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Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas III: Watershed-Based Prioritization

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1 Introduction

The Surface Water Protection Program (SWPP) of California Department of Pesticide Regulation (DPR) is developing a methodology and computer implementation to prioritize pesticides for surface water monitoring in agricultural and urban areas of California. The first two phases of this methodology generate priority lists and monitoring recommendations of pesticide active ingredients (AI's) and degradates (Luo et al., 2013; Luo et al., 2014). The prioritization process is mainly based on use data in the Pesticide Use Reporting (PUR) database and toxicological data in the USEPA Aquatic Life Benchmark database. In the current procedure, use data is aggregated at county level (for one county or a multi-county region). However, pesticide concentrations measured at monitoring sites are affected by pesticide use and transport within the hydrologic drainage areas. Therefore, the phase-3 scheme is proposed here for monitoring prioritization at watershed scale.

Most of the variables and procedures developed in the phase-1 and -2 of the methodology are applied in watershed-scale prioritization. In addition, the following new developments have been incorporated in the phase-3 prioritization:

a) Statewide watershed delineation and stream network are developed at the spatial resolution of USGS 12-digit hydrologic unit (HU12). User-defined watershed boundary is also allowed for a monitoring site associated with drainage area which cannot be appropriately represented by standard HU12 watersheds.
b) Watershed-based prioritization is initially designed for agricultural uses of pesticides. PUR data available at section level (1×1 mi^2) are aggregated for each watershed in the drainage area of a monitoring site.
c) Similar approach is applied to urban pesticides use data reported in PUR, by down-scaling county-level use data to sub-county districts (by population), then converted to watershed scale (by area intersection between the watershed and sub-county districts).
d) Watershed-based prioritization is developed in two forms: [1] prioritization for surface water monitoring in a given drainage area delineated by standard (HU12) or customized watersheds (this is similar to the county-based prioritization implemented in the previous

phases); and [2] statewide prioritization for surface water monitoring for pesticide(s) of interest.

e) Compared to county-based processes, watershed prioritization considers two additional factors of pesticide dilution and dissipation. Dilution is estimated based on total drainage area and predicted streamflow retrieved from the enhanced National Hydrography Dataset (NHDPlus). Dissipation is estimated based on total travel time in the drainage area and pesticide dissipation half-life in water-sediment system.

Mainly based on PUR data and spatial analysis, monitoring prioritization is not expected to predict pesticide concentrations and their spatiotemporal variability. The primary objective is to provide relative importance of pesticide AI's or monitoring sites to justify and optimize surface water monitoring studies conducted by DPR. The comparisons with previous chemical and site selections and monitoring results (in terms of detections or benchmark exceedances) are conducted for the evaluation of the proposed methodology.

2 Methodology

2.1 Delineation of watershed and water connectivity

Watershed delineation is based on Watershed Boundary Dataset (WBD) (USGS, 2014) with six nested levels of the Hydrologic Unit (HU) hierarchy. Each hydrologic unit is given a Hydrologic Unit Code (HUC). For example, the first level of the WBD, representing 21 "hydrologic regions" in the United States, has a 2-digit HUC (HUC2) such as "01" for New England and "02" for Mid-Atlantic region. The State of California is generally covered by HUC2 of "18" (hydrologic region of California, Figure 1).

Each hydrologic unit is subdivided into multiple units for the next level of hydrologic units. For example, 9 4-digit hydrologic units are nested in the hydrologic region of California, including HUC4=1801 (Klamath-Northern California Coast) to 1809 (North Mojave-Mono Lake). Each 4-digit hydrologic unit is further divided into 6-digit units, then 8-digit units, and so on. This watershed-based prioritization is based on 12-digit hydrologic units (HU12), which is the highest resolution available for California in the WBD. In this report, **"watershed" refers to a 12-digit hydrologic unit** defined in the WBD unless stated otherwise. In summary, there are about 4,415 watersheds in the hydrologic region of California (Figure 1), with areas ranging from 4.1 to 374 mi^2 (with a median size of 33.7 mi^2). There are about 200 watersheds located out of the state territory boundary of California (Figure 1). Those watersheds would not be associated with any PUR data, but used for the calculation of total drainage areas for potential downstream monitoring sites in California.

Figure 1. Hydrologic region of California (2-digit hydrologic unit code, HUC2=18) and its enclosed watersheds (12-digit hydrologic units), as delineated in the USGS Watershed Boundary Dataset

Pesticide observed in a watershed may be contributed by both the local watershed and all upstream watersheds. Given a watershed outlet, its **drainage area** (or "basin") can be defined by all contributing watersheds, connected by stream network. Stream network at HU12 level is characterized based on USGS National Hydrography Dataset (NHD) and its enhanced version NHDPlus (USGS, 2012). Upstream-downstream relationship is used for the determination of water connectivity. In NHD, each surface water channel between the conjunctions with other channels is called a NHD "flowline", indexed by a unique ID ("Common identifier", or "COMID"). NHD flowline characteristics required in watershed-based prioritization include length, stream order, cumulative drainage area, and predicted mean annual streamflow and velocity.

2.2 Aggregation of agricultural pesticide uses in a watershed

The PUR database provides agricultural pesticide uses at section level (approximately 1 mi^2). To simplify the data processing, each section is assigned to one watershed based on the majority of area coverage, and all reported uses in the section will be distributed to its assigned watershed.

This approach is justified by the fact that most of the watersheds are associated with total drainage areas significantly larger than the section size by at least one magnitude. More accurate use data distribution requires sub-section data to determine the spatial variations of pesticide uses within each section. These data are not publically available.

For a watershed, agricultural uses of pesticides are queried for all its associated sections according to user-selected years and months, and the total uses are reported as the agricultural uses in the watershed.

