PETALUMA TREE PLANTERS

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Diazinon and Chlorpyrifos in the Upper Petaluma River Watershed Petaluma, California

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ABSTRACT

Diazinon and chlorpyrifos are commonly used insecticides that can be toxic to aquatic organisms at relatively low concentrations. Other studies have demonstrated that these insecticides occur in urban creeks of the Bay Area at toxic concentrations, however, no monitoring prior to this study had been conducted in the upper Petaluma River Watershed. Storm-related and dry weather samples were collected from river, creek, and storm drain sampling locations in and around Petaluma as part of this investigation. All samples were analyzed for diazinon and chlorpyrifos using the enzyme-linked immunosorbant assay (ELISA) method. Results indicate that dry weather flows did not contain considerable concentrations of diazinon or chlorpyrifos. However, approximately 50 percent of samples collected from storm-related flows contained potentially toxic concentrations of either diazinon or chlorpyrifos or both. Residential and commercial land uses are dominant in the drainage areas of the sampling locations with the highest concentrations.

INTRODUCTION

Background

Diazinon and chlorpyrifos are widely used organophosphate insecticides. They are sold under the generic names "diazinon" and "chlorpyrifos" or as active ingredients in a variety of insecticide products. These products, which are sold as liquids, granules, dusts and sprays, are primarily used to kill ants, spiders, fleas, and grubs. Diazinon and chlorpyrifos are among the most widely used pesticides in the residential/urban setting and are used in agricultural crop protection. In addition, chlorpyrifos is an active ingredient in some pet flea shampoos.

Diazinon and chlorpyrifos in surface water systems (i.e., creeks and rivers) are of particular concern because they can be toxic to aquatic organisms at relatively low concentrations. Tests conducted on storm water runoff samples collected from Alameda and Santa Clara counties have demonstrated that samples are often toxic to small crustacean test organisms (Scanlin and Feng, 1997; Katznelson and Mumley, 1997). The San Francisco Bay Regional Water Quality Control Board has proposed that the San Francisco Bay and some tributary creeks be designated as impaired waterways due to the identified toxicity associated with diazinon (Mumley, 1999). The Petaluma River was not included in the proposed designation because there was no data available for that system (Tang, 1999).

The San Francisco Estuary Institute (SFEI) Regional Monitoring Program[1] indicates that water quality at the mouth of the Petaluma River is among the worst in the Bay Area. More exceedances of State water quality objectives were identified at the Petaluma River monitoring station than at any other station (except Coyote Creek in the South Bay Area) (Figure 1). This characterization is based on only one sampling location at the mouth of the River and provides no information on where the problem areas may be within the watershed.

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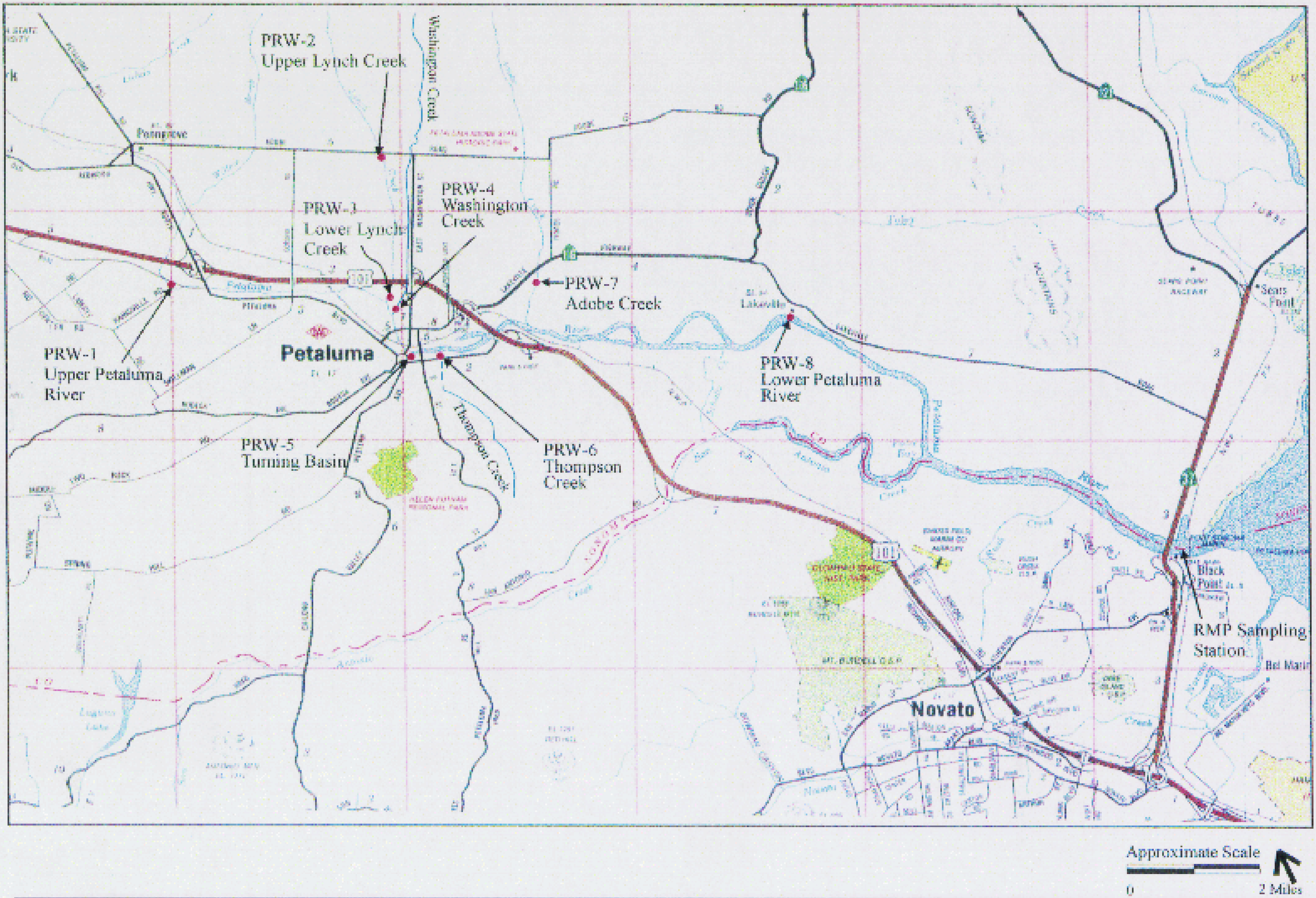
[1] The Regional Monitoring Program and the SFEI is further described under the "Previous Work" section of this report.

SAMPLING LOCATIONS
Petaluma River Watershed

Figure 1



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Watershed Description

The Petaluma River, which discharges directly to San Pablo Bay, drains an area of approximately 146 square miles. The basin is composed of hilly uplands in the headwaters and relatively flat lowlands on the valley floor. The Petaluma River is a tidal estuary that is regularly dredged between the downtown turning basin (just downstream of the Balshaw footbridge) and the river mouth to maintain adequate depths for commercial and recreational boating (Figure 1). The Petaluma River and its tributaries near the confluences contain water year round. During wet years (1998, for example) many of the tributaries flow year round. However, during dry years most of the tributaries stop flowing some time during the summer. Mean annual rainfall in Petaluma between 1948 and 1998 was 25 inches (WRCC, 1999).

Dominant land uses in the Petaluma River basin include residential, commercial, and industrial developments, open space, and agriculture (mostly dairy farms, cattle and sheep ranches, and poultry production). The City of Petaluma, located in the central to upper portion of the basin, supports a population of approximately 50,000 people.

Previous Work

Based on review of available documents and discussions with people involved with water quality issues in the North Bay region, there appears to be no existing data regarding the presence or absence of diazinon and/or chlorpyrifos in surface water in the upper Petaluma River watershed. Diazinon and chlorpyrifos concentrations have been evaluated in the Petaluma wastewater treatment plant influent and effluent. In addition, the Regional Monitoring Program for Trace Substances (RMP) conducted by the SFEI, monitors the San Francisco Bay for the presence of diazinon and chlorpyrifos and many other constituents. Monitoring conducted at the wastewater treatment plant and by SFEI is described below.

