±.3
Radium-226	^{226}Ra	2.70±.10	3.03±.11	3.33±.12	4.71±.18	5.10±.15	--	5.15±.19
Lead-210 excess	$^{210}\text{Pb}_{XS}$	2.48±.20	2.37±.21	3.59±.24	4.09±.34	5.00±.34	--	5.75±.36

[1] Two adjacent samples at site 5 were analyzed.

samples from the deepest interval, measurable concentrations are identical for 13 elements and differ by more than 10 percent for only 3 elements (nickel, niobium, and thorium).

Such small differences between duplicate sediment analyses provides strong evidence that the much larger site-to-site differences in surface sediments from the recharge basin (table 8) are real. Many of the trace elements whose concentrations are highest at the surface have concentrations at sites 5 and 6 that are about double those at sites 1 and 2. This trend of increasing concentration toward the south end of the recharge basin and away from the discharge pipe is consistent with a similar trend of increasing percentage of clay (table 5) to which these contaminants could be expected to adsorb.

Although the sediment at site 5 shows a marked decrease in many chemical concentrations with increasing depth (table 9 and fig. 4), the rather large variability in natural abundances and sharp change in lithology (from fine to coarse sediment) several centimeters below the recharge basin makes the assignment of background values somewhat uncertain. This variability in background concentrations is especially evident from the chemical differences between soil cores at five different depths (table 7), all of which must represent uncontaminated natural conditions. The concentrations of several elements are highest in the core interval from 10.9 to 11.3 m, which likely is related to the increased proportion of clay and silt in this sample relative to the other four samples (table 4). Radium-226 provides similar evidence of natural variability that probably implies differences in mineral assemblage. Concentrations of this naturally occurring radioisotope differ substantially between two of the soil cores (table 7), between the six surface-sediment sites in the recharge basin (table 8), and at different subbottom depths from site 5 beneath the recharge basin. On the basis of the particle-size distributions and selected chemical concentrations, as was noted in the section "Sampling of Sediments from the Recharge Basin," it was concluded that recharge-basin sediment below 16 cm is chemically most similar to soil between 5.5 and 5.8 m in test hole 1. However, the fact that chemical concentrations for a number of elements vary by a factor of 2 or more in uncontaminated soil from various depths in test hole 1 indicates that "background" for fine-grained basin deposits above 16 cm may be quite different from "background" for coarse-

Table 9. Concentrations of chemical constituents and radioisotopes in sediment and substrata at site 5 in the recharge basin

[Chemical concentrations in micrograms per gram dry weight; isotope concentrations in disintegrations per minute per gram dry weight. Data from 0-1 cm also are given in table 8. cm, centimeter; ~, approximate value; --, no data; <, less than indicated reporting limit]

Constituent	Symbol (where applicable)	Depth interval below recharge basin (cm)									
		0-1^{1}	0-1^{1}	1-2	2-4	4-8	8-16	16-32	32-64	120-150^{1}	120-150^{1}
Aluminum	Al	70,000	70,000	79,000	82,000	86,000	82,000	75,000	76,000	74,000	73,000
Arsenic	As	18	17	13	9.5	3.7	1.2	1.0	1.2	1.1	1.2
Barium	Ba	640	680	740	800	900	840	800	790	770	780
Beryllium	Be	1	1	1	1	2	2	1	1	1	1
Bismuth	Bi	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Boron	B	3.9	3.9	2.4	1.4	<.4	<.4	<.4	<.4	<.4	<.4
Cadmium	Cd	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Calcium	Ca	17,000	17,000	17,000	21,000	24,000	23,000	21,000	21,000	21,000	20,000
Cerium	Ce	54	53	63	67	66	58	59	52	56	55
Chromium	Cr	83	84	87	54	24	26	21	21	23	22
Cobalt	Co	17	17	17	13	10	8	6	6	6	6
Copper	Cu	140	140	120	52	13	10	6	5	6	6
Europium	Eu	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Gallium	Ga	16	16	18	18	17	16	14	14	13	14
Gold	Au	<8	<8	<8	<8	<8	<8	<8	<8	<8	<8
Holmium	Ho	<4	<4	<4	<4	<4	<4	<4	<4	<4	<4
Iron	Fe	38,000	39,000	44,000	34,000	22,000	19,000	19,000	18,000	24,000	23,000
Lanthanum	La	31	31	36	39	39	33	36	29	32	31
Lead	Pb	170	170	160	88	22	19	19	18	19	18
Lithium	Li	45	45	53	39	27	21	15	15	13	14
Magnesium	Mg	14,000	14,000	15,000	12,000	9,800	7,500	5,500	5,400	5,000	5,100
Manganese	Mn	640	650	700	620	550	450	370	350	370	370
Mercury	Hg	.22	.23	.22	.13	<.02	<.02	<.02	<.02	<.02	<.02
Molybdenum	Mo	6	5	4	<2	<2	<2	<2	<2	<2	<2
Neodymium	Nd	20	20	25	26	27	23	24	21	23	23
Nickel	Ni	66	68	70	39	12	11	10	10	9	8
Niobium	Nb	7	7	7	10	12	9	8	8	10	9
Phosphorus	P	2,200	2,300	2,100	1,200	1,000	700	500	500	300	300
Potassium	K	18,000	21,000	24,000	26,000	31,000	27,000	27,000	28,000	27,000	27,000
Scandium	Sc	10	10	11	10	9	7	5	5	5	5
Selenium	Se	1.0	1.0	<1.0	.8	<.2	<.2	<.2	<.2	<.2	<.2
Silver	Ag	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Sodium	Na	13,000	13,000	13,000	21,000	27,000	27,000	25,000	25,000	25,000	25,000
Strontium	Sr	270	270	280	340	410	400	380	380	370	370
Tantalum	Ta	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40
Thorium	Th	20.6	30.1	29.9	23.6	25.9	15.2	15.6	12.8	13.2	17.6

Footnote at end of table.

Table 9. Concentrations of chemical constituents and radioisotopes in sediment and substrata at site 5 in the recharge basin—*Continued*

Constituent	Symbol (where applicable)	Depth interval below recharge basin (cm)									
		0-1[1]	0-1[1]	1-2	2-4	4-8	8-16	16-32	32-64	120-150[1]	120-150[1]
Tin	Sn	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Titanium	Ti	2,900	3,100	3,500	3,500	3,300	2,800	2,200	2,100	2,200	2,200
Uranium	U	11.6	11.3	8.73	4.81	3.11	3.32	2.98	3.09	3.20	
3.08											
Vanadium	V	94	94	100	84	59	51	50	47	58	56
Ytterbium	Yb	1	2	2	2	2	2	2	2	2	2
Yttrium	Y	14	14	15	17	18	16	15	14	15	15
Zinc	Zn	1,200	1,200	760	390	71	49	31	33	33	30
Nitrite+nitrate (as N)		8	--	<2	<2	<2	3	2	3	9	--
Ammonium (as N)		1,100	--	960	560	230	97	32	170	1.2	--
Organic nitrogen (as N)		--	--	--	--	--	43	--	--	--	--
Phosphorus (as P)		87	--	2,600	990	1,300	730	690	760	470	--
Organic carbon (as C)		160,000	--	150,000	50,000	800	~600	~200	~900	~100	--
Inorganic carbon (as C)		200	--	300	200	100	<100	<100	<100	<100	--
Oil and grease		22,000	--	24,000	11,000	1,000	<1,000	<1,000	<1,000	<1,000	--
GC/FID (as $C_{10}D_8$ equivalents)		1,500	--	600	380	4.2	1.7	2.9	1.2	5.7	--
Aldrin		<.0005	--	<.0011	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	--
Lindane		.0011	--	.0071	.0032	.0003	<.0001	<.0001	<.0001	<.0001	--
Chlordane		.21	--	.35	.20	.001	.001	<.001	<.001	<.001	--
DDD		.035	--	.055	.067	<.0001	--	<.0001	<.0001	<.0001	--
DDE		.040	--	.072	.048	.0004	.0001	<.0001	<.0001	<.0001	--
DDT		<.0005	--	.10	.0021	.0001	<.0001	<.0001	<.0001	<.0001	--
Dieldrin		<.0005	--	.055	<.0001	.0001	<.0001	<.0001	<.0001	<.0001	--
Endosulfan		--	--	<.001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	--
Endrin		<.0005	--	.085	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	--
Heptachlor		.0021	--	.0021	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	--
Heptachlor expoxide		<.0051	--	<.0011	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	--
PCB		.039	--	.06	.04	<.001	<.001	<.001	<.001	<.001	--
PCN		<.005	--	<.01	<.001	<.001	<.001	<.001	<.001	<.001	--
Lead-210	^{210}Pb	10.1±.3	--	9.19±.23	6.68±.19	2.42±.11	2.17±.09	2.57±.10	2.57±.10	2.71±.11	--
Radium-226	^{226}Ra	5.10±.15	--	3.54±.11	3.92±.11	2.48±.09	2.53±.08	2.58±.08	2.27±.07	2.29±.07	--
Lead-210 excess	$^{210}Pb_{xs}$	5.00±.34	--	5.65±.25	2.76±.22	-.06±.14	-.36±.12	-.01±.13	.30±.12	.41±.13	--

[1] Analysis of two samples collected next to one another.