2.3 Aggregation of urban pesticide uses in a watershed

Urban pesticide use data is reported in PUR at county level. Sub-county population density data are used for the conversion of county-based use data to watershed scale. Population density data for the survey year 2012 are taken from U.S. Census Bureau, with 397 sub-county districts in California. A watershed may be covered by multiple sub-county districts, and its total population is calculated as the area-weighted sum of the population density in the corresponding districts. Similarly, total urban pesticide use (including structural pest control, landscape maintenance, and/or right-of-way applications, per user-selected use patterns) in each watershed is estimated based on the reported county-level data normalized by the population fractions of the watershed in each of the counties. The implied assumption is that, in each county, reported urban uses can be proportionally distributed to sub-county districts according to the corresponding population. For example, if a sub-county district explains 10% of the total county population, it's assumed that this district will use 10% of the reported urban uses of this county. Finally, the urban pesticide use in a watershed is calculated as,

$$USE(k) = \sum_{i=1}^{58} [f_i(k) \times PUR(i)] \quad (1)$$

where *k* is the index of the watershed of interest, *i* is a running index as California county code (i=1-58), f_i(k) is the population fraction of the county *i* in the watershed *k* (i.e., population in the intersected area between *i* and *k*, divided by the total population in *i*; f=0 for those counties not overlapping with the watershed *k*), USE(*k*) is the estimated urban pesticide use in the watershed *k* during the user-defined period, and PUR(i) is the reported urban uses in the PUR for the same period. Taking the "Coyote Creek – San Gabriel River watershed" (HUC12=180701060606) as an example, there are 339,534 people in Los Angeles portion of the watershed (3.4% of the total population in Los Angeles County, county code=19), and 95,669 people in Orange portion (3.0% of the total population in Orange County, county code=30). In this case, therefore, f_{19}=3.4%, f_{30}=3.0%, and all other f's are zero. More details for the calculation are demonstrated in Appendix 1.

2.4 Pesticide prioritization for monitoring of a watershed

Two types of prioritization are developed based on hydrologic orders: mainstream prioritization and tributary prioritization (Figure 2). While a tributary is only contributed by the local watershed, a mainstream receives water flows and pesticide residues from both local watershed and upstream watersheds. For this purpose, a traversal algorithm is used to search for all upstream watersheds for the watershed of interest, and the hydrologic sequence of the identified watersheds is developed based on the upstream-downstream relationship. Once pesticide uses are calculated for the drainage area of the watershed of interest, the mainstream prioritization for monitoring can be conducted following the same procedures developed for county-based procedures (Luo et al., 2013; Luo et al., 2014).

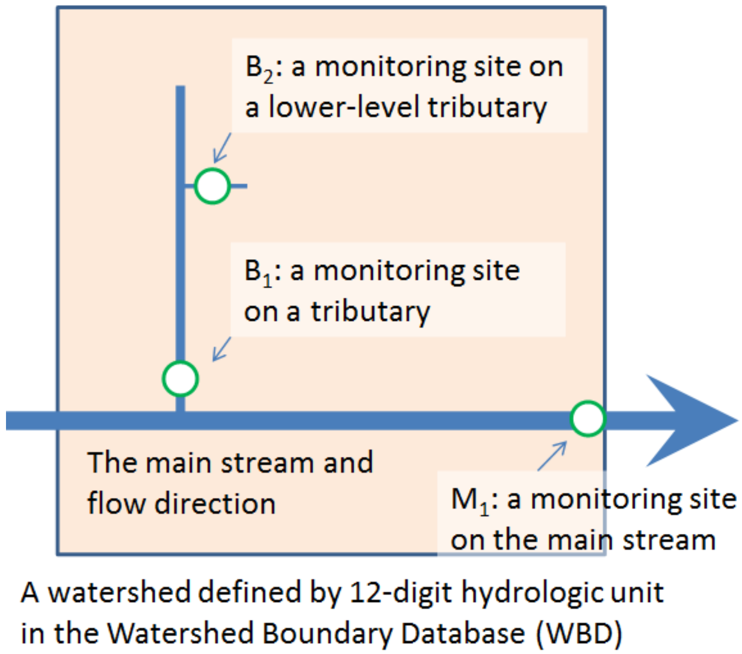


Figure 2. Demonstration of monitoring sites on the main stream and on tributaries of a watershed

The proposed method differentiates the mainstream sites and tributary sites by their drainage areas, but does not consider the geographic location of a monitoring site within the watershed. In the case of tributary prioritization, for example, the same results of prioritization would be generated for all tributary sites in the watershed by assuming that those sites potentially receive pesticide runoff from the entire watershed. This assumption may overestimate pesticide uses, especially for the monitoring sites with relatively small drainage areas (such as B2 in Figure 2). For agricultural uses, this could be refined when reliable watershed delineation for the monitoring site at sub-HU12 resolution is available (see Section 2.5).

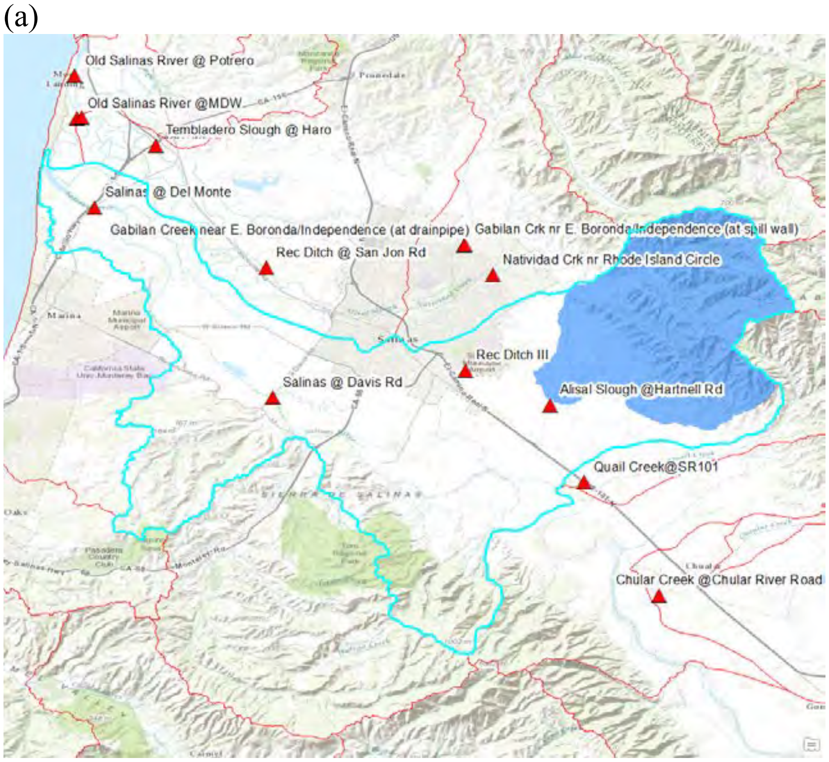
2.5 Customized prioritization at section level (for agricultural uses only)

In addition to HU12 scale, methodology is also developed for monitoring prioritization in a drainage area defined by Meridian-Township-Range-Section (MTRS) in the U.S. Land Survey System. An MTRS, referred as a section, is a fixed-boundary parcel of land approximately 1×1 mi^2 in area. The same geographic reporting unit is also used by the California Pesticide Use Reporting (PUR) system for agricultural uses.