Wastewater Treatment Plant

The City of Petaluma operates separate storm drainage and sanitary sewer systems. Storm water runoff enters gutters, culverts, creeks, and eventually the Petaluma River without treatment. During storms, a significant amount of storm water can enter the sanitary sewer lines through infiltration and inflow. This can occur when rainfall infiltrates the ground surface raising groundwater levels. A leaky sanitary sewer line below the groundwater table can allow infiltration of up to 100,000 gallons per day per mile of sewer (Metcalf and Eddy, 1972). The occurrence of substantial infiltration and inflow to the Petaluma sewer system is demonstrated by the fact that the average dry weather flow to the treatment plant is 4.5 million gallons per day and the peak wet weather flow is 30 million gallons per day (Brown and Caldwell, 1993). Treated effluent is discharged to the Petaluma River during the winter (October 21 through April 30) or used for irrigation of agricultural land and golf courses. Therefore, it is possible that diazinon and chlorpyrifos in storm water, as well as sanitary sewer sources (e.g. disposal of unused products, pet flea shampoo), could enter the sanitary sewer system, undergo treatment, and the residual amounts discharged to land or the Petaluma River.

The City of Petaluma, through U.S. Filter (the operator of the municipal wastewater treatment plant), participated in a regional study conducted by the San Francisco Bay Area Pollution Prevention Group (1998) designed to characterize treatment plant influent and effluent for diazinon and chlorpyrifos concentrations. A total of ten treatment plants located throughout the Bay Area participated in the study.

During August 1997 and March 1998, samples of wastewater influent and effluent were collected on a daily basis for seven days at each treatment plant and analyzed for diazinon and chlorpyrifos using the enzyme-linked immunosorbant assay (ELISA) method.[2]

The result for the Petaluma plant are summarized in Table 1. Based on these results, it appears that diazinon and chlorpyrifos are consistent components of the sanitary sewer waste stream, and that the treatment process is effective in reducing effluent concentrations of diazinon, but less effective in reducing chlorpyrifos concentrations.

Table 1
Concentrations of Diazinon and Chlorpyrifos in
Influent and Effluent from the Petaluma Wastewater Treatment Plant

Date Samples Collected	Influent- Diazinon (ng/L)	Effluent- Diazinon (ng/L)	Influent- Chlorpyrifos (ng/L)	Effluent- Chlorpyrifos (ng/L)
August 1997	950	91	63	25
March 1998	454	18	51	28

Source: San Francisco Bay Area Pollution Prevention Group, 1998.

Note: Samples analyzed using ELISA methodology.
ng/L = nanograms per liter (parts per trillion)

Regional Monitoring Program for Trace Substances

The San Francisco Bay Regional Water Quality Control Board (RWQCB) is the State agency responsible for regulating surface and groundwater quality in the San Francisco Bay and its watersheds. The RWQCB, recognizing the need for regional long-term monitoring of water quality conditions in the Bay, facilitated the creation of the Regional Monitoring Program for Trace Substances (RMP). The San Francisco Estuary Institute (SFEI) was chosen by the RWQCB to administer the RMP. Since 1993, the SFEI has conducted monitoring activities and published annual reports containing their findings. The RMP includes the Base Program monitoring activities and Pilot and Special Studies conducted to address specific concerns.

Base Program Monitoring Activities

From 1993 to 1997, the Base Program monitoring activities related to characterization of the presence of diazinon and chlorpyrifos in the San Francisco Bay have consisted of three sampling events per year (February, April and July/August of each year). Sampling is conducted from a boat at approximately two dozen predesignated sampling locations along the “spine” of the Bay. One of the sampling locations is at the mouth of the Petaluma River in San Pablo Bay (Figure 1).

[2] The ELISA method is discussed in further detail in the “Methods” section of this report.

Diazinon and chlorpyrifos concentrations have been measured in surface water samples at the mouth of the Petaluma River during each sampling event. The results for this sampling location are summarized in Table 2. Based on review of this data, it appears that discharge from the Petaluma River contains the highest concentrations of diazinon during the winter-period (February),[3] whereas trends in chlorpyrifos concentrations are less clear. Although concentrations of diazinon and chlorpyrifos identified in samples collected from the mouth of the River do not exceed existing water quality guidelines (Table 2), the concentrations were 30 times higher than concentrations identified in samples collected from the Golden Gate sampling station (SFEI, 1997). This concentration gradient indicates a considerable source in the Petaluma River watershed. The source of these contaminants is not identified by SFEI.

Table 2
Summary of Analytical Results for the
Mouth of Petaluma River at San Pablo Bay

Date Sample Collected	Total Diazinon (ng/L)	Total Chlorpyrifos (ng/L)
2/7/94	13.92	0.679
4/26/94	2.60	0.048
8/22/94	0.73	0.034
2/13/95	11.15	0.253
4/19/95	4.40	0.450
8/21/95	0.64	0.003
2/12/96	12.13	0.006
4/22/96	7.77	0.300
7/24/96	2.50	0.009
Water Quality Guidelines	–	–
Salt Water 4-day average[1]	40	5.6
Fresh Water 4-day average[1,2]	40	41

Source: SFEI Website, 1998.

Note: Samples analyzed using gas chromatograph. For detailed description of analytical methods seeSFEI, 1997.

1 From California Department of Fish and Game *in* SFEI, 1997. Salt waters are those with salinities greater than five parts per thousand (approximately equivalent to 7,500 µmhos/cm). The 4-day fresh water criteria for chlorpyrifos of 41 ng/L is listed as a "Recommended Criteria for Fresh Water" for protection of aquatic life by the US EPA in Marshack, 1998.

2 From RWQCB *in* SFEI, 1997. Fresh waters are those with salinities less than five parts per thousand (approximately equivalent to 7,500 µmhos/cm).

3 This trend is similar to most sampling stations throughout the Bay Area.

Pilot and Special Studies
The RMP collects samples three times each year at one location directly relevant to the Petaluma River Watershed (at the mouth of the River). The RMP data demonstrates that diazinon and chlorpyrifos concentrations vary dramatically at some sampling locations with time. Elevated concentrations of pesticides in the Bay system tend to occur in pulses as the contaminants enter and then flow through the system. The RMP is conducting special studies at particular locations where many more samples are collected (relative to the sampling frequency of the Base Program) to further document event-based episodic toxicity. Pulses of pesticides (particularly diazinon) have been demonstrated to associated with in toxic conditions at particular locations that may last up to several days (SFEI, Pesticide Work Group, 1999).

DIAZINON AND CHLORPYRIFOS IN THE UPPER PETALUMA RIVER WATERSHED

Objectives

The primary objective of this investigation was to determine whether diazinon and/or chlorpyrifos occur in creeks, storm drains, and the Petaluma River at concentrations of concern. There are two parts to this stated objective:

1) <u>Characterize the variability of the concentration of diazinon and chlorpyrifos in creeks, storm drains, and the Petaluma River.</u> Water chemistry and pollutant concentrations vary with space and time in natural water systems. That is, samples collected at the same time from different locations within the same creek or river are likely to have different chemical characteristics *and* samples collected from the same location at different times are likely to have different chemical characteristics. In addition, the sources of diazinon and chlorpyrifos fluctuate with time as users apply these products in different locations at different times. Therefore, it is not possible to identify a single consistent pollutant concentration for the waters of the upper Petaluma River Watershed. Selected samples for which concentrations have been determined by an analytical laboratory must be viewed as indicators of variability within a constantly changing system.

2) <u>Determine whether the identified concentration ranges are "of concern."</u> This determination is subjective (even water quality objectives established by regulatory agencies have a subjective component), but generally focuses on evaluation of potential impacts to beneficial uses of the waterways. The RWQCB has identified beneficial uses for Petaluma River and its tributaries as cold freshwater habitat, marine habitat, fish migration, navigation, preservation of rare and endangered species, water contact recreation, noncontact water recreation, fish spawning, warm freshwater habitat, and wildlife habitat.