Table 10. Concentrations of extractable priority pollutants, organochlorine compounds, and organophosphorus insecticides in sediment from depths of 0-1 and 8-16 cm at site 5 in the recharge basin

[Concentrations in micrograms per gram dry weight. cm, centimeter; ; <, less than indicated reporting limit]

Organic constituent	Concentration	
	0-1 cm	8-16 cm
Extractable Priority Pollutants		
Acenaphthylene	<0.2	<0.2
Acenaphthene	<.2	<.2
Anthracene	.46	<.2
Benzo (a) arthracene	3.9	<.2
Benzo (b) arthracene	9.2	<.4
Benzo (k) fluoranthene	6.4	<.4
Benzo (g,h,i) perylene	11	<.4
Benzo (a) pyrene	6.5	<.4
bis (2-Chloroethyl) ether	<.2	<.2
bis (2-Ethylhexyl) phthalate	6.2	<.2
Chrysene	9.7	<.4
Diethylphthalate	<.2	<.2
Dimethylphthalate	<.2	<.2
di-n-Butyl phthalate	<.2	<.2
Fluoranthene	9.4	<.2
Fluorene	<.2	<.2
Hexachlorobenzene	<.2	<.2
Hexachlorobutadiene	<.2	<.2
Hexachlorocyclopentadiene	<.2	<.2
Hexachloroethane	<.2	<.2
Indeno (1,2,3,ed) pyrene	9.5	<.2
Isophorone	<.2	<.2
n-Nitrosodi-n-propylamine	<.2	<.2
n-Nitrosodiphenylamine	<1.5	<.2
n-Nitrosodimethylamine	<.2	<.2
Naphthalene	.15	<.2
Nitrobenzene	<.2	<.2
p-Chloro-m-cresol	<.6	<.6
Phenanthrene	2.7	<.2
Pyrene	15	<.2
1,2-Dichlorobenzene	<.2	<.2
1,2,4-Trichlorobenzene	<.2	<.2
1,2,5,6-Dibenzanthracene	<.4	<.4
1,3-Dichlorobenzene	<.2	<.2
1,4-Dichlorobenzene	<.2	<.2
2-Chloronaphthalene	<.2	<.2
2-Chlorophenol	<.2	<.2
2-Nitrophenol	<.2	<.2
Di-n-octylphthalate	<.4	<.4
2,4-Dichlorophenol	<.2	<.2
2,4-Dinitrotoluene	<.2	<.2
2,4-Dinitrophenol	<.6	<.6
2,4,6-Trichlorophenol	<.6	<.6
2,6-Dinitrotoluene	<0.2	<0.2
4-Bromophenyl phenyl ether	<.2	<.2
Chlorophenyl phenyl ether	<.2	<.2
4-Nitrophenol	<1.2	<.6
4,6-Dinitro-o-cresol	<.6	<.6
Phenol	<.2	<.2
Pentachlorophenol	<.6	<.6
Organochlorine Compounds		
Aldrin	<0.0005	<0.0001
Lindane	.0011	<.0001
Chlordane	.21	.001
DDD	.035	--
DDE	.040	.0001
DDT	<.0005	<.0001
Dieldrin	<.0005	<.0001
Endosulfan	--	<.0001
Endrin	<.0005	<.0001
Ethion	<.0005	<.0001
Toxaphene	<.05	<.01
Heptachlor	.0021	<.0001
Heptachlor epoxide	.0051	<.0002
Methoxychlor	<.025	<.0001
Mirex	<.0005	<.0001
Perthane	<.005	<.001
PCB	.039	<.001
PCN	<.005	<.001
Organophosphorous Insecticides		
Malathion	<0.0005	<0.0001
Parathion	<.0005	<.0001
Diazinon	<.0005	<.0001
Methyl parathion	<.0005	<.0001
Methyl trithion	<.0005	<.0001
Trithion	<.0005	<.0001
Chlorophenoxy Acid Herbicides		
2,4-D	<0.0001	<0.0001
Dicamba	<.0001	<.0001
2,4-DP	<.2	<.2
Pichloram	<.0001	<.0001
Silvex	<.0001	<.0001
2,4,5-T	<.0001	<.0001

grained basin deposits below 16 cm. Sampling of near-surface soil in the vicinity of the study basin that could have established more suitable background levels for the shallower basin sediment was not done. Extensive tilling and grading in the area indicated that nearby soil would not have been suitable for direct comparison because reworking is likely to have mixed contaminated (by atmospheric deposition) and uncontaminated soil, and soil of differing texture, in variable proportions.