Section-based prioritization requires a list of sections representing the total drainage area of a sampling site. The geographic coverage of the listed sections is considered as a customized watershed, where monitoring prioritization is conducted based on the same methodology previously developed for the standard watershed (HU12). This function is mainly designed for the following conditions:

a) Drainage area of a tributary monitoring site is significantly smaller than the enclosing HU12. Figure 3a shows an example of Alisal Slough @ Hartnell Rd (DPR site code: 27_70), with drainage area of 77 km^2, compared to 293 km^2 for the entire HU12 of 180600051509.
b) HU12-defined drainage area for a site is significantly different from that determined based on more information such as irrigation districts and irrigation tailwater collection. For example, the drainage area of Orestimba Creek @ River Rd (DPR site code: 50_28) is defined by 4 HU12 (180400020101 to -04) covering a very small agricultural area. Based on monitoring results, however, this site is observed with a greater variety of agricultural pesticides compared to other regions in the San Joaquin Valley (Dubrovsky et al., 1998). More realistic drainage area for this site (mainly for the lower portion) has been delineated by USGS, California Water Boards and UCD (Kratzer et al., 2003; Chu and Marino, 2004; SWRCB, 2007; Luo and Zhang, 2009) (Figure 3b).
c) Monitoring sites located within the State of California but outside of California hydrologic region (HUC2="18"). Examples are DPR sites (DPR site code: 13_24, 13_81, 33_11, 33_30, and 33_31) on Palo Verde Valley of Colorado River basin (HUC2="15").

(a)



(b)

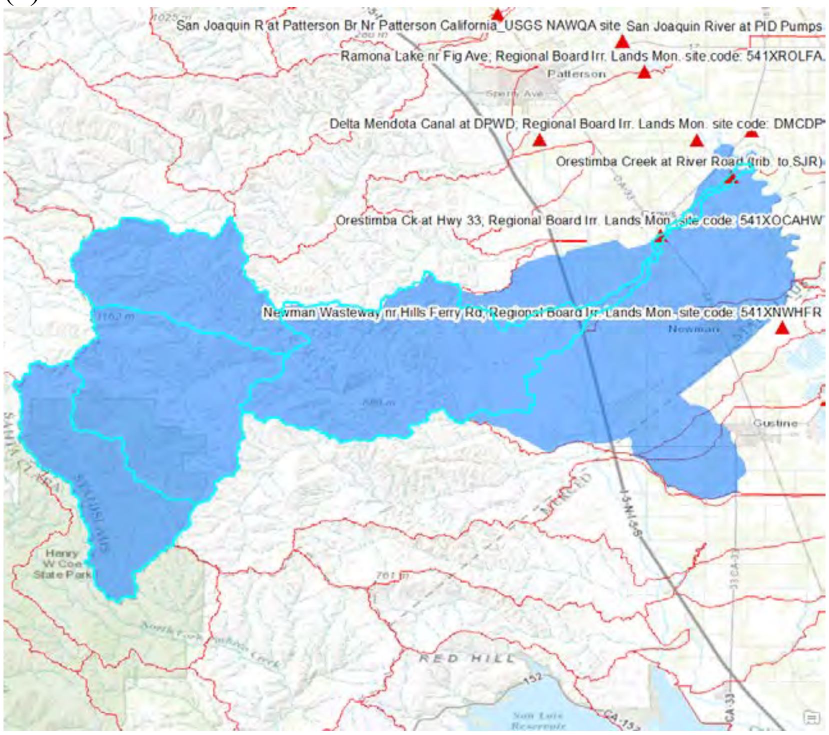


Figure 3. Actual drainage areas (blue) and drainage areas defined by HU12 (highlighted): (a) Slisal Slough @ Hartnell Rd (HUC12=180600051509), and (b) Orestimba Creek @ River Rd (HUC12=180400020101-0104)

2.6 Statewide mapping for monitoring prioritization

With the watershed-based prioritization developed above, it's possible to map pesticide use data at watershed scale throughout California. Unlike the procedures for a specific region of interest (counties or watersheds), statewide mapping is designed to identify areas with relatively high uses of a given pesticide (or a pesticide group). To make comparable data of pesticide uses over watersheds with various sizes, total pesticide uses (in lb[AI]) is normalized by the total drainage area (mi^2) of the watershed. In another words, pesticide use density (lb/mi^2) is used in priority mapping. For tributary sites, both use data and drainage area are defined within the corresponding watershed, while, for main-stream site, its entire hydrologic contributing area will be considered. For cross-pesticide comparison, the pesticide use density is further normalized by the toxicity benchmark value (ppb) and defined as a "Priority Mapping Index" (PMI) for an individual pesticide,

$$PMI(k) = \begin{cases} USE(k)/AREA(k)/TOX & \text{tributary mapping} \\ USE(K)/AREA(K)/TOX & \text{mainstream mapping} \end{cases} \qquad (2)$$

where k is the watershed of interest with an area of AREA(k), USE(k) is the use amount of the pesticide of interest in k, K is the total drainage area for k (including k and all upstream watersheds), USE(K) and AREA(K) are total pesticide uses and total watershed size in K, respectively, and TOX is the aquatic life benchmark of pesticide that is defined in the previous prioritization studies (Luo et al., 2013; Luo et al., 2014). The priority mapping index has a unit of lb/mi^2/ppb. The normalization by TOX in Eq. (2) is designed for the convenience of mapping for multiple pesticides. In this case, the priority mapping index of pesticide mixtures is calculated as the sum of individual indices, by following the “pesticide toxicity index” approach (Nowell et al., 2014).