It is unlikely that elevated concentration of diazinon and/or chlorpyrifos would have any impact on navigation. Furthermore, surface waters of the Petaluma River system are not identified as municipal, industrial, or agricultural water supply sources, and therefore impacts to existing water supply systems and users is unlikely. The remaining beneficial uses that could be impacted can be divided into two broad categories: 1) impacts to aquatic habitat and organisms, and 2) impacts to contact and noncontact water recreationists (e.g., anglers, boaters, people or pets swimming or walking in the water, pets drinking the water). If identified concentrations of diazinon and/or chlorpyrifos in the Petaluma River system could be interpreted to be a source of impact to aquatic organisms or water recreationists, then the concentrations would be "of concern."

In addition to impacting beneficial uses, concentrations of diazinon and chlorpyrifos in surface water would be "of concern" if they exceeded established water quality objectives. In general, water quality objectives are established to protect beneficial uses. However, numerical objectives for diazinon or chlorpyrifos are not included in the San Francisco Bay Water Quality Control Plan (1995). Nor does the California Toxics Rule (US EPA, 1997) contain water quality objectives for these compounds. The only water quality objectives available are those proposed by California Department of Fish and Game (for diazinon) and by the US EPA National Ambient Water Quality Criteria (for chlorpyrifos) (in Marshack, 1998). These values are included at the bottom of Table 2. Since both salt and fresh surface water systems occur in the upper Petaluma Watershed, numerical guidelines for both are provided in Table 2.

Methods

The monitoring program focused on quantifying concentrations of diazinon and chlorpyrifos in the River, tributaries, and storm drain systems of the upper Petaluma River Watershed during dry weather and storm-related flows. A total of four sampling events were conducted. During the first event on 21 July 1998 samples were collected to characterize dry weather base flows in the creeks and culverts. These base flows are maintained by groundwater flow and water use by people in the basin (e.g., runoff from over-irrigation, runoff from car washing, leaking pipes). The first storm-related sampling event occurred on 24 October 1998; this storm could be characterized as the "first flush."[4] The last two sampling events occurred during subsequent storms on 7 and 21 November 1998. Efforts were made to collect the storm-related samples within a few hours of the start of rainfall events so that the data would be comparable (it has been demonstrated by other investigators that diazinon and chlorpyrifos concentrations can vary significantly at the same location as the storm progresses [Scanlin and Feng, 1997]).

Eight locations were selected for sampling and are shown on Figure 1. Sampling locations were selected to be representative of varying land uses (i.e., residential, commercial, industrial, and agricultural) within the greater Petaluma area (Table 3), and allow characterization of the greatest amount of runoff within the upper watershed for the limited number of sampling stations. Figures showing sampling locations PRW-1 through PRW-7 are included in Appendix A.

Samples were collected in 500 milliliter amber glass bottles supplied by an analytical laboratory at a depth of 0.5 to 1.0 foot below the water surface. All samples were labeled, stored in a cooled container, and transported under chain-of-custody protocols to AQUA-Science Laboratories of Davis, California for analysis. Each sample was analyzed for diazinon and chlorpyrifos using the enzyme-linked immunosorbant assay (ELISA) method. The practical detection limits for diazinon and chlorpyrifos

[4] "First flush" refers to the first storm of a given rainy season that washes accumulated pollutants on paved and unpaved surfaces, roof tops, and plant material into the storm drainage system and to surface water bodies.

using the ELISA method are 30 nanograms/liter (ng/L).[5] Quality assurance and quality control is discussed in Appendix B.

Table 3
Land Uses within Subbasins Monitored

Sampling Station	Land Use in Subbasin above Sampling Station
1) Upper Petaluma River	**Open space** and low intensity **agriculture** in the immediate vicinity of sampling station (minor residential and commercial). Town of Penngrove approximately two miles upstream.
2) Upper Lynch Creek	**Open space** and low intensity **agriculture** (minor residential).
3) Lower Lynch Creek	Retail **commercial** and suburban **residential**. Highway 101 crosses creek less than one-half mile upstream of sampling station. Open space and low intensity agriculture (i.e. grazing land) and minor residential in upper portion of subbasin.
4) Washington Creek	Retail **commercial** and suburban **residential**. Highway 101 crosses creek approximately one-half mile upstream of sampling station. Athletic playing fields and a new golf course approximately two miles upstream. Open space, low intensity agriculture (i.e. grazing land), and minor residential in upper portion of subbasin.
5) Turning Basin	Downtown Petaluma (**commercial**) and suburban **residential.** This sampling station is at a culverted outfall; there is no creek. This is entirely an underground storm drainage system.
6) Thompson Creek	Suburban **residential**, **commercial**, minor light industrial. The lower 2,000 feet of this creek is culverted underground.
7) Adobe Creek	**Commercial**, light **industrial**, **residential**. A golf course approximately 1.5 miles upstream of sampling station. Open space, low intensity agriculture (i.e., grazing land), and minor residential in upper portion of subbasin.
8) Lower Petaluma River	Sampling station in main stem of Petaluma River approximately five miles downstream of the City of Petaluma, primarily **agriculture**.

Occurrence of Diazinon and Chlorpyrifos

The analytical results are summarized in Table 4. Graphical representations of diazinon and chlorpyrifos concentrations identified at each sampling station are presented on Figure 2 (for diazinon) and Figure 3 (for chlorpyrifos). To provide context for the identified concentrations, the minimum concentrations expected to result in toxicity to test organisms are also shown on the graphs. Reportable concentrations of diazinon were identified in 16 of the 32 samples collected (50 percent); reportable concentrations of

[5] ng/L is equivalent to parts per trillion (ppt).

Table 4
Summary of Analytical Results
Petaluma River Watershed

Sample ID	Date	Time (24-hr)	Diazinon (ng/L)	Chlorpyrifos (ng/L)	Electrical Conductivity (µmhos/cm)	pH	Temperature (c)
Upper Petaluma River:							
PRW-1	7/21/98	8:35	<30	<30	900	7.65	18.8
	10/24/98	7:20	<30	<30	--	--	--
	11/7/98	2:20	<30	<30	1,200	8.13	12.1
	11/21/98	20:40	<30	31	1,020	7.72	13.7
Upper Lynch Creek:							
PRW-2	7/21/98	9:00	<30	<30	550	7.38	19.4
	10/24/98	8:05	<30	<30	--	--	--
	11/7/98	2:37	<30	<30	600	7.42	13.1
	11/21/98	20:55	<30	<30	650	7.88	14.3
Lower Lynch Creek:							
PRW-3	7/21/98	9:15	<30	<30	850	7.35	17.6
	10/24/98	8:34	--	--	--	--	--
	11/7/98	3:00	118	63	500	6.38	12.7
	11/21/98	21:20	86	<30	670	7.25	14.2
Washington Creek:							
PRW-4	7/21/98	9:25	<30	<30	1,150	7.81	17.6
	10/24/98	8:20	58	31	--	--	--
	10/24/98[1]	8:25	49	31	--	--	--
	11/7/98	2:52	45	<30	8,000	7.17	12.7
	11/21/98	21:10	888[2]	39	1,320	7.70	14.0
Turning Basin:							
PRW-5	7/21/98	9:50	<30	<30	700	8.23	19.3
	10/24/98	7:30	420	<30	--	--	--
	11/7/98	2:09	1088	57	2,100	8.13	14.4
	11/21/98	20:25	415	77	400	6.67	14.5
Thompson Creek:							
PRW-6	7/21/98	10:03	<30	<30	1,150	8.26	18.7
	10/24/98	7:20	1368	47	--	--	--
	11/7/98	1:54	100	<30	15,000	7.14	13.6
	11/7/98[1]	1:58	120	<30	15,000	7.14	13.6
	11/7/98[3]	10:10	480	53	680	8.16	13.5
	11/21/98	20:05	56	<30	950	7.46	13.3
Adobe Creek:							
PRW-7	7/21/98	10:15	<30	<30	650	8.06	18.7
	10/24/98	8:50	716	43	--	--	--
	11/7/98	3:13	157	<30	475	7.10	13.1
	11/21/98	21:36	42	34	320	7.68	14.5
	11/21/98[1]	21:41	<30	30	320	7.68	14.5
Lower Petaluma River:							
PRW-8	7/21/98	10:30	<30	<30	13,000	7.52	20.5
	7/21/98[1]	10:36	<30	<30	13,000	7.48	21.0
	10/24/98	9:02	<30	<30	--	--	--
	11/7/98	3:20	<30	<30	21,000	7.69	12.8
	11/21/98	21:50	35	<30	9,500	7.70	13.8

Notes:

Sampling locations shown on Figure 1. Results presented graphically on Figures 2 and 3.