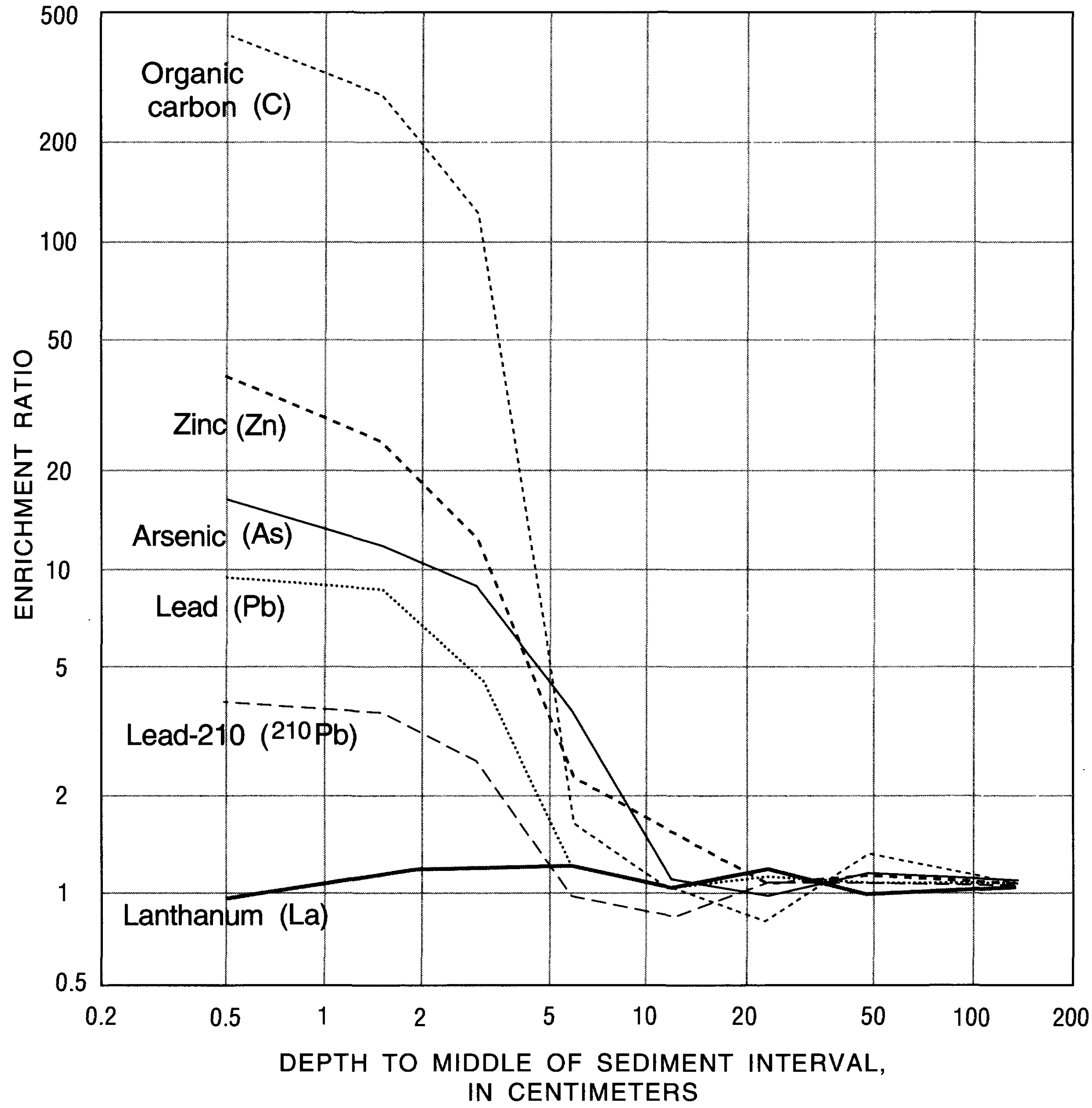

Figure 4. Enrichment ratios for selected constituents in subbottom sediment at site 5 in the recharge basin.

ORGANIC CHEMICALS

The results for organic carbon, oil and grease, GC-FID organic carbon, and organochlorine compounds in near-surface (0-1 cm) sediments at the six recharge-basin sites are given in table 8. Table 9 gives results for the same suite of organic constituents with increasing subbottom depth at site 5. Results for analysis of extractable priority pollutants, organochlorine compounds, organophosphorus insecticides, and chlorophenoxy-acid herbicides at depths of 0 to 1 cm and 8 to 16 cm at site 5 are given in table 10. The pattern of results for organic chemicals generally is similar to that shown by inorganic elements, although there exists considerably less uniformity in either the areal trend (table 8) or the profile (table 9) for the organic chemical constituents. No pesticides were detected below 16 cm at site 5, and only two, chlordane and DDE, were identified (at their reporting limits of 0.001 μg/g and 0.0001 μg/g, respectively) in sediment from the 8- to 16-cm interval.

The only pesticides that were found in basin sediment are the long-lived organochlorine compounds. It was anticipated that some of the more widely used organophosphorus insecticides, on the basis of their abundance in rainfall and runoff (Oltmann and Shulters, 1989), also might be present in sediment, but none were detected (table 10). Similarly, their absence in sediment from five recharge basins in residential and commercial catchments during the Fresno NURP study was attributed to probable degradation (Nightingale, 1987c). A large number of phosphorus-containing organic compounds were reported during the gas-chromatographic analyses for this study, but they could not be specifically identified because of poor resolution and many interferences (M.P. Schroeder, USGS, oral commun., 1987). High organic content and the anaerobic nature of the sediment—which made cleanup of the sample extracts difficult and may have interfered with detection of organophosphorus insecticides—is the cause of the variable analytical reporting limits for the organochlorine compounds that are listed in the tables.

Chlordane was the organochlorine compound reported in highest concentration, a finding similar to that obtained during monitoring for the NURP study (Oltmann and Shulters, 1989). However, one of the more puzzling results obtained by this study is the finding of DDT itself as opposed to only its metabolites, DDD and DDE, which are more commonly present in environmental samples today. The highest DDT concentration of 0.10 µg/g was found not in surface sediment but rather in sediment from a depth of 1 to 2 cm at site 5. Use of DDT was banned in the United States about 10 years prior to the Fresno NURP study and the operation of this recharge basin in its present configuration. Confirmation of DDT's presence is strong, as shown by its detection in several of the sediment samples analyzed (tables 8 and 9). Furthermore, the Fresno NURP study found that DDT concentrations consistently exceeded DDD and DDE concentrations in street sweepings from residential, commercial, and industrial catchments (Oltmann and Shulters, 1989).

Of 50 extractable organic priority pollutants analyzed, 13—including 12 polycyclic aromatic hydrocarbons and 1 phthalate ester—were detected in surficial sediment from site 5 (table 10). None were detected in sediment from the 8- to 16-cm interval. Total concentration of all the identified organic compounds in the surficial interval is slightly less than 100 µg/g, nearly all of which consists of the polycyclic aromatic hydrocarbons listed in table 10. Comparison with data given in table 9 shows that this represents only about 5 percent of the organic carbon reported by the GC-FID analysis, and less than 0.1 percent of total organic carbon. Although two additional polycyclic aromatic hydrocarbons (dimethyl-substituted napthalenes) and at least 20 compounds belonging to the broad classes of alkanes and alkenes (or cycloalkanes) were identified by GC-FID analysis, virtually all the organic matter in the basin sediment remains uncharacterized. It seems likely that much of it may be generated by biological activity in the overlying water column; however, the organic nitrogen data that might have supported this assertion with the observation of low carbon/nitrogen ratios are lacking because all sediment samples but one listed in table 9 were accidentally destroyed in the laboratory during analysis.

ASSESSMENT OF ANTHROPOGENIC INPUTS

Chemical profiles that show a decrease in concentration with increasing sediment depth not only are strong evidence for sorptive removal of contaminants but also can be used, with some assumptions, to quantify the relative importance of anthropogenic (human-related) and natural (background) sources. The concept of enrichment ratios, defined herein as the concentration in a particular sediment interval divided by the mean concentration for all intervals below a depth of 16 cm (considered background concentration), is useful for this discussion. Profiles of enrichment ratios for selected constituents are shown in figure 4. If the surficial (0 to 1 cm) sediment is presumed to represent the combined inputs of current anthropogenic and natural sources, then decreases below this depth represent removal of contaminants, and possibly dilution by mixing with deeper soil that is free of anthropogenic influence. As expected, for rare-earth elements such as lanthanum, which has very few industrial uses, the concentration profile shows no change and represents only the natural abundance of this element. Two other rare earths that are present above reporting limits, cerium and neodymium, also show no change in concentration with depth (table 9).

Surface-enrichment ratios for all elements were calculated and are reported to the nearest whole number in table 11 for those values that differ from 1. These values include about half the elements analyzed. For those elements not listed in table 11, either there is no anthropogenic source or (1) concentrations are uniformly below detection, (2) natural levels are so high that they mask any anthropogenic input, or (3) variability in mineralogy or lithology exerts the predominant influence on concentrations. Just as an enrichment ratio of 1 does not preclude an anthropogenic component—conversely, an

Table 11. Surface-enrichment ratios for selected elements and radioisotopes in sediment at site 5 in the recharge basin

[Surface-enrichment ratio is concentration of 0-1 centimeter interval divided by mean concentration of all intervals below 16 centimeter. >, greater than indicated value]

Constituent	Symbol	Enrichment ratio
Arsenic	As	16
Boron	B	>9
Chromium	Cr	5
Cobalt	Co	3
Copper	Cu	25
Iron	Fe	2
Lead	Pb	9
Lithium	Li	3
Magnesium	Mg	3
Maganese	Mn	2
Mercury	Hg	>11
Molybdenum	Mo	>2
Nickel	Ni	7
Phosphorus	P	5
Scandium	Sc	2
Selenium	Se	>5
Thorium	Th	2
Uranium	U	4
Vanadium	V	2
Zinc	Zn	38
Lead-210	^{210}Pb	4
Radium-226	^{226}Ra	2

enrichment ratio greater than 1 is not necessarily conclusive proof of anthropogenic contamination, especially when these ratios are low. Such results could be an artifact of natural variability, as already discussed, or the results could be unique to the geochemical behavior of individual elements.