Here drainage area is used as a surrogate of total runoff volume for the estimation of pesticide dilution in streams. Therefore, the ratio between total pesticide use and drainage area conceptually represents the average pesticide concentration in surface water bodies of the watershed, and the mapping index is in the format of risk quotient or toxicity index. Although the association between drainage area and mean streamflow is not always confirmed at watershed scale, it’s consistent with the hydrologic modeling results in NHDPlus, where a regression between the predicted mean annual streamflow (cfs, cubic feet per second) and cumulative drainage areas (km^2) is observed for California: flow=0.394*area-7.475 (R^2=0.92). Processes of runoff generation, pesticide offsite movement, and in-stream transport are not simulated in this methodology. The statewide mapping is proposed for an initial assessment of the spatial variability on pesticide risks in aquatic ecosystems, which could be refined with modeling efforts for hydrology and pesticide transport.

2.7 Travel time and pesticide dissipation in stream network

Travel time and associated pesticide dissipation between the treated locations to a downstream monitoring site are considered for watershed-based prioritization. Pesticide uses in any location within the drainage area will finally contribute to the concentration measured at a monitoring site. However, the relative contributions are not only related to the total use amounts in the drainage area, but also adjusted by pesticide dissipation as a function of travel time. Travel time (T, hour) in a watershed is estimated based on the data provided in the NHDPlus,

$$T = \frac{\text{LengthKM}}{\text{MAVelU}} \times 0.911 \tag{3}$$

where LengthKM and MAVelU are NHDPlus parameters of length (km) and predicted annual mean flow velocity (ft/s) for each NHD “flowline” (i.e., river segment), and 0.911 is a factor to convert the resulting T to the unit of hour. Usually, there are multiple NHD flowlines in each watershed, the median flowline length of each stream order is selected for the calculation of total travel time in a watershed. With T for each watershed, pesticide dissipation in stream network is estimated with the first-order kinetics,

$$\begin{aligned} USE_{eff}(k) &= USE(k) \times \exp\left(\frac{\ln 2}{HLWD} \cdot \frac{\sum T}{24}\right) \\ \mathrm{USE}_{eff}(K) &= \sum_k USE_{eff}(k) \end{aligned} \tag{4}$$

where USE(k) is the actual pesticide use (lb[AI]) in a watershed *k*, $\mathrm{USE}_{\mathrm{eff}}$ (k) and $\mathrm{USE}_{\mathrm{eff}}$(K) is the adjusted pesticide uses (lb[AI]) for each watershed and for the entire drainage area, respectively, HLWD (day) is the "water-sediment DT50" of the pesticide according to the definition in IUPAC FOOTPRINT Pesticide Property Database (FOOTPRINT, 2014), and 24 is an unit conversion factor for travel time from hour to day. ΣT is the cumulative travel time between k and the watershed for monitoring prioritization (Figure 4). Travel time in the local watershed (where the monitoring site is located) is not accounted for conservative estimation. If HLWD is not reported in PPDB, this pesticide is assumed to be persistent and no dissipation will be estimated, i.e., $USE_{eff}(k)=USE(k)$. Calculation for pesticide dissipation according to travel time is developed as an option in the watershed-based prioritization. If the option is selected, pesticide use amounts, such as USE(k) for tributary prioritization or USE(K) for mainstream prioritization in Eq. (2), will be replaced by their effective values $USE_{eff}(k)$ or $USE_{eff}(K)$, respectively. In the computational implementation of the prioritization methodology, travel time is pre-calculated for each HU12. Therefore, pesticide dissipation could be incorporated in the proposed prioritization with HU12-based watersheds (as described in sections 2.4 and 2.6), but not be used with user-defined watersheds (section 2.5).

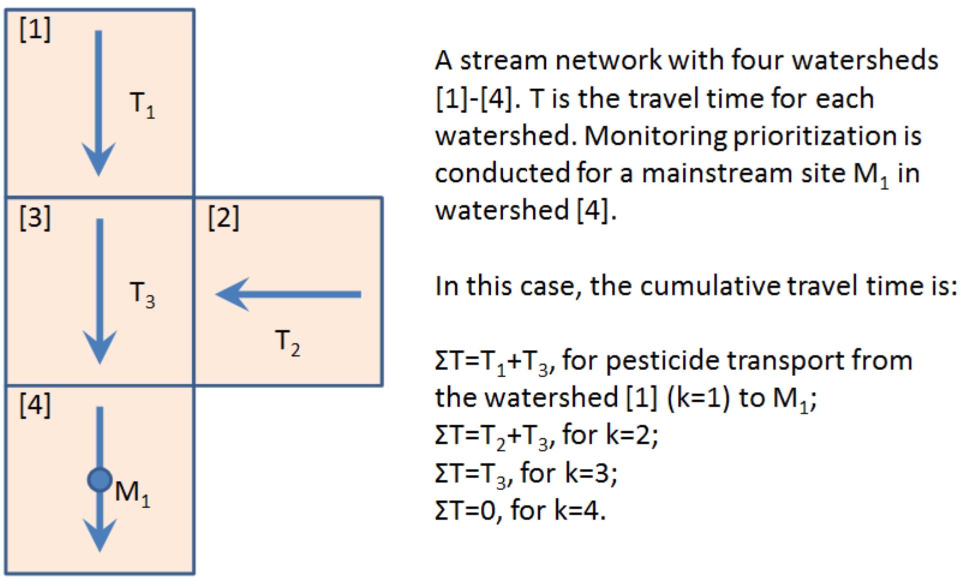


Figure 4. Demonstration of the calculating process for pesticide dissipation at watershed scale

3 Model testing

3.1 Characterization of monitoring sites for watershed-based prioritization

For a given monitoring site (or site group), required information for prioritization include coordinates, the name and type of water body to be sampled, primary land use in the drainage area, and sampling schedule. Those site-specific data can be retrieved from previous monitoring data reporting (Ensminger, 2015). With the data prepared, monitoring prioritization could be developed with the following steps:

1) Determine the HUC12 of the watershed enclosing the monitoring site, in GIS desktop applications or with online tools (see Appendix 2).
2) Classify the monitoring site as mainstream site or tributary site.

