

RMP REGIONAL MONITORING PROGRAM FOR WATER QUALITY IN SAN FRANCISCO BAY

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Small Tributaries pollutants of concern reconnaissance monitoring: Application of stormevent loads and yields-based and congener-based PCB site prioritization methodologies

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Preface

With RMP funding allocated in 2017 and 2018, a pilot study was completed using a subset of data from watersheds in San Mateo and Santa Clara Counties to build new methods for organizing and analyzing the existing stormwater reconnaissance data that will provide further evidence to support decisions about which watersheds may be of interest for prioritized management focus. The pilot study resulted in two new analysis methodologies outlined in two companion reports:

- Davis, J.A. and Gilbreath, A.N., 2019. Small Tributaries Pollutants of Concern Reconnaissance Monitoring: Pilot Evaluation of Source Areas Using PCB Congener Data. SFEI Contribution No. 956. San Francisco Estuary Institute, Richmond, California. <u>https://www.sfei.org/documents/small-</u> <u>tributaries-pollutants-concern-reconnaissance-monitoring-pilot-evaluation-source</u>
- McKee, L.J., Gilbreath, A.N., Hunt, J.A., Wu, J., Yee, D., and Davis, J.A., 2019. Small tributaries pollutants of concern reconnaissance monitoring: Loads and yields-based prioritization methodology pilot study. SFEI Contribution No. 817. San Francisco Estuary Institute, Richmond, California. https://www.sfei.org/documents/small-tributaries-pollutants-concern-reconnaissance-monitoring-loads-and-yields-based

In this final report, we describe a few enhancements to the storm-event loads and yields method and then apply both methods to a much larger data set and provide the resulting database to support stormwater management and decision making.

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Executive summary

Stormwater agencies in the San Francisco Bay Area are identifying watershed areas that are polluted with PCBs in order to prioritize management efforts to reduce impairment in the Bay caused by PCBs carried in stormwater. Water sampling during storms has been used to characterize PCB concentrations but management prioritization based on the comparison of concentrations between watersheds is made difficult due to variations in flow and sediment erosion between storms and in relation to varying land use. In addition, identifying PCB source areas within priority watersheds has proven complex and costly. To address these challenges, the San Francisco Bay Regional Monitoring Program (RMP) has developed two new interpretive methods based on storm-event PCB yields (PCBs mass per unit area per unit time) and fingerprints of Aroclors (commercial PCB mixtures) that make existing data more useful for decision-making.

The objectives of this study were to:

objective was not fully completed.

- 1. Apply the yield method to the regional stormwater dataset and provide new rankings,
- 2. Estimate the presence of Aroclors in samples where congener data are available
- 3. Evaluate data weaknesses and recommend watersheds to resample, and

4. Classify watersheds into high, medium, and low categories for potential management. Due to the lack of thresholds and the limitations of the currently available data set, the fourth

Ranking watersheds by concentrations, loads, and storm-event yields

The dataset for this comparative analysis contains 137 watersheds. Sampled watersheds range in size from 0.016-232 km², impervious cover ranges from 2-91%, and the sum of PCB source areas and older industrial, commercial and transportation land use distributions in these watersheds range from 3-100%. PCB event mean concentrations (EMCs) in water ranged from 106-308,000 pg/L, whereas the estimated particle concentrations (EPCs) ranged from 4.0-9,300 ng/g. Watersheds were ranked based on EMCs and EPCs. For sites that had been sampled during two storms, the sample with the highest EMC was retained in the ranking database since it is most likely indicative of the greatest number of contributing PCB source areas. For 14 out of 15 watersheds, the sample with the greatest EMC also exhibited the greatest EPC.

Storm-event loads for each watershed were estimated using storm-specific rainfall, a modeled estimate of runoff, and the PCB EMCs measured during storms. Load estimates were adjusted for a standard sized storm. The standardized load estimates were then normalized to the portion of a watershed composed of PCB-associated land uses (Old Industrial and source areas plus Old Commercial and Old Transportation). Storm-event yields computed in this way allow for the direct comparison and ranking of PCB source areas one to another rather than whole watersheds (as is the case with ranking based on concentrations). Thus, the information is more relevant at the scales where management actually occurs. Yields (PCBs mass (grams) per square kilometer per standardized storm-event) ranged between 0.00069-1.45 g/km². Comparing the sites using this PCBs storm-event yield indicator revealed that a number of watersheds that ranked relatively low priority in terms of EMC or EPC are ranked relatively high

priority for yields in their older industrial areas. For example, 18 watersheds that ranked in the bottom two thirds of the dataset for either EMCs or EPCs were ranked in the upper 50 watersheds for yields.