Despite these limitations on interpretation, it is clear from some of the very large enrichment ratios listed in table 11 that anthropogenic fluxes to the recharge basin far exceed natural fluxes for several trace metals that are in widespread industrial use. Results for three elements at this recharge basin (copper=25, lead=9, and zinc=38) can be compared with the enrichment ratios for these same elements (Cu=6, Pb=15, and Zn=5) in sediment from Irondequoit Bay, New York (Schroeder, 1985), which also was one of the NURP study sites (Kappel and others, 1986).

The results for four elements (As, Cu, Pb, and Ni) from this study also can be compared with those from a previous investigation at five other recharge basins in the city of Fresno, the oldest of which has been in use for about 20 years. The five basins are in predominantly residential catchments that include some commercial land use and minimal industry. Surface-enrichment ratios, calculated by comparing published data for depths of 0-2 and 90-120 cm in the five basins (Nightingale, 1987b), range from 1 to 18 for arsenic, 3 to 13 for copper, 60 to 400 for lead, and 2 to 4 for nickel. Values for this study (table 11) are arsenic = 16, copper = 25, lead = 9, and nickel = 7. Enrichments are greater for the trace metals copper and nickel and much less for lead in the industrial catchment in comparison with the residential/commercial catchments, a pattern which is similar to that found during direct monitoring of runoff in the NURP study (Oltmann and Shulters, 1989).

Surface-enrichment ratios can be calculated similarly for organic priority pollutants and organochlorine compounds; however, the calculations yield only minimum estimates of 10^2 and 10^3, respectively, because these compounds are below detection levels in the deeper sediment. Organic carbon, analyzed by combustion and by GC-FID (fig. 4 and table 9), also yields surface-enrichment ratios of almost 10^3; for organic carbon, detectable concentrations exist below 16 cm for both methods of analysis.

The data presented and the foregoing discussion indicate that a wide variety of trace elements and synthetic organic chemicals from the industrial catchment are removed within the top 16 cm of sediment in the recharge basin. Given the existence of nearly 8 m of soil between the basin and the water table and such effective removal of contaminants for the 4 years of operation in the basin's current configuration (since last scraped), local ground-water quality should be afforded protection during continued operation of the basin for a very long time. A similar inference can be made on the basis of results of studies at five other recharge basins in the city of Fresno (Nightingale, 1987a,b,c, and 1989)—although it was suggested by Nightingale (1989) that periodic monitoring of organic contaminants in soil would be advisable because of their known presence in storm runoff.

LABORATORY ELUTRIATION EXPERIMENTS

The potential for movement of urban-runoff contaminants through the unsaturated zone can be evaluated by means of laboratory experiments that simulate processes of sorption from the aqueous onto the solid phase and desorption from the solid into the aqueous phase. Both types of experiments were done for this study. As conducted, the experiments were intended to provide only a qualitative rather than a quantitative assessment. They were adapted from

Table 12. Chemical concentrations in water from the recharge basin equilibrated (mixed for 0, 1, 2, and 4 days) with surface (0-1 centimeter) sediment from near site 5 in the recharge basin

[Water from recharge basin collected April 29, 1986, and stored frozen until beginning of laboratory experiment 4 months later. µS/cm, microsiemens per centimeter at 25° Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; --, no data; <, less than indicated reporting limit]

Constituent	Equilibration time			
	0 day	1 day	2 days	4 days
Specific conductance (µS/cm)	346	638	660	696
pH (standard units)	6.2	7.7	6.9	7.3
Calcium (mg/L)	8.0	29	25	29
Magnesium (mg/L)	5.0	--	--	13
Sodium (mg/L)	16	22	21	22
Potassium (mg/L)	26	--	--	30
Chloride (mg/L)	21	23	22	24
Sulfate (mg/L)	33	120	120	110
Silica (mg/L as SiO_2)	5.9	11	14	16
Alkalinity (mg/L as $CaCO_3$)	7	8	8	--
Ammonium (mg/L as N)	11	26	25	29
Kjeldahl nitrogen (mg/L as N)	15	48	42	41
Nitrate + nitrite (mg/L as N)	<.1	<.1	.2	<.1
Orthophosphate (mg/L as P)	5.0	2.7	3.5	4.2
Organic carbon (mg/L as C)	24	--	--	66
Arsenic (µg/L)	3	--	--	11
Boron ((µg/L)	80	--	--	620
Cadmium (µg/L)	1.4	--	--	.15
Chromium (µg/L)	2.2	--	--	2.1
Cobalt (µg/L)	.5	--	--	1.5
Copper (µg/L)	10.0	--	--	3.1
Iron (µg/L)	140	6,300	4,300	1,000
Lead (µg/L)	1.4	--	--	2.7
Manganese (µg/L)	40	370	330	290
Mercury (µg/L)	.1	--	--	<.1
Molybdenum (µg/L)	2	--	--	9
Nickel (µg/L)	5.7	--	--	10
Zinc (µg/L)	30	540	290	110
Tannin & lignin (mg/L as tannic acid)	4.3	--	--	9.0
Phenols (µg/L as phenol)	2	--	--	18
MBAS detergents (mg/L)	.09	--	--	.27

methods commonly used to determine sorption isotherms (Harter, 1983) and from elutriation tests used to determine short-term water-quality conditions associated with dredging operations (Fuhrer and Rinella, 1983; Palermo, 1986). In one set of experiments, samples of highly contaminated surface sediment from the recharge basin were mixed with water from the recharge pond to test the ability of the sediments to desorb contaminants into the water with which it is in contact. In another experiment, water from the recharge basin was mixed with clean soil from the unsaturated zone deep beneath the recharge basin to examine the potential for removal of aqueous contaminants by the soil.

Water for the experiment was collected from the recharge basin on April 29, 1986, and stored frozen until its use 4 months later. It generally was similar in composition to water collected from the basin on January 29, 1986, as indicated by comparison of chemical concentrations in tables 6 and 12 (in table 12, see values for zero-day equilibration time). The most obvious difference between the two samples is the absence of nitrate (plus nitrite, which likely is negligible) in the water used for the laboratory experiment. Although this difference may be a consequence of seasonal variations, it seems more likely that it is the result of biological degradation because the water used for the laboratory experiment

Table 13. Chemical concentrations in water from the recharge basin equilibrated (mixed for 4 days) with aquifer soil from 10.9-11.3 meters in test hole 1, in deionized water equilibrated (mixed for 4 days) with surface (0-1 centimeter) sediment from near site 5 in the recharge basin, and in a deionized-water blank

[μS/cm, microsiemens per centimeter at 25° Celsius; mg/L, milligrams per liter; μg/L, micrograms per liter; --, no data; <, less than indicated reporting limit. MBAS, methylene blue active surfactants.]

Constituent	Basin water equilibrated with aquifer soil	Deionized water equilibrated with basin sediment	Deionized-water blank
Specific conductance (μS/cm)	548	197	2
pH (standard units)	7.8	7.1	6
Calcium (mg/L)	35	10	<.1
Magnesium (mg/L)	18	5.0	<.1
Sodium (mg/L)	29	4.0	.4
Potassium (mg/L)	14	7.8	.3
Chloride (mg/L)	27	3.5	<.1
Sulfate (mg/L)	130	11	.2
Silica (mg/L as SiO_2)	38	9.9	<.1
Alkalinity (mg/L as $CaCO_3$)	139	82	2
Nitrite + nitrate (mg/L as N)	<.1	<.1	<.1
Ammonium (mg/L as N)	13	12	.03
Kjeldahl nitrogen (mg/L as N)	20	20	.7
Orthophosphate (mg/L as P)	2.1	3.9	.041
Organic carbon (mg/L as C)	39	16	--
Arsenic (μg/L)	35	12	<1
Boron (μg/L)	320	60	10
Cadmium (μg/L)	.66	.4	.02
Chromium (μg/L)	1.2	2.2	.06
Cobalt (μg/L)	10	1.0	<.20
Copper (μg/L)	4.5	4.5	--
Iron (μg/L)	150	850	10
Lead (μg/L)	.30	3.4	.20
Manganese (μg/L)	890	140	<10
Mercury (μg/L)	--	<.1	<.1
Molybdenum (μg/L)	18	5.0	<1
Nickel (μg/L)	58	8.6	<.5
Zinc (μg/L)	30	50	<10
Tannin & lignin (mg/L as tannic acid)	4.1	7.4	--
Phenols (μg/L as phenol)	6	4	--
MBAS detergents (mg/L)	.09	.36	--

was neither preserved with the mercuric chloride biocide nor filtered prior to its storage for later use.