3) (Optional) for the convenience of site visiting and chemical analysis, monitoring sites are usually grouped by their common drainage basin. In this case, prioritization will be conducted for the site group, which could be characterized by the most downstream sites for HUC12 and mainstream/tributary classification.
4) For agricultural monitoring on a drainage ditch or small tributary, if possible, try to delineate the drainage area of a monitoring site, and list all included sections.
5) Conduct watershed-based prioritization for the monitoring site (or site group) with suggested settings in Table 1.

Table 1. Suggested settings for monitoring prioritization according to water body type and land use associated with monitoring sites

Water body type of the monitoring site	Suggested settings for monitoring prioritization [1]	
	Use pattern	Drainage area
Drainage ditch	Agriculture	Use section-based prioritization, if the drainage area can be estimated. Otherwise, use tributary prioritization.
Receiving water, tributary in an agriculture dominated watershed	Agriculture	Generally, use tributary prioritization. May consider section-based prioritization, if its drainage area is significantly smaller than the watershed.
Storm drain outfall	Urban	Use tributary prioritization. [2]
Receiving water, tributary in an urban area	Urban	Use tributary prioritization.
Receiving water, mainstream	According to the land use type in the drainage area (agricultural, urban, or both)	Use mainstream prioritization.

Notes:
[1] Not shown in the table is the setting for the period of PUR data query, which does not change with water body type and landuse: year = the latest 3 years with officially posted PUR data (http://www.cdpr.ca.gov/docs/pur/purmain.htm); month = the month or antecedent months of preschedule sampling. If sampling schedule is not determined, annual pesticide uses could be considered for initial planning.
[2] Due to PUR limitations in urban use data, the proposed methodology may not be appropriate for small urban drainage areas, such as a residential community. By using tributary prioritization for monitoring at storm drain outfalls, the implied assumption here is that the area of interest generally follows the average conditions of urban pesticide uses in the watershed.

3.2 DPR surface water monitoring for agricultural pesticide uses

Watershed-based prioritization has been implemented in the proposed DPR study 297, the primary surface water monitoring study by DPR in the 2015 sampling season for pesticides in agricultural areas of California. Prioritization results are used in the study designs of monitoring schedule and required chemical analysis (Deng, 2015).

In summary, 30 monitoring sites (Figure 5) are grouped by 7 drainage areas (Palo Verde Drain, Alamo River, New River, Salinas River, Tembladero Slough, Orcutt Creek, and Oso Flaco Creek). Prioritization was conducted for each drainage area based on the 2010-2012 pesticide uses data in the antecedent months of each sampling month. For example, pesticide use data from January to March of 2010-2012 were considered in the monitoring prioritization for March 2015. Prioritized pesticides were presented as the corresponding analytical groups of chemicals in the monitoring schedules.

3.3 Statewide priority mapping

Statewide priority mapping is demonstrated with [1] main-stream prioritization for total chlorpyrifos uses, and [2] main-stream prioritization for urban (including right-of-way applications) bifenthrin uses.

[1] Chlorpyrifos

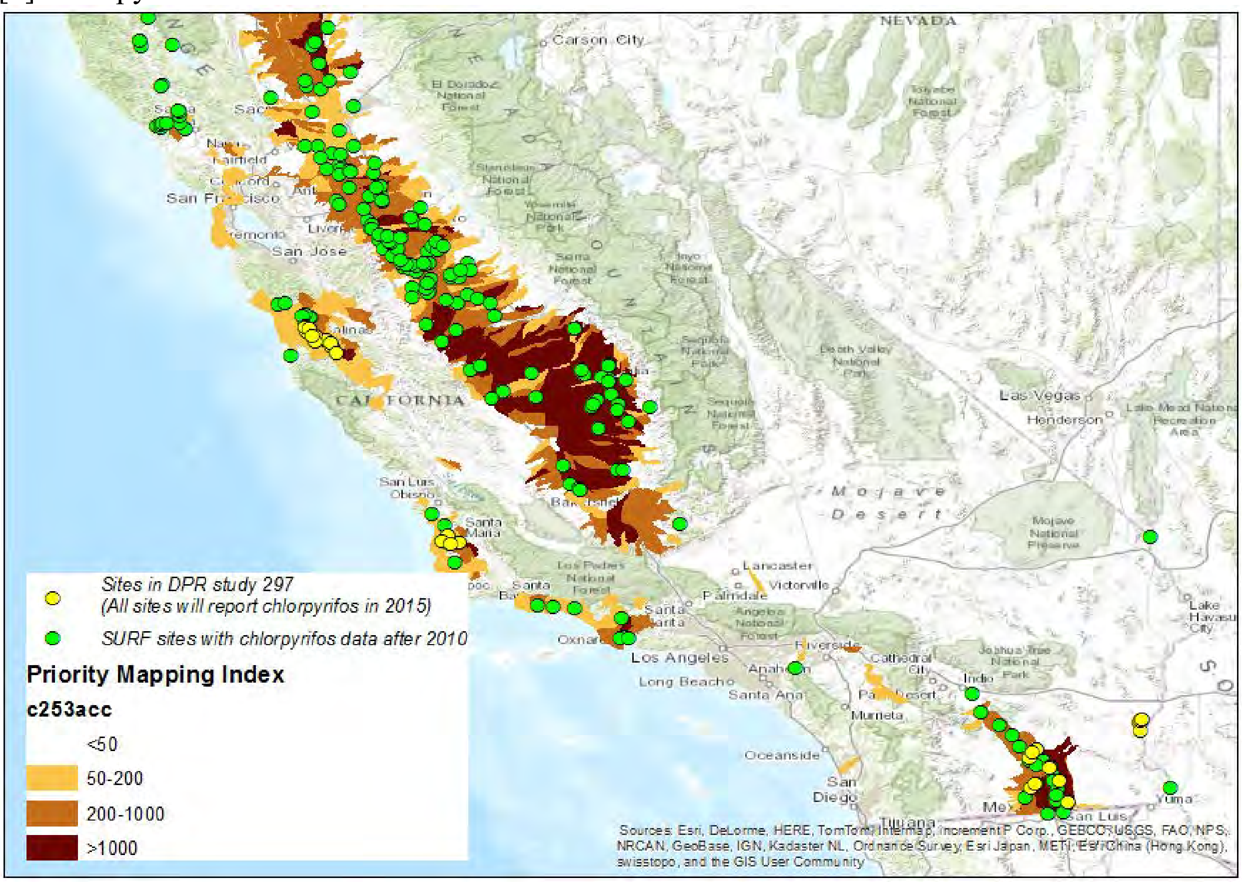


Figure 5. Monitoring priority mapping for chlorpyrifos in main streams of 12-digit hydrological units, based on total (agricultural, urban, and right-of-way) uses of chlorpyrifos. “c253acc” is the priority mapping index of chlorpyrifos (lb/mi^2/ppb), with 253 for the PUR chem_code of chlorpyrifos, and “acc” for main-stream prioritization with accumulated uses in all upstream

watersheds. Priority mapping index values are only calculated for California hydrologic region (HUC2=18), so not covering the sites in Colorado River basin.