Diazinon and chlorpyrifos analyzed by ELISA methodology

Electrical conductivity, pH, and temperature measured in the field.

-- = not analyzed

<30 = compound not detected above 30 ng/L

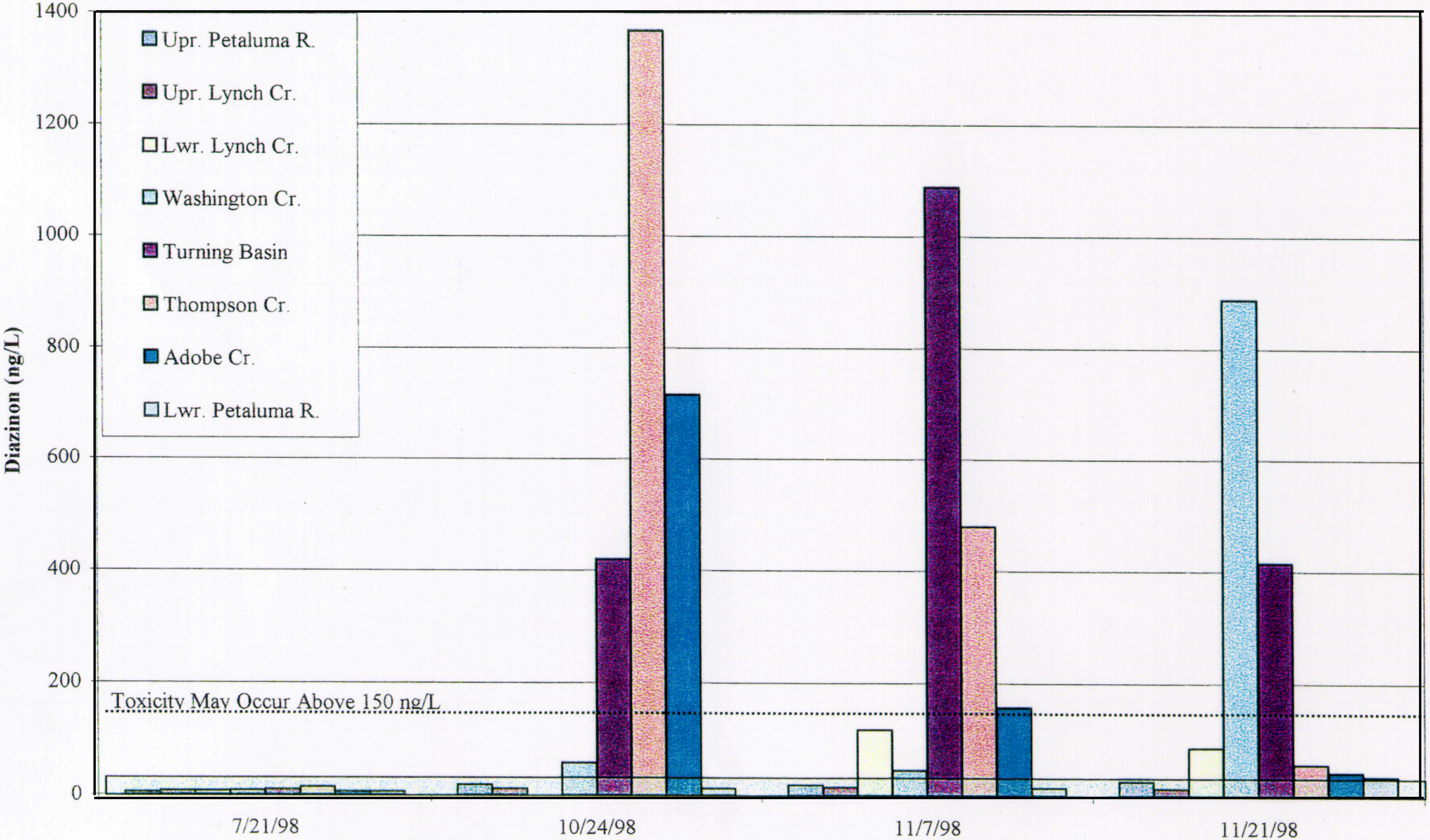
[1] Duplicate sample collected and analyzed as part of quality assurance/quality control program.

[2] This result was outside the range of the calibrated curve for the test method and no dilution was performed. This value should be considered approximate

[3] This sample was collected later in the storm (during low tide) since the samples collected at 1:58 and 1:54 on 11/7/98 were collected during high tide and Petaluma River water had backed up to the sampling station (note high electrical conductivity of high tide samples)

Diazinon in Upper Petaluma River Watershed, 1998

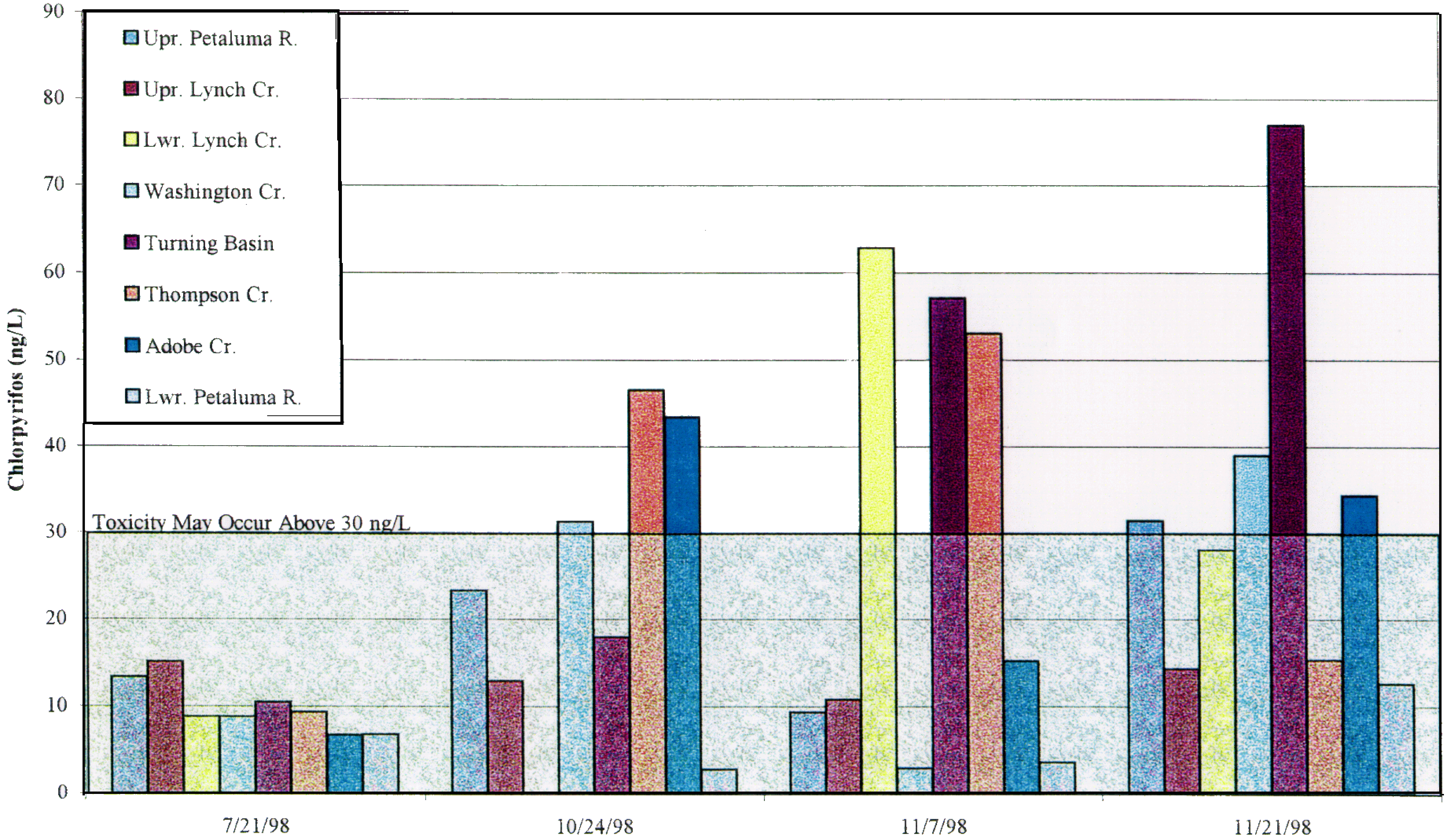
Figure 2



Note: Concentrations were generated for all samples as a result of the test method. The practical laboratory reporting limit is 30 ng/L; concentrations below 30 ng/L (shaded area) should be considered "non-detect".