One experiment was carried out by using a magnetic stirrer to continuously mix recharge-basin water and recharge-basin surficial sediment, in an approximately 10-to-1 gravimetric ratio, for as long as 4 days. The sediment-water slurry was contained in a covered, cylindrical glass chromatography jar and was continuously bubbled with nitrogen gas to maintain an oxygen-free environment throughout the experiment. Aliquots for chemical analysis were removed after 1, 2, and 4 days. The aliquots (also the initial, or zero-day, water) were centrifuged for 1 hour at 5,000 times gravity, but they were not filtered. Although the solutions appeared visually to be free of suspended solids, the possible presence of colloidal material cannot be excluded. The increase in specific conductance from 346 to 638 μS/cm after 1 day, and a smaller increase to only 696 μS/cm after 4 days (table 13) shows that dissolution is initially rapid and then slows.

Calcium and sulfate were the main contributors to the increase in specific conductance. Despite a very large increase in dissolved (supernatant after centrifugation) iron and manganese during the experiment, the increase in all other cationic trace-metal concentrations, with the exception of zinc, was comparatively modest. Most chemical concentrations changed little between days 1 and 4. Iron is an obvious exception—its concentration decreased from 6.3 to 1.0 mg/L during this period. Failure of the needle valve that regulated release of nitrogen gas several hours before termination of the experiment may have allowed entrance of some oxygen to the chamber, with the consequent precipitation of iron.

Increases were measured in tannin and lignin, total phenols, and MBAS detergents during the 4-day experiment. However, given the potential for analytical artifacts in the colorimetric methods used for these broad-indicator constituents (Wershaw and others, 1987), their precise concentrations and detection at these low concentrations is uncertain. Nightingale (1989) reported the movement of phenols in soil moisture beneath one recharge basin in the city of Fresno that had very coarse substrata. The solubility and negative polarity of phenols make them one of the few relatively mobile classes of compounds analyzed for in this study. However, specific phenols were not detected in sediment samples from the recharge basin (table 10) and, therefore, their presence and downward transport remain uncertain.

Surficial sediment for the laboratory experiment was taken from a location near site 5 in the recharge basin and was collected in a slightly different manner than was used for all other samples of surficial sediment described elsewhere in this report. Instead of removing the entire 1-cm-thick polygonal plate, the sample was obtained by scraping the sediment surface with a Teflon-coated spatula at several locations over a wide area near site 5. Chemical composition of this composite sample (table 14) is remarkably similar to composition of the duplicate samples from 0 to 1 cm at site 5 (tables 8 and 9). For 35 detectable elements, the average (unsigned) difference in concentration is 5.4 percent between the duplicate samples and only slightly larger at 7.7 percent between the composite sample and the mean value of the duplicate samples.

Table 14. Concentrations of elements in recharge-basin sediment and in aquifer soil used for the laboratory elutriation tests

[Concentrations in micrograms per gram dry weight. Sediment is from top 1 centimeter near site 5; soil data, also given in table 7, are from depth of 10.9-11.3 meters in test hole 1. <, less than indicated reporting limit]

Element	Symbol	Concentration	
		Basin sediment	Aquifer soil
Aluminum	Al	74,000	89,000
Arsenic	As	18	4.2
Barium	Ba	710	510
Beryllium	Be	1	<1
Bismuth	Bi	<10	<10
Boron	B	2.6	1.9
Cadmium	Cd	2	<2
Calcium	Ca	16,000	24,000
Cerium	Ce	57	37
Chromium	Cr	87	140
Cobalt	Co	17	19
Copper	Cu	140	26
Europium	Eu	<2	<2
Gallium	Ga	17	16
Gold	Au	<8	<8
Holmium	Ho	<4	<4
Iron	Fe	38,000	38,000
Lanthanum	La	33	19
Lead	Pb	170	14
Lithium	Li	46	30
Magnesium	Mg	14,000	15,000
Manganese	Mn	630	590
Mercury	Hg	.27	<.02
Molybdenum	Mo	4	<2
Neodymium	Nd	21	18
Nickel	Ni	66	140
Niobium	Nb	7	5
Phosphorus	P	2,000	300
Potassium	K	22,000	18,000
Scandium	Sc	10	14
Selenium	Se	.8	<.2
Silver	Ag	<2	<2
Sodium	Na	14,000	19,000
Strontium	Sr	270	280
Tantalum	Ta	<40	<40
Thorium	Th	29.0	4.7
Tin	Sn	<10	<10
Titanium	Ti	3,200	3,100
Uranium	U	11.4	2.24
Vanadium	V	97	91
Ytterbium	Yb	2	2
Yttrium	Y	15	17
Zinc	Zn	1,200	69

In addition to the equilibration between surface sediment and water from the recharge basin, the sediment also was mixed with deionized water for about 4 days as a further check for desorption of contaminants into the aqueous phase. The results given in table 13 (results for a deionized-water blank also are shown in the table) lead to the conclusion already stated that evidence exists for possible transfer of some chemical constituents from sediment to the aqueous phase. Wigington and others (1983) also reported the potential for leaching of four inorganic urban contaminants (Cd, Cu, Pb, and Zn) from sediment in a recharge basin in Washington, D.C. They found that as much as 2 percent of these elements was removed by a 0.01M $Ca(NO_3)_2$ solution; of the four elements tested, zinc was the most readily solubilized. Because solid-phase concentrations typically exceed aqueous concentrations by three orders of magnitude or more, the amount leached during the experiment represents a very large input to the aqueous phase. However, their experimental procedure likely overstates the potential for leaching in the environment because $Ca(NO_3)_2$ is expected to hydrolyze to form a weakly acidic solution.

For the laboratory experiment in which water from the recharge basin was mixed with natural uncontaminated soil, the core from a depth of 10.9-11.3 m in test hole 1 was selected. Soil from this depth was chosen because its generally higher silt-plus-clay content—in comparison with other, sandier, core samples (table 4)—would be expected to favor increased sorption. Results from this experiment to check for removal of aqueous contaminants by clean soil were inconclusive. An increase in mineral dissolution, as indicated by the increase in specific conductance from 346 (table 12) to 548 µS/cm (table 13), was measured. The major ions that showed the largest increase are calcium, sulfate, and bicarbonate (alkalinity).

Concentrations of many minor constituents, including tannin and lignin and MBAS detergents, changed little. Some constituents, such as phenols and arsenic, actually show substantial increases. The increase from 2 to 6 µg/L for phenols is, if anything, another indication of the uncertainty in the colorimetric test for phenols at this low level. And the increase in arsenic from 3 to 35 µg/L indicates the potential for leaching of selected trace elements from even uncontaminated soil.

In summary, the batch-elutriation experiments done for this study demonstrate the potential for leaching of urban-runoff contaminants as water in recharge basins infiltrates the basin's sediment. However, the results of similar experiments to test the ability of uncontaminated substrata to remove those contaminants were inconclusive—in part, because of the significant natural abundances of some inorganic elements; because of limitations on the colorimetric methods used to analyze broad organic indicators; and because of the possible presence of colloidal material in the centrifuged elutriate itself. Theoretical considerations based on the physical and chemical properties of contaminants in a circumneutral (or slightly alkaline) environment and monitoring of soil moisture and ground-water chemistry provide more reliable support for evaluating transport of urban-runoff contaminants to the water table than do the results of these elutriation experiments. The observation that concentration gradients show a sharp decrease in sediment beneath the recharge basin, and the likelihood that water-infiltration rates are sufficiently slow for the soil moisture to, in effect, undergo a series of "batch-removal" processes as it percolates downward through the soil, ensures the effective removal of all urban runoff contaminants, with the possible exception of those having negative charge (anions) or negative polarity.