For chlorpyrifos, PMI values (lb[AI]/mi^2/ppb) are calculated at watershed outlets and displayed in a color map over the corresponding watersheds for visualization purpose (Figure 5). In each watershed, the priority mapping index reflects total chlorpyrifos uses, transport, and dissipation in its drainage area. Relatively high PMI values are observed in the Central Valley, Salinas Valley, Santa Maria, and Imperial Valley. Most of these areas are actively monitored by DPR and other agencies according to SURF data, and by the proposed DPR study 297 for 2015 sampling. Some closed basins with less potentials for agricultural runoff and discharge to surface water are not considered in chlorpyrifos monitoring even they are associated with very high PMI values, such as the cropland in the former lakebeds of Kern Lake and Buena Vista Lake (south to Bakersfield). Additional data analysis on the modeled PMI values and observed benchmark exceedances for chlorpyrifos are provided in Appendix 3.

[2] Bifenthrin (non-agricultural uses)

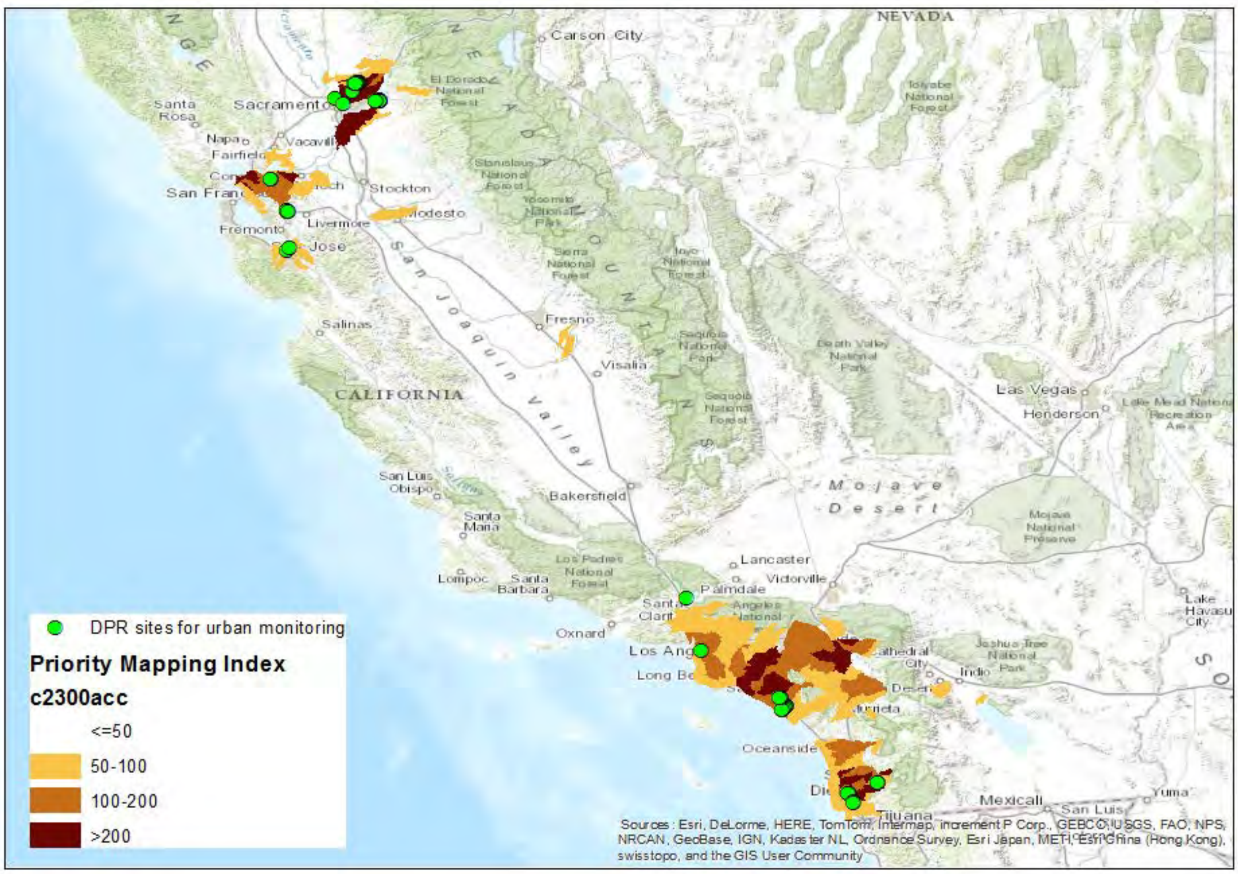


Figure 6. Monitoring priority mapping for bifenthrin in main streams of 12-digit hydrological units, based on urban and right-of-way uses of bifenthrin. “c2300acc” is the priority mapping index of bifenthrin (lb/mi2/ppb) with 2300 for the PUR chem_code of bifenthrin, and “acc” for main-stream prioritization with accumulated uses in all upstream watersheds.

For bifenthrin, relative high PMI values are observed in the areas of Sacramento County and east Placer County, Alameda County and Contra Costa County, South Coast, and east Riverside County (Figure 6). There are 58 sites for urban pesticide monitoring in the historical and active DPR studies (#249, 264, 265, 269, and 270, http://www.cdpr.ca.gov/docs/emon/pubs/protocol.htm). Most of them are captured by the regions with high priority mapping index (Figure 6), and reported with high detections for bifenthrin (Ensminger and Kelley, 2011a, b; Ensminger et al., 2012).