Chlorpyrifos in Upper Petaluma River Watershed, 1998

Figure 3



Note: Concentrations were generated for all samples as a result of the test method. The practical laboratory reporting limit is 30 ng/L; concentrations below 30 ng/L (shaded area) should be considered "non-detect" chlorpyrifos were identified in 10 of the 32 samples collected (31 percent). Concentrations of diazinon ranged from below laboratory reporting limits to 1,368 ng/L, and chlorpyrifos ranged from below reporting limits to 77 ng/L. Highest concentrations of both diazinon and chlorpyrifos were identified at the Turning Basin storm drain, Thompson Creek, Adobe Creek, and Washington Creek. Lowest concentrations of diazinon and chlorpyrifos (near or below the laboratory reporting limits) were identified at the Upper and Lower Petaluma River stations and the Upper Lynch Creek station.

Samples collected from dry weather flows (sampling date 21 July 1998) did not contain reportable concentrations of diazinon or chlorpyrifos. Of the three storm-related monitoring events, 16 of the 24 samples (67 percent) contained reportable concentrations of diazinon, and 10 of the 24 samples (42 percent) contained reportable concentrations of chlorpyrifos.[6] Copies of the laboratory reports are included in Appendix C.

Discussion of Potential Toxicity and Exceedance of Water Quality Guidelines

The toxicity of water can be evaluated by performing toxicity testing at a qualified laboratory. At the laboratory, specific test organisms (in the case of diazinon and chlorpyrifos toxicity testing, typically small invertebrate crustaceans) are placed in a sample of the water (at 25 degrees centigrade) and their responses documented on a daily basis. If all the test organisms survive and reproduce normally, the water would not be considered toxic to that particular organism. If, however, a statistically significant portion of the organisms die within the period of the test, the sample would be considered toxic. The two most important factors in determining toxicity are 1) the concentration of a potentially toxic chemical (the higher the concentration, the higher the level of toxicity), and 2) the duration of exposure, or how long the organism is exposed to the chemical (the longer the exposure the more likely toxicity would be observed).

No toxicity testing was conducted as part of this investigation due to budgetary constraints (the appropriate test cost hundreds to thousands of dollars to perform). However, many toxicity tests have been conducted by other investigators on runoff samples collected from Bay Area watersheds (though none from the Petaluma River Watershed). The results of the toxicity tests indicate that concentrations of less than 150 ng/L diazinon were not lethal to *Ceriodaphnia dubia,* a fresh water invertebrate test organism, within seven days, 150 to 300 ng/L diazinon were lethal after four to seven days of exposure, and 300 to 500 ng/L diazinon were usually lethal within two days (Katznelson and Mumley, 1997). Chlorpyrifos has been demonstrated to be toxic to *Ceriodaphnia dubia* at concentrations above 80 ng/L and *Palaemon macrodactylus* or *Mysidopsis bahia*, invertebrate salt water crustaceans, at concentrations of 10 to 30 ng/L (Barron and Woodburn, 1995), which is below the detection limit of the analytical method used in this study. Therefore, any reportable concentration of chlorpyrifos would be considered potentially toxic to these invertebrates. Sensitivity of both fresh and salt water organisms was considered in the toxicity discussion since both conditions can occur at many of the sampling stations.

Approximately 50 percent of samples collected from storm-related flows contained potentially toxic concentrations of either diazinon or chlorpyrifos or both. Eight of the samples collected as part of this investigation contained greater than 150 ng/L of diazinon and 10 samples contained concentrations of

[6] Results of duplicate (QA/QC) samples were not included in this, or subsequent, numerical summaries.

chlorpyrifos greater than 30 ng/L. If these concentrations persisted (not confirmed by this study), then creek conditions where they were collected would be expected to be toxic to identified test organisms and perhaps to other lower food chain organisms with similar sensitivity. The levels of diazinon and chlorpyrifos identified in this study would not be considered toxic to fish, amphibians, reptiles, birds, or mammals (Novartis, 1997; Barron and Woodburn, 1995).

In this study, concentrations were determined at various times and locations within the watershed. The duration of exposure was not determined. A previous study conducted in the Castro Valley Creek Watershed in Alameda County (Scanlin and Feng, 1997) determined that diazinon concentrations generally follow one of two patterns through the course of a storm; they either 1) peak early in the storm runoff event and then decrease rapidly, or 2) they remain relatively consistent. If concentrations peak at the onset of the storm (probably due to the "first flush" phenomena) and then rapidly decline in the Petaluma River Watershed, then duration of exposure to diazinon and/or chlorpyrifos may not be long enough to cause toxicity. However, if the concentrations persist through the storm, then exposures may be adequate to cause significant toxicity to aquatic organisms.

Approximately 33 percent of the storm-related samples collected contain potentially toxic concentrations of diazinon[7] (100 percent of the samples collected from the Turning Basin outfall and 66 percent of the samples collected from Thompson and Adobe creeks were potentially toxic due to the presence of diazinon). Approximately 42 percent of the storm-related samples collected contained potentially toxic concentrations of chlorpyrifos[8] (66 percent of the samples collected from Washington Creek, the Turning Basin outfall, Thompson Creek and Adobe Creek were potentially toxic due to the presence of chlorpyrifos).

Concentrations of diazinon in samples collected during this study exceeded existing water quality guidelines (40 ng/L for fresh or salt water) on 15 occasions (of a total of 32 samples collected). Concentrations of chlorpyrifos exceeded existing water quality guidelines (41 ng/L for fresh water and 5.6 ng/L for salt water) on five occasions. However, more samples may have exceeded the chlorpyrifos salt water criteria that could not be identified since the reporting limit of 30 ng/L for the test method used far exceeds the water quality guideline of 5.6 ng/L. All the samples collected from the Lower Petaluma River station and individual samples collected from the Washington Creek and Thompson Creek stations would be considered salt water based on the electrical conductivity (greater than 7,500 µmhos/cm) measured during sample collection.

CONCLUSIONS

C Neither diazinon nor chlorpyrifos was identified in any of the samples collected during the dry weather sampling event. This may indicate that discharge of these pollutants in wash water and irrigation overflow (typical summertime gutter flow) is not widespread and/or persistent within the watershed. However, the results of one sampling event do not rule out the possibility that significant discharges occur in the dry weather flows.

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[7] Concentrations potentially toxic to *Ceriodaphnia dubia*.

[8] Concentrations potentially toxic to *Palaemon macrodactylus* or *Mysidopsis bahia*.

- Diazinon and chlorpyrifos are present at reportable concentrations in much of the storm water runoff in the Petaluma River Watershed. Samples collected from the Turning Basin outfall, Thompson Creek, and Adobe Creek contained diazinon concentrations potentially toxic to standard test organisms (*Ceriodaphnia dubia*) during at least two of the three storm-related sampling events. Chlorpyrifos was detected in two of the three storm-related sampling events in Washington Creek, the Turning Basin Outfall, Thompson Creek, and Adobe Creek.

- The levels of diazinon and chlorpyrifos identified in the upper Petaluma River Watershed in this study would not be considered toxic to fish, amphibians, reptiles, birds, or mammals.

- The levels of diazinon and chlorpyrifos identified in some creeks of the upper Petaluma River Watershed in this study would likely be toxic to standard test organisms, and therefore may be toxic to naturally-occurring sensitive species. If so, the entire food chain could be negatively impacted by the presence of these pesticides. Residential and commercial land uses dominate within the subbasins demonstrating highest potential toxicity. The likely source of diazinon and chlorpyrifos in runoff from residential and commercial areas is the outdoor use of these products for pest control.