Perhaps the most important finding obtained from these laboratory experiments comes from analyses of the sediment and soil before (table 14) and after (table 15) the elutriation tests. The data in table 14 were obtained from complete mineral digestion with strong acids, whereas those in table 15 are based on oxidation of organic matter with H_2O_2 followed by only partial digestion with 0.3M HCL (Fishman and Friedman, 1989). The mild-acid digestion is intended to remove only surface layers while leaving the aluminosilicate mineral matrix itself largely intact. Among the alkali- and alkaline-earth elements, the mild-acid treatment removed virtually no calcium, magnesium, and sodium but did leach a substantial proportion of the total potassium. Percent recoveries from the contaminated basin sediment at 0 to 1 cm near site 5 and from clean aquifer soil at 10.9-11.3 m in test hole 1 can be obtained by dividing concentrations for partial digestion (table 15) by concentrations for complete digestion (table 14). Results of this calculation for several elements are summarized in table 16. These results show that a number of elements having high enrichment ratios (the contaminants in urban runoff) are almost entirely recoverable by the mild treatment and therefore are presumed to be present in surface coatings on mineral grains and in organic matter (Horowitz and Elrick, 1987). Percent recoveries for mild-acid digestion of the uncontaminated aquifer soil are somewhat less, but they also indicate that a substantial proportion of selected trace elements is likely associated with

Table 15. Concentrations of chemical constituents in recharge-basin sediment and aquifer soil after the laboratory elutriation tests

[Element concentrations, in micrograms per gram dry weight, are based on analysis of mild-acid leachate from sediment and soil. Pesticide concentrations are in micrograms per kilogram dry weight.]

Constituent	Basin sediment equilibrated with deionized water	Aquifer soil equilibrated with basin water
Calcium	<10	<10
Magnesium	10	<10
Sodium	<10	<10
Potassium	8,400	3,300
Aluminum	22,000	8,200
Arsenic	15	4
Boron	20	<10
Cadmium	5	<1
Chromium	40	20
Cobalt	<50	<50
Copper	180	17
Iron	36,000	13,000
Lead	200	<10
Manganese	580	260
Mercury	.24	.02
Molybdenum	3.8	<1
Nickel	50	60
Zinc	1,600	35
Nitrite + nitrate (as N)	6,000	3,000
Ammonium (as N)	380	160
Kjeldahl nitrogen (as N)	13,000	460
Phosphorus (as P)	2,300	1,000
Organic carbon (as C)	140,000	3,000
Inorganic carbon (as C)	100	100
Oil and grease	20	<1
Organochlorine Compounds		
Aldrin	<0.1	<0.1
Lindane	51	<.1
Chlordane	<1	1
DDD	17	.8
DDE	50	.6
DDT	.6	<.1
Dieldrin	5.3	<.1
Endosulfan	10	<.1
Endrin	<.1	<.1
Ethion	<.1	<.1
Toxaphene	<10	<10
Heptachlor	52	<.1
Heptachlor epoxide	8.1	<.1
Methoxychlor	<.1	<.1
PCN	<1	<1
PCB	26	<1
Organophosphorus Insecticides		
Malathion	<0.1	<0.1
Parathion	<.1	<.1
Diazinon	<.1	<.1
Methyl parathion	<.1	<.1
Mirex	<.1	<.1
Ethyl trithion	<.1	<.1
Methyl trithion	<.1	<.1
Perthane	<1	<1

Table 16. Percent extractable for selected elements in recharge-basin sediment and aquifer soil by digestion with hydrogen peroxide plus mild acid

[Calculated from data in tables 14 and 15. Basin sediment is from top 1 centimeter near site 5, and aquifer soil is from 10.9–11.3 meters in test hole 1. >, greater than; <, less than; --, indeterminate value]

Element	Percent extractable	
	Basin sediment	Aquifer soil
Aluminum (Al)	30	9
Arsenic (As)	83	>100
Chromium (Cr)	46	14
Copper (Cu)	>100	69
Iron (Fe)	95	34
Lead (Pb)	>100	<71
Manganese (Mn)	92	44
Mercury (Hg)	89	--
Nickel (Ni)	76	43
Potassium (K)	38	18
Zinc (Zn)	>100	51

hydrous ferromanganese oxides present either as coatings on mineral grains or disseminated throughout the uncontaminated soil.

TRANSPORT AND LOADING OF CONTAMINATED SEDIMENT

When results of this study are compared with results from the NURP study, some differences emerge that raise questions about how contaminants in the urban environment are delivered to the recharge basin and about the quantity of contaminants actually present in the basin. Although these are important questions, it is emphasized that they do not change this study's principal conclusion that urban contaminants are not reaching the ground water, nor do they affect sediment-disposal considerations (following periodic scraping of the basin's floor) that are based on compliance with sediment-quality criteria or standards.

Table 17. Annual loads to the industrial recharge basin determined from runoff monitoring and sediment inventories

[Annual loads in kilograms per year. Inventory loads are converted to values based on mild-acid, partial digestion (see text) for direct comparison with runoff loads, adjusted to mean annual rainfall in Fresno, obtained by Oltman and Shulters (1989)]

Element	Annual load, determined from:		Inventory/runoff ratio
	Runoff	Inventory	
Aluminum (Al)	340	1,300	3.7
Arsenic (As)	.93	.57	.6
Organic carbon (as C)	11,000	5,700	.5
Chromium (Cr)	1.1	1.8	1.6
Copper (Cu)	3.5	5.1	1.5
Iron (Fe)	570	2,000	3.5
Lead (Pb)	4.5	7.0	1.6
Manganese (Mn)	19	33	1.8
Mercury (Hg)	.013	.0088	.7
Nickel (Ni)	1.3	2.3	1.8
Zinc (Zn)	26	38	1.4
Sediment	30,000	56,000	1.8

COMPARISON OF BASIN-SEDIMENT INVENTORIES AND STORM-RUNOFF LOADS

Storm-runoff loads to the industrial basin, calculated from average-annual constituent loads estimated by Oltmann and Shulters (1989, table 25) on the basis of monitoring for the NURP study during the 1981-82 and 1982-83 wet seasons, are given in table 17. Quantities of constituents found in this study to have accumulated in the recharge-basin's sediment during operation in its present configuration from 1982 to 1986 also are given in the table. In order to compare annual loads estimated by means of the two methods, it is necessary to adjust the sediment inventories for differences in recovery between the mild-acid digestion used during the NURP study to analyze runoff samples and the complete mineral digestion used in this study to analyze basin sediment. This was done by multiplying total-constituent amounts mea sured in the sediment by recovery percentages from the "Basin sediment" column in table 16, thereby providing a comparison that is based on element recoveries from the partial-digestion analytical method. [Alternatively, an equivalent comparison could be based on loads determined from complete-digestion methods by dividing the runoff-load values of Oltmann and Shulters (1989) reproduced in table 17 by the recovery percentages.] Complete recovery (100 percent) was used in the calculation for organic carbon, copper, lead, and zinc. The concentration profiles at site 5, given in table 9, were used to calculate constituent quantities in the basin sediment. Quantities are calculated by multiplying concentrations, basin area, sediment dry-bulk density, and subbottom depth. The error that is propagated by uncertainty in each of these parameters is discussed below.

The uncertainty in element concentrations that results from analytical imprecision is small: an average of only about 5 percent on the basis of analysis of duplicate samples. The error that results from spatial variability in concentration is much greater: as much as a factor of about 2 (100 percent) for many of the urban contaminants in surface sediment (0-1 cm) at six locations in the recharge basin (table 8). However, the effect of such large spatial variability is deceptive because nearly all of the basin floor's area is in the south end, where the variability obtained by comparing surficial concentrations at sites 5 and 6 is only about 5 percent (table 8), and by comparing concentrations at site 5 with those from a broad area near site 5 (table 13) is only about 8 percent. The area of the basin floor that contains contaminated sediment is difficult to estimate because the sediment reaches an indeterminate distance up the sloping sides of the basin. The basin-floor area was measured in the field to be about 3.72×10^7 cm^2 (40,000 ft^2 or about 1 acre) with a possible error of about 25 percent.