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Appendix 1 Demonstration of the estimation of urban pesticide uses for a watershed

The following paragraph explains the procedure to convert county-based urban use data to watershed scale. The “Coyote Creek – San Gabriel River” watershed (12-digit hydrologic unit code, HUC12=180701060606) is demonstrated as an example. This watershed is located in Los Angeles County and Orange County, and covered by 6 sub-county districts with population density data. Details of the calculation are provided in the following tables.

	Sub-county district	Population density (people/mi^2) [1]	Area of the watershed		Population within the watershed [1]*[2]
			mi^2 [2]	%	
	East San Gabriel Valley	4422.6	1.77	3.0%	7,836
	Upper San Gabriel Valley	6572.6	0.12	0.2%	788
	Whittier	5285.8	15.33	25.5%	81,039
	Downey Norwalk	9556.4	21.13	35.2%	201,952
	Long Beach Lakewood	8984.4	5.33	8.9%	47,919
Subtotal			43.68	72.8%	**339,534**
	Anaheim Santa Ana Garden Grove	5786.2	13.15	21.9%	76,079
	North Coast	6136.8	3.19	5.3%	19,591
Subtotal			16.34	27.2%	**95,669**
Total			60.03	100%	435,204

County	Total population in the county [3]	Population in the watershed (from the above table) [4]	Fraction [4]/[3]
Los Angeles	10.0 million	339,534	3.4%
Orange	3.1 million	95,669	3.0%

Finally, the urban pesticide use in the watershed (HUC12=180701060506) is calculated as 3.4%*PUR(Los Angeles)+3.0%*PUR(Orange), where PUR(county) is the reported urban uses from the PUR database during the user-defined period.

Appendix 2 Geo-coding a monitoring site to USGS Watershed Boundary Database (WBD) and National Hydrography Database (NHD)

This procedure is to locate a monitoring site in a USGS 12-digit hydrologic unit (HU12). Input data include the site coordinates, or a site map in GIS format.

With desktop GIS applications such ESRI ArcMap

WDB in shapefile format can be downloaded from USGS site (http://nhd.usgs.gov/wbd.html). Watershed can be located by putting the WDB and site map layers together. In addition, NHD map layer (http://nhd.usgs.gov/data.html) could be helpful to align monitoring sites with river/ditch channels.

With online GIS tools

The USGS National Map Viewer provides base maps for NHD and WBD (http://viewer.nationalmap.gov/viewer/nhd.html?p=nhd). The screenshot in Figure 7 shows Quail Creek watershed and Chualar Creek watershed in Salinas Valley. Watersheds (purple polygons, labeled with 12-digit hydrologic unit code, HUC12) and NHD flowlines (green polylines, labeled with stream names if available) are displayed in the map. Some useful tools are provided: [1] "Fine Coordinates" by clicking on the map, and [2] "Add Data" to import a site GIS map in KML (Keyhole Markup Language) format.

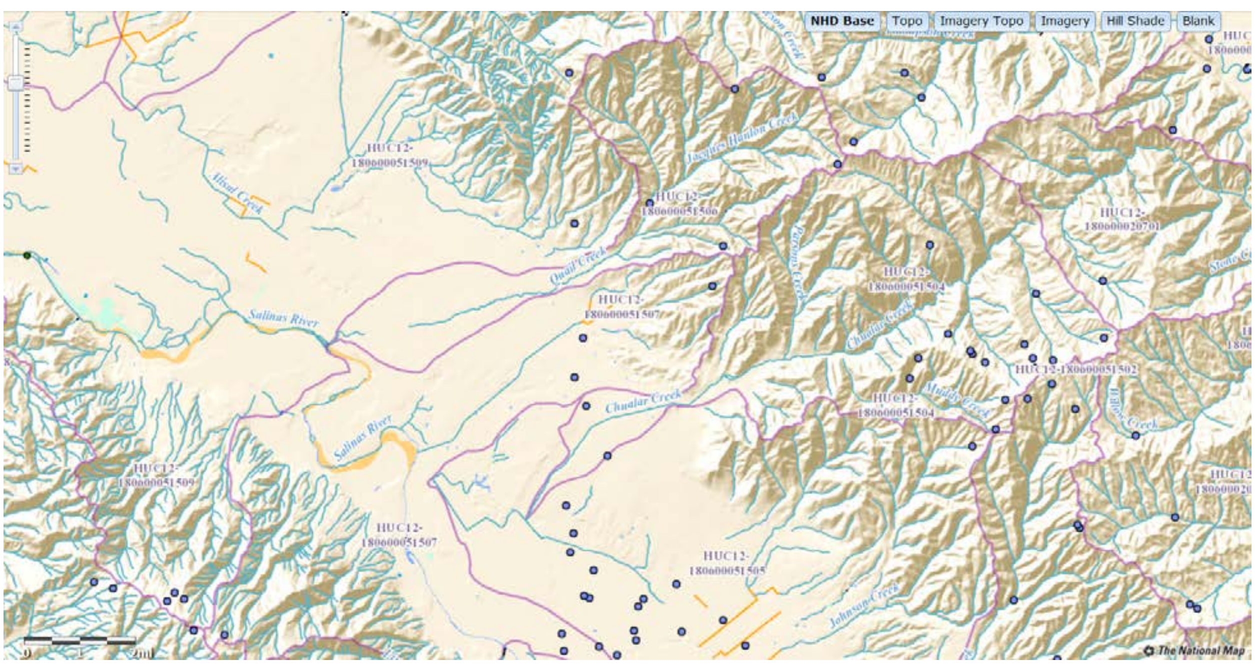

Figure 7. Locating USGS 12-digit hydrologic unit for a sampling site with National Map Viewer

A special case: a mainstream site located close to the outlet of an upstream watershed

a) If there is only one upstream watershed (Figure 8a), the monitoring site should be assigned to the upstream watershed for prioritization.
b) If there are multiple upstream watersheds (Figure 8b), independent prioritization for all relevant upstream watersheds should be conducted, and then the results are combined for monitoring prioritization at this site.