Characterizing watersheds for Aroclors to support source property identification

There were four main Aroclors produced and sold in the United States (1242, 1248, 1254, 1260). Although Aroclors were used for a wide variety of applications and thus are not perfect indicators of a source type upstream, with the exception of 1260, the other three Aroclors have some unique applications and the presence of two or three Aroclors at a site can also be indicative of potential sources to consider. Suitable data to generate estimates of Aroclor contributions to the sum of PCB congeners were available for 74 watersheds. Fingerprinting analysis for these watersheds revealed that Aroclor 1254 was commonly dominant, showing up as a primary component (>40%) in 46 of the 74 watersheds and a secondary component (20-40%) in a further 27 of the 74 watersheds. Aroclor 1242 and 1248 were primary components in just one watershed each. Aroclor 1260 was more common than 1242 and 1248, being a primary component at 16 sites and a secondary component at 46 sites. At seven of the 15 sites, congener data were available for two duplicate samples. At five of the seven sites, identical Aroclor indicators occurred during both storms providing an indication for confidence in the method. In many instances, watersheds high in yields exhibited Aroclors other than 1254.

Evaluating data weaknesses

In order to support decisions about site priorities, the data were evaluated to identify sites sampled under conditions that might have led to a falsely low EMC, EPC, or storm-event yield. A decision tree was developed to provide a consistent rationale for identifying sites that may have been incorrectly ranked as a low priority. Watersheds in the lower third of the data set (based on EMC and storm-event yield) were selected for evaluation via the decision tree. In addition, thresholds of 0.5 inches of total storm rainfall, 0.15 inch/hour rainfall intensity, and 20 mg/L SSC were used. Using this decision tree, 13 sites were recommended for resampling to verify if these sites should be ranked as low priority for management action.

Prioritizing watersheds for potential management

Due to a lack of well-defined thresholds to define sites of high, medium, and low management interest, a more advanced classification beyond just proposing sites that might be falsely ranked low priority due to storm size was not possible at this time. Another decision tree was developed to support a future effort of watershed classification (Appendix A). It is quite likely that many of the sites recommended for resampling due to storm size might end up being classified as low management interest. Further sampling would help to confirm this.

Introduction

Stormwater contains many pollutants washed from sources in the urban landscape that contribute to downstream water quality problems and permit compliance challenges. Often, however, it is difficult to identify the primary source areas that produce the majority of pollutant mass. Yet, identifying and managing these areas is more cost-effective than management of less polluted areas because more mass can be captured, removed, or abated from these "high leverage" areas per unit of effort. The San Francisco Bay Regional Water Quality Control Board (Water Board) Municipal Regional Stormwater Permit (MRP) calls for identifying watersheds, source areas, and source properties that are potentially most polluted with PCBs and prioritizing such areas for elevated management effort (SFBRWQCB, 2015).

To support this focus, a stormwater reconnaissance PCBs monitoring program was implemented by the San Francisco Bay Regional Monitoring Program (RMP), and the Santa Clara and San Mateo Countywide Clean Water Programs in water years (WYs) 2015-2021 (SMCWPPP 2020; SCVURPPP, 2020a, 2021; Gilbreath and McKee, 2021). Time-interval composite samples were collected during single storms at sites with greater areas of older industrial land use or suspected sources and analyzed for 40 PCB congeners¹, total Hg, suspended sediment concentration (SSC), and other pollutants. Sites were then ranked from high to low by both event mean concentration (EMC) and estimated particle concentrations (EPC) (the concentration of Σ PCBs in water divided by suspended sediment concentration) to help identify areas for management consideration (e.g. Gilbreath and McKee, 2021).

The separation of a class of high PCB concentration watersheds, as distinguishable from medium and low PCB concentration watershed works reasonably well since the variation in EMC between storms within a single watershed typically varies by <90-fold (<11-fold if Pulgas South Pump Station and Sunnyvale East Channel watersheds are excluded), whereas variation between watersheds is known to be >300-fold (Gilbreath and McKee, 2021). Therefore, when EMCs are high and coupled with other evidence², the small industrial watersheds and, by extension the source properties within them, can be prioritized for management. About 20% of watersheds have high EMCs and/or EPCs and fall into an "obvious management attention category" (Gilbreath and McKee, 2021).