Sediment dry-bulk density (ρ in equation 1 later) was not measured in this study, but a value of 1.5 g/cm^3 was chosen because it was measured by Nightingale (1989) for a sediment with similar grain-size distribution from another recharge basin in the city of Fresno. True density of well-homogenized sediment samples is likely to differ little from this estimate, although minor fluctuations with depth can be expected. A far greater error arises from the unusual open texture of sediment in the top few centimeters referred to in the "Sampling of Sediment from the Recharge Basin" section of this report.

These irregularities in sediment texture, and thinning of the contaminated zone along the sideslopes and channel in the northern part of the basin, create a rather large uncertainty in precise assignment of subbottom depths as well as some ambiguity in choosing the maximum depth to be used in calculating sediment inventories. Four centimeters was chosen as the maximum depth to use because sediment below this depth contained no excess (atmospheric) lead-210 ($^{210}Pb_{xs}$).

When each of the various sources of error is considered, the accuracy of calculated annual-contaminant inventories in the sediment is thought to be no better than a factor of 2 or 3. As noted, most of the imprecision is attributable to uncertainty in the determination of depth and bulk density related to the unusual sediment texture. Guay and Smith (1988) also recognized the large error in simulating a relation between quantity and quality of storm runoff in the industrial catchment and therefore developed simulations for residential and commercial catchments only. Failure of their model for the industrial catchment may be caused by discharge from large point sources unrelated to rainfall, in contrast to residential and commercial catchments, where nonpoint (as numerous small-point) contributions predominate. Median errors using data from individual storms for their simulation in a commercial catchment were 11 percent for lead and 54 percent for suspended sediment. However, even these rather large errors in estimating urban-runoff loads are much less than differences between the results obtained using the two methods described in this report. The differences for selected constituents are expressed as a ratio between the sediment-inventory and runoff-monitoring load and are given in table 17. Possible reasons for the differences include: (1) errors in one, or both, of the methods used to estimate annual loads; (2) real differences between the period of storm monitoring during 1981-83 and the period of sediment accumulation during 1982-86; and (3) substantial delivery of sediment containing urban contaminants by some mechanism in addition to storm runoff, such as overland flow and erosion on the perimeter of the basin or atmospheric transport (dryfall).

Contaminated sediment contained in the recharge basin exceeds the amount delivered as suspended sediment in storm runoff by a factor of 1.8 (table 17). The difference is only slightly less for several elements (Cr, Cu, Pb, Mn, Ni, and Zn), possibly reflecting minor dilution with sediment (soils or substrata) containing little or no urban contaminants. The close similarity in loading patterns for these elements and for sediment is especially surprising given the very different procedures and assumptions used to obtain the two estimates. These results suggest that a single explanation may exist for the differences, such as a systematic error in the estimated quantity of sediment. Furthermore, there are simple explanations to reconcile inventory-runoff differences that are either much greater (aluminum and iron) or much less (arsenic, organic carbon, and mercury) than 1.8 for five other elements.

The amount of recoverable aluminum and iron contained in basin sediment relative to runoff apparently is overestimated because the digestion procedure produced uncharacteristically high recoveries for the strongly anaerobic sediments from the basin in comparison with the much lower recoveries of both aluminum and iron for clean aquifer soil (table 16). Possible explanations for those elements that appear to be depleted in the basin sediment (arsenic, organic carbon, and mercury) are much more varied.

The subbottom concentration profile from site 5 (table 9 and fig. 4) clearly shows that some arsenic has migrated beyond the 4-cm depth. The amount of arsenic that migrated was not included in the inventory calculation, which was cut off at 4 cm to maintain internal consistency among all elements. The greater mobility for arsenic, in comparison with many other trace elements that exist as cations, may be attributed to its possible existence as the more soluble oxyanion.

Mercury concentrations are so low that analytical errors and loss during storage and processing of the sediment samples must be considered; however, natural loss by volatilization of the element or its methylated form within the basin (Compeau and Bartha, 1985) also is possible.

Because the concentration of dissolved organic carbon in soil water (and ground water) generally is low and sorption of organic carbon to solid-particle surfaces typically is high, transport of organic carbon with downward-percolating recharge is likely to be a minor mechanism for its removal. The main removal mechanism for organic carbon is believed to be biological degradation within the subbottom sediment; the data in table 17 indicate that at least one-half the organic carbon delivered in runoff must be decomposed. In fact, the fraction of organic carbon actually mineralized (degraded) must be even greater than one-half because not only allochthonous carbon in runoff but also autochthonous carbon produced biologically within the pond itself is delivered to the subbottom sediment. The basin receives an average annual load of 730 kg total nitrogen. Dissolved phosphorus also was noted to be especially high in runoff from the industrial catchment in comparison with runoff from the residential and commercial catchments (Oltmann and Shulters, 1989). It is this rich supply of nutrients which results in the deep green color (from algae) of the pond itself and in the existence of strongly anaerobic sediment beneath the basin, and which provides an environment that supports extensive degradation of organic carbon.

LEAD-210 CONSTRAINTS ON ORIGIN AND LOADING OF CONTAMINATED SEDIMENT

Lead-210 occurs naturally as a product of the uranium-238 decay series and has a half-life of 22 years. Lead-210 has been used widely for dating lacustrine and coastal sediments that have accumulated during the last 100 years (Faure, 1977). For this study, the primary purpose in obtaining ^{210}Pb data was to ascertain the maximum depth at which inorganic elements from urban runoff occur in basin sediment. This radioisotope is especially well suited to this purpose because (1) its chemical and physical properties are expected to be similar to those of other inorganic cations, especially nonradiogenic lead, and thus it would be expected to transport similarly and (2) that portion of the sedimentary ^{210}Pb derived from atmospheric fallout, the $^{210}\text{Pb}_{xs}$ (excess lead-210), will be completely absent in the much older substrata that lie beneath the basin's recently deposited sediment if no downward transport of the isotope has occurred. Lead-210 also may provide useful insight into the origin (mechanism of delivery) and loading of urban-contaminated sediment to recharge basins.

Atmospheric ^{210}Pb is produced when ^{226}Ra in the Earth's crust decays to ^{222}Rn, an inert gas that effuses into the atmosphere, where it subsequently decays through a series of very-short-lived daughters to ^{210}Pb and falls back to the Earth's surface. Because secular (long-term) equilibrium is presumed to exist between sedimentary (or soil) ^{226}Ra and its decay products, the $^{210}\text{Pb}_{xs}$ activity can be calculated as total ^{210}Pb activity minus ^{226}Ra activity (see Graustein and Turekian, 1986, for a more complete discussion). For this study, activities are given in dpm (disintegrations per minute), which can be converted to other units of activity commonly used in the literature with the relation: 1 pCi (picocurie) = 2.2 dpm = 37 mBq (millibecquerels). Crustal variations in concentration of the parent isotope from which ^{210}Pb is derived and rapid removal of ^{210}Pb from the atmosphere in comparison with global circulation times causes regional variations in the flux of atmospheric ^{210}Pb. On the basis of measurements in soil and precipitation, Moore and Poet (1976) reported values of 0.53 to 1.0 (dpm/cm^2)/yr for oceanic fluxes, 0.8 to 2.0 (dpm/cm^2)/yr for continental fluxes in the north temperate zone, and 1.6 (dpm/cm^2)/yr from surface-soil profiles in Colorado, Texas, and Kansas. Graustein and Turekian (1986) reported values ranging from 0.6 to 1.2 from undisturbed soil in 19 locations throughout the central and eastern United States. Published data from several locations on the west coast yield a range of about 0.2 to about 0.7 (dpm/cm^2)/yr, with latitude, longitude, and precipitation quantity influencing the flux (Fuller and Hammond, 1983)—and a value of about 6 (dpm/cm^2)/yr in Emerald Lake (calculated from data in Holmes and others, 1989, fig. 2). Although Emerald Lake is only 110 km east-southeast of Fresno in an alpine watershed on the west slope of the Sierra Nevada, its high ratio of watershed to lake area (almost 50) and the steep slopes of this cirque lake are likely to result in an anomalously high atmospheric-flux estimate. Although data are not available for the city of Fresno, proximity to the Pacific Ocean suggests that the ^{210}Pb flux should be near the low end of the range of continental values and likely no greater than about 1 (dpm/cm^2)/yr. Data from undisturbed soil or from atmospheric precipitation (wet and dry deposition) in the Fresno area would be needed to determine the local flux more accurately.