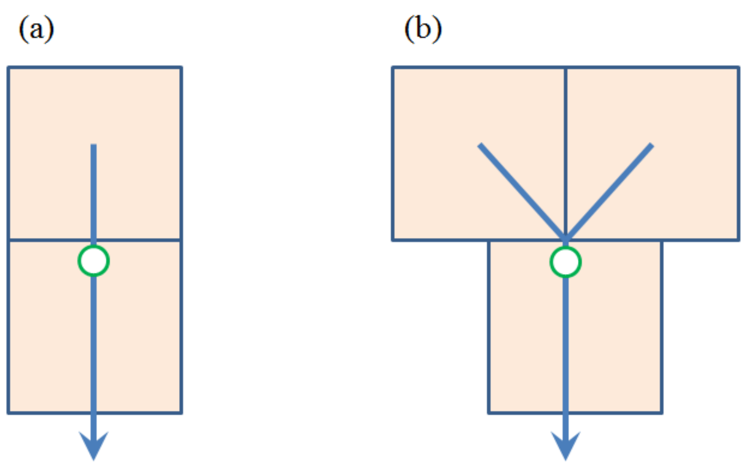

Figure 8. Monitoring sites located close to the outlet of upstream watershed(s)

Appendix 3 Comparison between Priority Mapping Index and observed benchmark exceedance for chlorpyrifos

For further investigation, priority mapping index values are compared with observed benchmark exceedances (BE) of chlorpyrifos (Figure 9). Please note that the comparison is used to provide supporting information for future selection and optimization of monitoring sites. The resulting relationship may not be appropriate in predicting pesticide concentration level at a specific site.

Prioritization is based on chlorpyrifos uses reported in 2010-2012, while SURF data (version "Apr2014") show benchmark exceedance of chlorpyrifos in only 4 sites during the same period, based on the lowest acute aquatic life benchmark of 0.05 ppb for chlorpyrifos (USEPA, 2015). Therefore, all available data during 1990-2012 in the SURF database are used for better geographic coverage of historical surface water monitoring in California. Selected sites, based on the following considerations, are used for the comparison with modeling results:

a) Site with at least 30 samples, or with at least 5 benchmark exceedances. Those values are arbitrarily selected here for demonstration purpose only.
b) Sites with small drainage areas are excluded. Those sites are mathematically identified by critical drainage area of 33.7 mi^2 (i.e., the median size of HU12) or equivalently by the mean annual streamflow predicted in NHDPlus <26 cfs (cubic feet per second). The regression relationship between cumulative drainage area and mean annual streamflow derived from NHDPlus for California is applied here.

Finally, 74 sites are selected. If BE=0 for a site, it's set as 0.1% for the convenience of plotting in logarithmic scale (0.1% is the lowest non-zero BE observed for chlorpyrifos). Each site is assigned to a watershed and determined to be a mainstream site or tributary site. For a mainstream site, its BE value is related to the mainstream priority mapping index (Figure 5) by considering chlorpyrifos uses in all drainage areas. For a tributary site, otherwise, its BE value is compared with the priority mapping index determined from chlorpyrifos uses in the local watershed only. There is a significant positive correlation between priority mapping index and benchmark exceedance in logarithmic scale ($r=0.74$, $p<0.001$) based on the historical monitoring data for selected sites in California (Figure 6). It's worthwhile to note that the priority mapping index (x axis) is calculated based on chlorpyrifos uses during the latest 3 years of available PUR data (2010-2012), while the benchmark exceedance (y axis) is calculated from all available monitoring data in the SURF database. The general agreement between modeling and monitoring results suggests the importance of pesticide use in the drainage area and routing in stream network for determining its surface water risks observed in a downstream site.

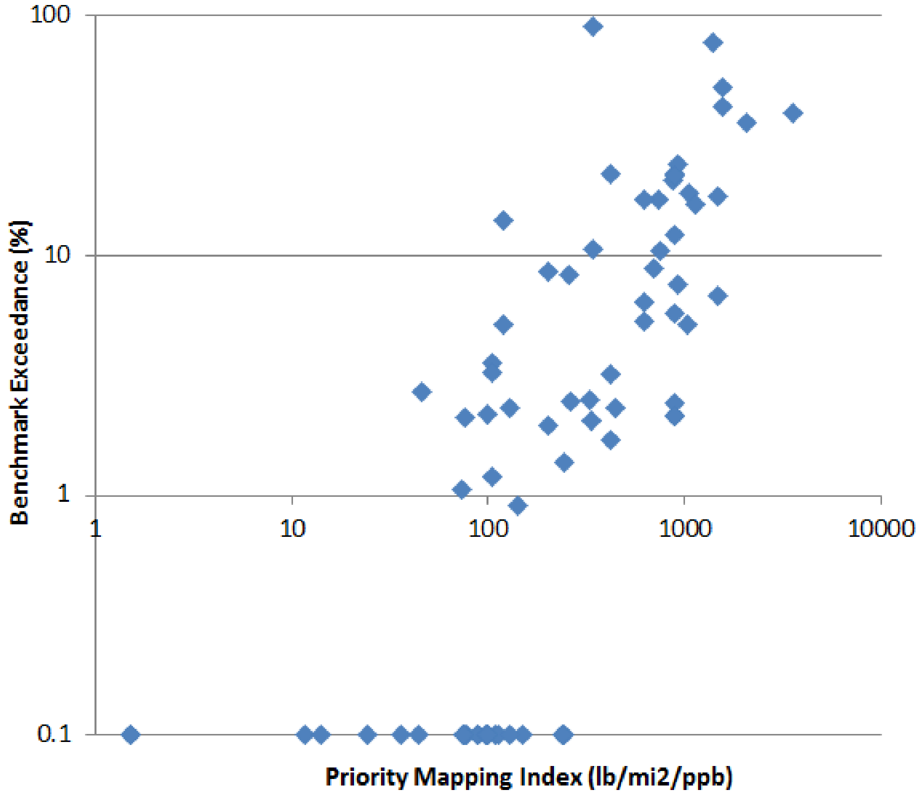

Figure 9. Priority mapping index and observed Benchmark Exceedance for chlorpyrifos in 74 monitoring sites throughout California. Monitoring data are based on DPR surface water database, version Apr. 2014, and 0.1% benchmark exceedance is assigned for all sites where no exceedance was observed.