- It appears that low intensity agriculture and open space areas contribute little, if any, diazinon and chlorpyrifos to the system. Samples collected from the Upper Petaluma River and Upper Lynch Creek stations (largely agriculture and open space) did not contain reportable concentrations of diazinon and only one positive result (near the detection limit) for chlorpyrifos.

- Water quality monitoring at the Turning Basin sampling station helped demonstrate that residential and commercial land uses are a significant source of diazinon and chlorpyrifos in the basin. Consistently toxic concentrations of diazinon and chlorpyrifos were sampled at the outfall, and therefore this drainage area does contribute a potentially significant load of these compounds to the system. However, concentrations would be expected to be quickly diluted as they enter the main stem of the River and it is unlikely that significant habitat would be present in the storm drainage system represented by and upstream of this sampling station.

UNANSWERED QUESTIONS AND FURTHER WORK NEEDED

Are diazinon and chlorpyrifos persistent in these urban creeks throughout the rainy season? How long do toxic concentrations persist in these systems?

This question could best be answered with continued water quality monitoring. In practical terms, it would probably require that one or two creek systems be selected for more intensive study, and that many more samples be collected through the rainy season at the selected creek(s). We suggest that Thompson Creek and Adobe Creek would be logical candidates for additional study. Thompson Creek contained the highest mean concentration of diazinon (and the highest single value) of any of the creek sampling stations monitored in this study. Adobe Creek water was potentially toxic, either from diazinon or chlorpyrifos concentrations, during each storm-related monitoring event (none of the other creek sampling stations were identified to be potentially toxic during every storm-related sampling event).

Is there habitat value in these creeks that would benefit from a reduction in diazinon and chlorpyrifos concentrations?

A common argument against the use of, or reliance upon, toxicity testing using sensitive species is that "there are no such species in the system, and therefore no impact exists." In many cases, the very reason the basic food chain components are absent is that continuous flushing of the system with pesticide-laden runoff kills them. At the same time there may be a whole range of other physical and chemical conditions in the urban creeks of Petaluma that discourage the presence of lower food chain aquatic organisms (e.g. lack of physical habitat sites, temperature of the water, poor water quality caused by other chemicals).

Prior to initiating any efforts to reduce the pollutant concentrations, the potential habitat value of the systems should be determined. The activities associated with the fish hatchery on Adobe Creek has generated some biological characterization of that system, but based on available information, it does not appear that any rigorous biological monitoring of Thompson Creek has occurred. We recommend that all the available biological data on these two systems be compiled and analyzed in light of the new water quality data generated as part of this study. A systematic approach to determine whether the biological diversity of these systems could benefit from reduced pesticide levels in the water should be undertaken.

If it is determined that habitat could benefit from a reduction in the level of these pesticides, what is the most effective method of achieving this reduction?

Often, the first response to the identification of damaging pollutants in the environment is a move to ban the particular chemical causing the most recently identified problem. The short-coming of this approach is, if banned, another pesticide that may be equally or more damaging to aquatic habitat would probably be introduced to take its place. This repeated cycle of product introduction, problem identification, and product removal could continue indefinitely with no substantial progress being made toward habitat improvement. The underlying issue that needs to be resolved is the relationship of people to pests (in the case of pesticide use). We believe that the residents of this community should be informed that 1) a valuable resource is in their community is at risk, and 2) that their individual actions can have significant impacts on the health of that resource. This may be the only practical way to achieve lasting improvement of the health of the system. Educational programs may include formation of watershed partnerships, educational mailers, creek programs, and volunteer monitoring. We believe that the watershed planning effort being initiated by the local Resource Conservation District, which may include the formation of a watershed council, or another watershed partnership which focuses on urban pollutants, should consider the results of this study and decide on the best approaches to public outreach and education, and continue monitoring activities to demonstrate changes in water quality conditions with the selected subbasins.