Annual deposition of $^{210}\text{Pb}_{xs}$ in a sediment profile can be calculated from:

$$^{210}\mathrm{Pb}_{xs}\ \text{flux} = \frac{\lambda \sum_{i} [^{210}\mathrm{Pb}_{xs}]_{i} L_{i} \rho_{i}}{1 - e^{-\lambda t}} \ , \qquad (1)$$

where λ is the decay constant (0.0311 yr^{-1}), ρ is dry-bulk density (1.5 g/cm^3), t is 4 years, and the other terms are defined in the following paragraph. The above formulation yields the same result as an alternative method chosen to illustrate more clearly the effect of errors in basin area and sediment mass on the result. The method also is analogous to that used for calculating element inventories in table 17.

Annual deposition of $^{210}Pb_{xs}$ to the basin also can be calculated by substituting data (in table 9) from site 5, where a complete activity profile exists, into the equation:

$$^{210}\mathrm{Pb}_{XS}\ \text{flux} = \frac{M}{t \cdot A \cdot L} \sum_{i} [^{210}\mathrm{Pb}_{XS}] L_{i} \ , \qquad (2)$$

where

$[^{210}Pb_{XS}]$ is the activity in sediment interval i,
L_i is the length of sediment interval i
L is the sediment depth (4 cm) to which $^{210}Pb_{xs}$ is present,
M is mass of sediment in the basin,
t is length of time (4 years) the basin has been operated since last scraped, and
A is area of the basin (3.72×10^7 cm^2).

Using the estimated sediment-accumulation rate (M/t) of 56,000 kg/yr given in table 17, and adjusting upward for the small amount of decay that took place during 4 years, yields a $^{210}Pb_{XS}$ deposition rate of 6.4 $(dpm/cm)^2/yr$. This value is markedly higher than the expected atmospheric flux of about 1 $(dpm/cm^2)/yr$. Fluxes determined from sediment data in surface-water bodies often are higher than atmospheric deposition rates and the difference is attributed to sediment "focusing"—the preferential scavenging on fine-grained material at the location of the cored sediment. For example, in four cores from the NURP study site in Irondequoit Bay, New York, fluxes were found to range from about 1 to 3 $(dpm/cm^2)/yr$ (Schroeder, 1985). The spatial trend shown by surficial activities that are given in table 8 provides evidence that focusing occurs in the recharge basin. However, the equation above hints at a simpler explanation that reconciles the difference—a decrease in the sediment mass by a factor of 2 and an increase in the effective basin area by a factor of 3.

Monitoring of suspended-sediment concentration in runoff yielded the lower estimate (in relation to inventory estimate) for average annual sediment delivered to the recharge basin, and because total rainfall in Fresno during 1982-86 was only a little above average, annual sediment deliveries during this period also should be near the annual average. Erosion from the sideslopes and perimeter to the floor of the recharge basin plausibly could increase the effective area of deposition by a factor of 3 (compare total basin area to bottom area in figure 2). Such sediment may have been deposited initially as dryfall, whose contribution must be small in comparison with that of runoff, or the pattern and level of contamination in the dryfall and overland flow on the sideslopes must be similar to that in runoff in order to maintain the similarity in pattern shown by several different elements that is indicated in table 17.

The discussion above illustrates how, with relatively few measurements in comparison with much more intensive monitoring of runoff, reasonable estimates can be obtained for the quantity of contaminated sediment in an urban-runoff recharge basin. More detailed studies are needed to refine and test the validity of the method. Such studies might preferably be done in turfed basins that have been operated for a much longer time than was the subject basin in this study, thereby minimizing possible effects of erosion from the sides of the basin and providing a much thicker sediment veneer in which depths and bulk density could be measured more accurately.

SUMMARY AND CONCLUSIONS

Previous monitoring of storm-runoff quantity and quality, during 1981-83, in Fresno revealed elevated concentrations of urban contaminants in residential, commercial, and industrial catchments. The monitoring was accompanied by studies that confirmed the presence of these contaminants within the top few centimeters of sediment beneath recharge basins constructed to dispose of runoff from residential and commercial catchments. This study extends those previous studies to a 0.4-ha industrial-catchment basin where some urban contaminants were expected to be present at even higher concentrations than in residential- and commercial-catchment basins. This study also shows that a wide variety of inorganic and organic contaminants generated in the 1.13-km^2 industrial catchment are removed by sorption within the top 4 cm of sediment in the recharge basin, and that the contaminants have not degraded ground-water quality beneath the basin.

The absence of local ground-water-quality impairment is documented by comparing chemical concentrations in two water-table monitoring wells to aqueous concentrations in the recharge basin. Shallow ground water near the basin contains a significant proportion of partly evaporated runoff from the basin as shown by measured delta-deuterium values of about -50 permil in both monitor wells in comparison with reported values of about -90 permil in regional ground water and -16 permil in the recharge basin itself. Because aqueous zinc concentration is about 100 times higher in the recharge basin than in the monitor wells, this element is an especially sensitive surrogate for assessing potential ground-water degradation by inorganic cations. Organic contaminants either were absent or were detected at such low concentrations (near reporting limits) that evidence for their presence in the monitor wells is questionable.

The range in chemical concentration of many urban contaminants in surface (0-1 cm) sediment from six locations on the floor of the recharge basin was a factor of about 2. Concentrations were lowest in channels at the north end of the basin nearest the pipe from which runoff discharges, and highest at the south end in the broad, topographically lowest part of the basin. The proportion of fine sediment also is highest at the south end, as would be expected. Profiles at a representative location in the south end of the basin show that concentrations of nearly all contaminants decrease to background levels at a depth of 4 cm, which also was the maximum depth to which atmospheric ^{210}Pb (excess ^{210}Pb) penetrates; no contaminants generated in the urban environment were detected below a depth of 16 cm.

Surface-enrichment ratios, defined as the ratio of concentrations in the top centimeter to concentrations in substrata below 16 cm, provide a quantitative means to compare anthropogenic (human related) and natural sources. Accordingly, a ratio of 2 is consistent with equal inputs from human and natural sources. Twenty inorganic elements were found to have enrichment ratios of 2 or greater. The value for zinc, which had the highest ratio, was 38. Values for several other elements were: arsenic=16, chromium=5, copper=25, lead=9, mercury>11, nickel=7, phosphorus=5, and organic carbon$\approx 10^3$.

Enrichment ratios cannot be calculated for the approximately 20 organic compounds identified in sediment because the compounds are absent at depth. Nearly all the organic compounds detected in sediment are either organochlorine pesticides or polycyclic aromatic hydrocarbons. Among compounds in these two groups, chlordane and pyrene show the highest concentrations. Curiously, concentrations of the banned pesticide DDT exceed those of its possible metabolites DDD and DDE, a finding also noted in previous studies of urban runoff in the city of Fresno.

Estimates of sediment quantity and element load (total recoverable by mild-acid digestion) loads obtained in this study from a single core in the recharge basin exceed previously published estimates that were based solely on storm-runoff monitoring by a factor of 1.8. Possible explanations for this study's higher estimates are imprecision in the determination of sediment depths, the unusually open texture of the sediment veneer that had accumulated during the 4-year period the basin was operating, and thinning of the sediment layer in parts of the basin.

The flux of atmospheric ^{210}Pb, calculated to be 6.4 (disintegrations per minute/cm^2)/yr using data from the only core obtained in the basin, is much higher than the maximum expected atmospheric flux of about 1 (disintegrations per minute/cm^2)/yr. This difference can be reconciled if 1982-86 sediment contained in the basin is reduced by half and if the effective area of deposition is increased to 3 times larger than the approximately 0.4-ha floor of the basin. Erosion from the perimeter and sideslopes of the basin could provide the additional area required. This discussion illustrates how acquisition of ^{210}Pb data can be used to check estimated loads of sediment and urban contaminants delivered to recharge basins without the numerous analyses and intensive sample collection necessary to monitor runoff itself. However, additional data collection is needed to confirm and refine the method.

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