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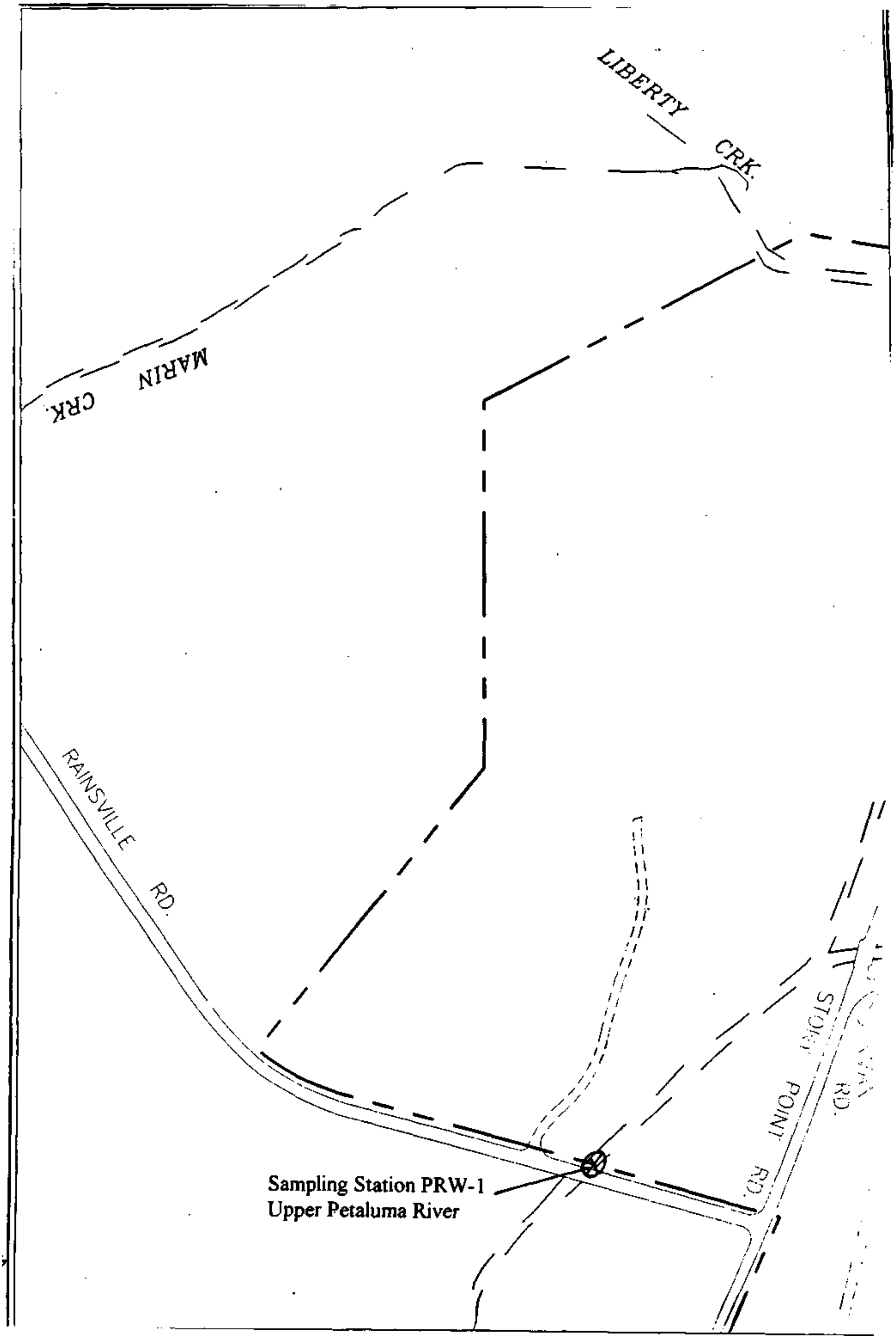
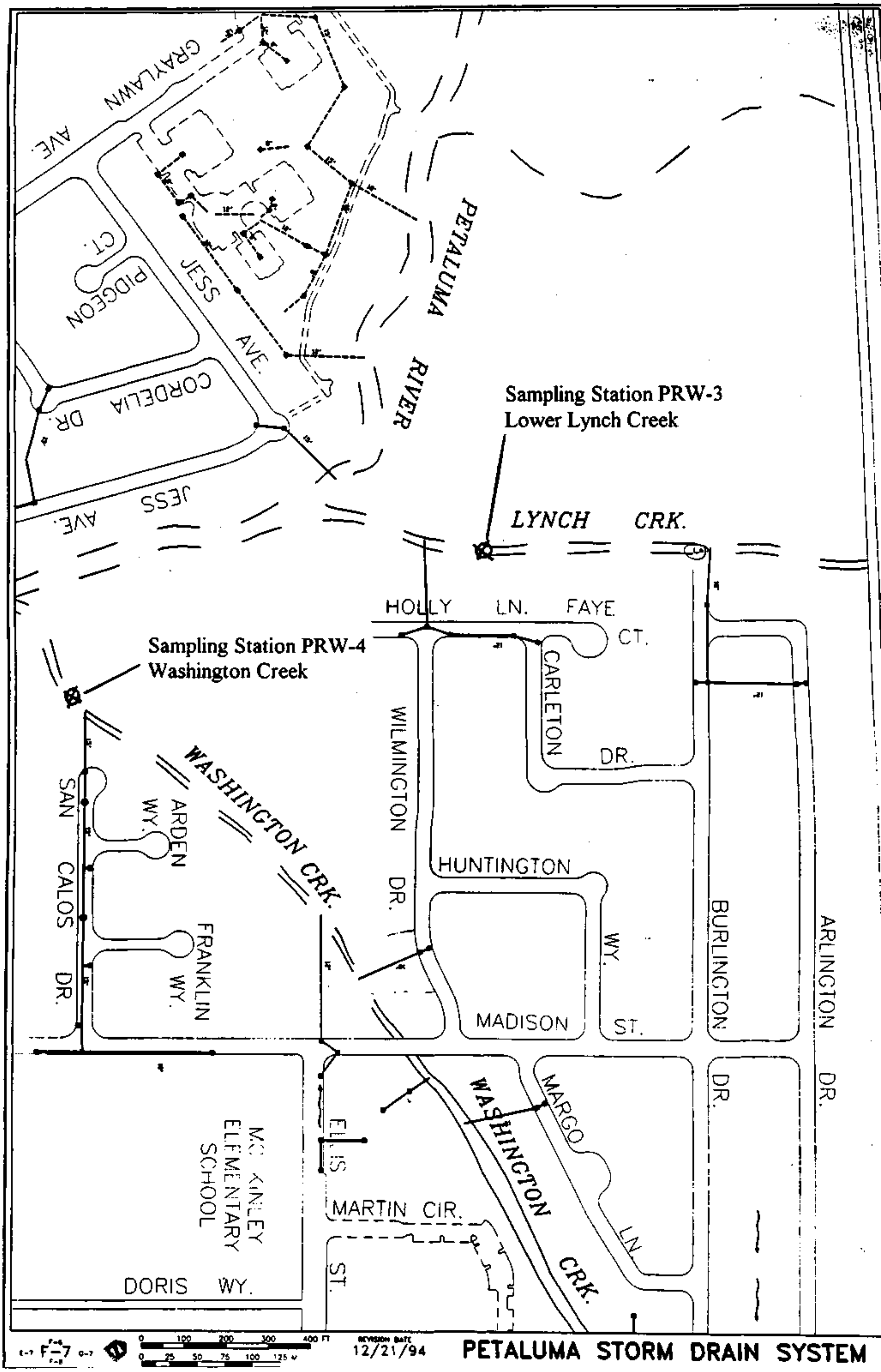
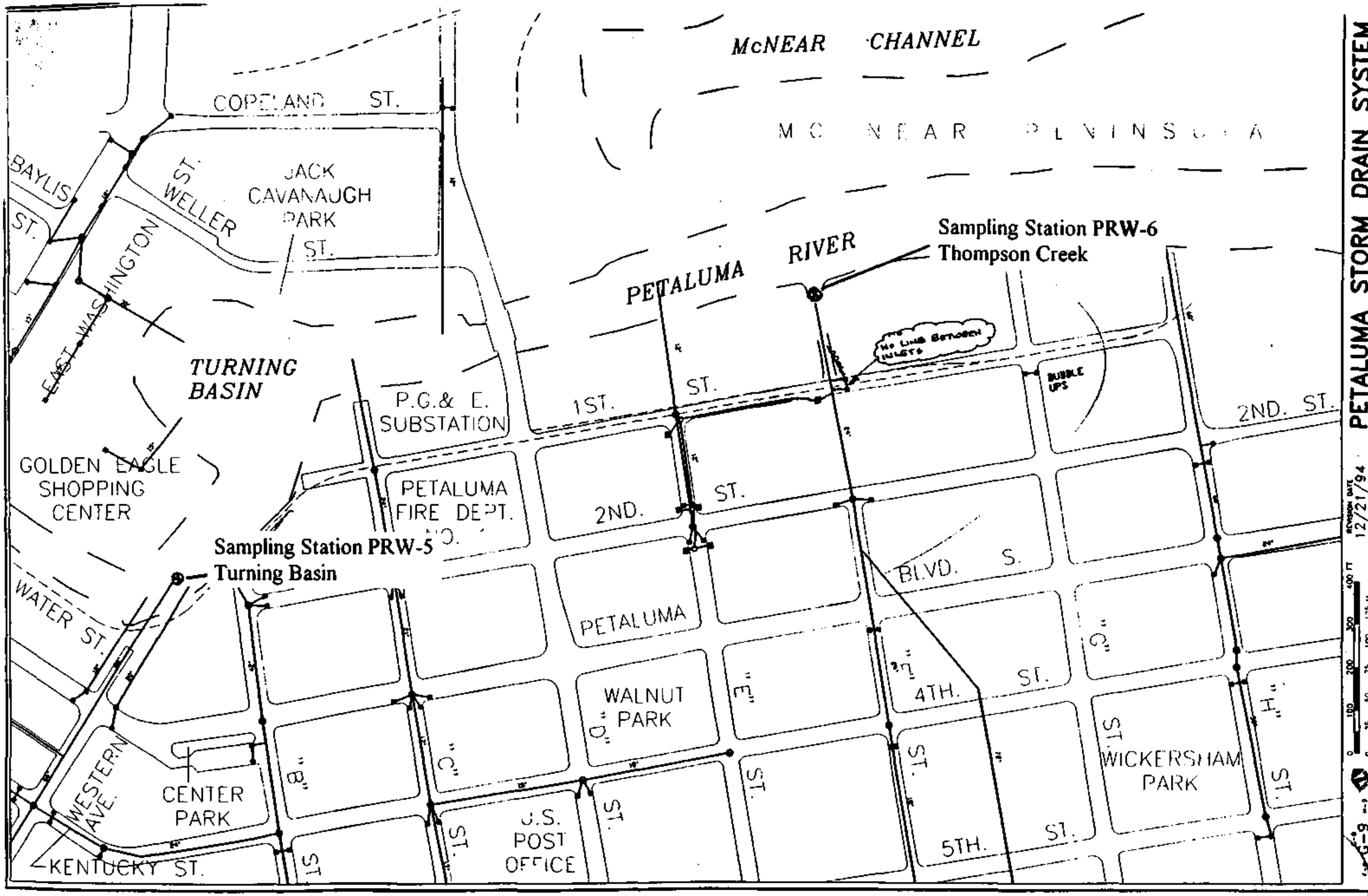
Appendix A
Sampling Station Locations

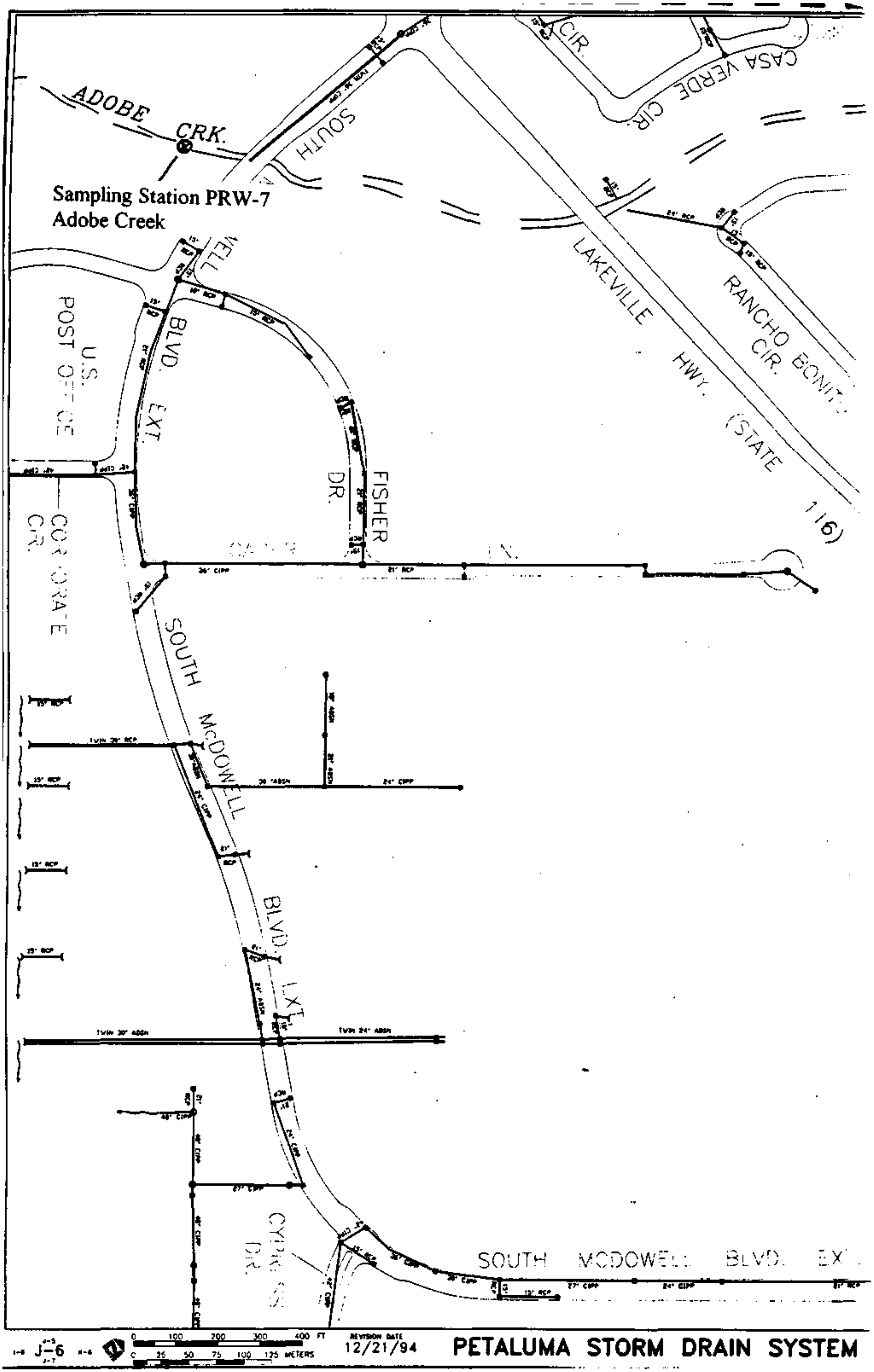
Source of base maps: City of Petaluma Storm Drain System, Department of Engineering (1994).

Sampling stations PRW-2 and PRW-8 are outside the boundaries of storm drain system map coverage, and therefore not shown on the enclosed maps. Sampling station PRW-2 is at the intersection of Adobe Road and Lynch Creek; PRW-8 is at the floating dock on the Petaluma River at Gilardis.


LIBERTY CRK.
MARIN CRK.
RAINSVILLE RD.
STONY POINT RD.
Sampling Station PRW-1
Upper Petaluma River


GRAYLAWN AVE.
PIDGEON CT.
JESS AVE.
CORDELIA DR.
JESS AVE.
PETALUMA RIVER
Sampling Station PRW-3
Lower Lynch Creek
LYNCH CRK.
HOLLY LN.
FAYE CT.
Sampling Station PRW-4
Washington Creek
CARLETON DR.
WILMINGTON DR.
WASHINGTON CRK.
SAN CALOS DR.
ARDEN WY.
FRANKLIN WY.
HUNTINGTON WY.
MADISON ST.
BURLINGTON DR.
ARLINGTON DR.
MARGO LN.
WASHINGTON CRK.
ELLIS ST.
MARTIN CIR.
MC KINLEY ELEMENTARY SCHOOL
DORIS WY.
F-7
0 100 200 300 400 FT
0 25 50 75 100 125 M
REVISION DATE 12/21/94
PETALUMA STORM DRAIN SYSTEM


McNEAR CHANNEL
MC NEAR PENINSULA
COPELAND ST.
BAYLIS
ST.
ST. WELLER
JACK CAVANAUGH PARK
ST.
EAST WASHINGTON
TURNING BASIN
PETALUMA RIVER
Sampling Station PRW-6
Thompson Creek
BUBBLE UPS
P.G.& E. SUBSTATION
1ST. ST.
2ND. ST.
GOLDEN EAGLE SHOPPING CENTER
PETALUMA FIRE DEPT.
2ND. ST.
Sampling Station PRW-5
Turning Basin
BLVD. S.
WATER ST.
PETALUMA
"G"
"F"
4TH. ST.
"E"
WALNUT PARK
"D"
ST.
WICKERSHAM PARK
"H"
"B"
"C"
ST.
WESTERN AVE.
CENTER PARK
U.S. POST OFFICE
ST.
5TH. ST.
KENTUCKY ST.
ST.
PETALUMA STORM DRAIN SYSTEM
REVISION DATE 12/21/94
G-9



ADOBE CRK.
Sampling Station PRW-7
Adobe Creek
SOUTH
CASA VERDE CIR.
CIR.
LAKEVILLE HWY. (STATE 116)
RANCHO BONITO CIR.
U.S. POST OFFICE
BLVD. EXT.
FISHER DR.
CORPORATE CIR.
LN.
SOUTH McDOWELL BLVD. EXT.
CYPRESS DR.
SOUTH MCDOWELL BLVD. EXT.
TWIN 30" RCP
TWIN 30" ABSN
TWIN 24" ABSN
24" CIPP
27" CIPP
36" CIPP
21" RCP
15" RCP
J-6
0 100 200 300 400 FT
0 25 50 75 100 125 METERS
REVISION DATE 12/21/94
PETALUMA STORM DRAIN SYSTEM

Appendix B
Quality Assurance/Quality Control Provisions

Quality Assurance/Quality Control

The objective of the Quality Assurance/Quality Control (QA/QC) plan is to ensure that all technical data generated during this investigation are accurate, representative, technically defensible, and appropriate for project objectives. The components of the QA/QC plan are summarized below:

- All sample collection were conducted by, or under the supervision of, a qualified water quality professional (in this case, a California Certified Hydrogeologist);
- All samples were be collected in pre-cleaned glass bottles supplied by an analytical laboratory;
- All samples were labeled immediately after sample collection and placed in a cooler containing blue ice;
- Sample custody was documented and maintained from the time of sample collection through completion of laboratory analysis. A chain-of-custody record was prepared following sample collection and accompanied the samples at all times;
- During each sampling event, one quality control sample was submitted with the environmental samples. In this case, one field duplicate (used to demonstrate the precision of the analytical data and sampling technique) was collected during each event. ;
- Standard laboratory analysis procedures include QA/QC reporting for each batch of samples. These procedures include lab spikes and lab duplicates. In a lab spike, a known concentration of the analyzed compound (i.e. 0.1 ppb diazinon) is added to the sample. The sample is then analyzed to determine whether the analytical procedure is able to quantify the spiked contaminant concentration and the concentration contained within the environmental sample. A lab duplicate procedure simply analyzes another portion of the environmental sample as a separate sample to evaluate reproducibility of the procedure.

  Field duplicates ranged from 3.0 to 18 percent of the concentration identified in the primary sample. Lab duplicates were all non-detect, as were the primary samples they were used to evaluate. Spike samples demonstrated a precision between 2.0 and 11 percent (i.e. comparing the concentration of the primary sample to the spike concentration after subtracting the known concentration of added analyte). These QA/QC values indicate adequate accuracy and precision of the analytical method used for the purposes of this investigation.

Appendix C
Laboratory Reports

Not available for this KRIS edition of this paper