The challenge then is how to prioritize the other 80% of watersheds with medium or lower EMCs and EPCs that can contain relatively polluted patches of land within them and may, in some cases, deliver substantial and potentially controllable loads to the Bay even though EMC and EPCs in these watersheds can be low and diluted by the flow of water and clean sediment from less polluted areas (see McKee et al. (2019) for a detailed discussion).

¹ The RMP 40: PCBs 8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74, 87, 95, 97, 99, 101, 105, 110, 118, 128, 132, 138, 141, 149, 151, 153, 156, 158, 170, 174, 177, 180, 183, 187, 194, 195, 201, and 203.

² The current weight-of-evidence standard decision-making approach typically includes evaluating factors including land use and source area characteristics and history, records review, age and condition of infrastructure, soil and stormwater concentration surveys, erosion factors, and facility inspections.

Once a watershed or a patch of land use within that watershed is identified as a priority, the other challenge is how to identify the sources and source properties that are the highest leverage (most mass for the smallest area) where management effort will be most cost-effective. PCBs were manufactured and used as complex mixtures of individual PCBs, referred to as PCB congeners. In North America, the only producer of PCBs was the Monsanto Company, which marketed them under the trade name Aroclor from 1930 to 1977. A series of different mixtures was produced, each referred to as an Aroclor, and each with varying degrees of overall chlorine content (Erickson and Kaley, 2011). Since the different mixtures were used for different purposes and these mixtures are found in more pure form nearer to where the PCBs were used or spilled, it is possible to use congener patterns in each watershed sample as indicators for possible upstream PCB uses. It is not a perfect indicator, however, since stormwater flowing out of the watersheds has a congener profile that is an aggregation of the combined contributions of inputs from multiple source areas. But it does provide a further indication of source characteristics especially when one particular Aroclor is dominant.

To address this challenge of making management decisions for the 80% of watersheds that don't fall into the "obvious priority" category, and to provide new information about the character of PCB sources of interest in watersheds, in 2018, the RMP developed two new interpretative methods based on storm-event yields (McKee et al., 2019) and congener patterns and dominant Aroclors (Davis and Gilbreath, 2019). These methods were piloted in a small number of watersheds.

The objectives of this study were to:

- 1. Apply these methods to the large regional dataset for which there are presently data available, and rank the data using all indicators of watershed contamination (storm-event yields, EMCs, and EPCs),
- 2. Estimate the presence of Aroclors in samples where congener data are available,
- 3. Determine which watersheds to resample based on data gaps associated with PCB detection limits, SSC, or storm size,
- 4. Classify watersheds into areas of high, medium, or low management interest.
 - a. High: Those where there may be a property or properties within a watershed that may be good to further investigate. What is the threshold where we can say there is likely a source in the watershed?
 - b. Low: Those where the watershed has background or relatively low EMCs suggesting that the watershed is one of the last places we would implement management action. What is the threshold where we can say there is likely no source in the watershed?
 - c. Medium: No suggestion of a main source but the watershed is still producing loads at a moderate rate.

Unfortunately, it was not possible to address this last objective despite this being of stakeholder interest due to a lack of a suitable rationale for thresholds but it is quite possible that many of the sites recommended for resampling may, in the future, be categorized as low management interest if they consistently show low storm yields, EMCs, and EPCs even after resampling.

Methods

Overview of interpretive methods

Key points: Two new interpretive methods are summarized here, however, for details, the interested reader should review one or both of the technical reports that describe how the methods were developed (Davis and Gilbreath, 2019; McKee et al., 2019).

During 2018 and 2019, the RMP developed two new interpretive methods for comparing and characterizing watersheds based on EMC data obtained from the single storm reconnaissance sampling method.

Method 1: Ranking watersheds by storm-event yields

The details of the storm-event loads and yields method have been reported (McKee et al., 2019) but are described briefly here. Method 1 has four basic steps:

- Using storm-specific rainfall data and estimates of the portion of rainfall that becomes runoff from the regional watershed spreadsheet model (RWSM) (Wu et al., 2017; SFEI, 2018), storm volume was estimated for watersheds where a watershed boundary layer was available in GIS format, and where reliable rainfall data could be obtained for the sampled storm from a nearby or representative rain gauge.
- 2. Storm volume was combined with field measured EMC data to estimate storm specific loads for each watershed in the dataset.
- 3. Storm loads were then adjusted up or down to a standard sized storm to derive a <u>standard storm load</u> that allows for direct comparisons among watersheds. To minimize the size of the adjustment, and the uncertainties associated with that adjustment, all loads for the sites were adjusted up or down to the median storm size found in the data set. The median for the data used in the pilot study (McKee et al., 2019) was a storm size of 0.5 annual return frequency (the storm that on average occurs twice in any one wet season). However, with the inclusion of the majority of the RMP and Santa Clara and San Mateo Countywide Clean Water Programs data sampled up to WY 2019, the median storm size was 0.3 annual return (the storm that on average occurs a little more than thrice in any one wet season). If the sampled storm was larger than the median, the storm loads were adjusted down; if the storm size was smaller, the storm loads were adjusted up.
- 4. <u>Standard storm yield</u> for each watershed was then computed by normalizing the <u>standard storm load</u> to both the whole watershed area and the source areas of interest in the given watershed or subwatershed. Consistent with the pilot approach (McKee et al., 2019), the source area of interest in each watershed was assumed to be the area in each watershed associated with the RWSM parameters (Old Industrial and Source Areas and Old Commercial and Old Transportation) (Wu et al., 2017; SFEI, 2018).

Method 2: Characterizing watersheds for Aroclors

The second method applied in this report was also developed by the RMP in 2018 and 2019 and has been reported in detail (David and Gilbreath, 2019). For method 2, the relative

contributions (or "fingerprints") of four different Aroclor mixtures (1242, 1248, 1254, and 1260) in stormwater and sediment were estimated using the following four basic steps:

- 1. The percent contributions of four relatively unique indicator congeners for each Aroclor that are a major contributor to the overall sum of PCBs were determined (Davis and Gilbreath, 2019):
 - a. Aroclor 1242: PCBs 18, 28, 31, 33;
 - b. Aroclor 1248: PCBs 44, 49, 66, 70;
 - c. Aroclor 1254: PCBs 87, 101, 110, 118; and
 - d. Aroclor 1260: PCBs 149, 170, 180, 187.
- 2. For each water sample, an index was computed as the sum of the percent contributions for each set of congeners.
- 3. The index was then standardized for each Aroclor as a % of the sum of the four indices.
- 4. The data for the Aroclor contributions were then binned into the following categories
 - a. greater than or equal to 40% of the sum of Aroclor indices (primary contributor);
 - b. greater than or equal to 20% and less than 40% of the sum of Aroclor indices (secondary contributor); and
 - c. less than 20% of the sum of Aroclor indices (minor contributor).

Data sources

PCB stormwater data

Key points: About 160 watersheds have been sampled for PCBs but only 137 watersheds were included in the current application due to a lack of suitable rainfall data. Congener data have been compiled for 74 watersheds.

Monitoring data were collated from three major studies: Water year 2011 pollutants of concern loads monitoring (McKee et al., 2012), Water years 2015-2019 pollutants of concern reconnaissance monitoring (Gilbreath and McKee, 2021), and Water years 2016-2019 Santa Clara and San Mateo Counties pollutants of concern monitoring (SMCWPPP 2020; SCVURPPP 2020a; 2021). The dataset collated includes 137 unique watersheds, 15 of which have been sampled twice. A further 23 sites have been sampled for PCBs but were not included in this current analysis due to lacking rainfall data (Figure 1)³. Of these 137 watersheds, congener data have been compiled for 74 watersheds with seven of these having duplicate congener data available. The selection of monitoring locations was biased towards small watersheds with proportionally greater areas of older industrial land use in municipal jurisdictions covered under the Phase 1 permit (SFBRWQCB, 2015).

Rainfall data for each storm and recurrence intervals

Key points: Rainfall information was obtained for a small number of sites, quality assured, and extrapolated to estimate storm rainfall for each sampling location.

³ In the future other sources of rainfall data that might be considered are the source data set for PRISM and NLDAS (Jon Butcher, personal communication, January 2022), and the Weather Underground data.



Figure 1. Map of sampled locations included in this analysis or in method development. Some sites were not included due to lacking rainfall data.

Estimates of rainfall for a sampled storm for each sampling site are needed. To get a reasonable estimate for a storm, only rain gauges with published records at a 1-hour time interval or less were considered (McKee et al., 2019). Because there were no rain gauges at the majority of sampling sites, estimates of storm rainfall were made by extrapolating rainfall data from sources, including local government agencies, NOAA cooperative observation sites, and the California Data Exchange Center (CDEC) (Table 1). The rainfall gauge used at each sampling location is noted in the project database provided in a separate <u>Excel Spreadsheet</u>. Return frequencies for each sample site and for each rainfall data location were estimated using a published tool called <u>NOAA Atlas 14</u> (Perica et al., 2014).

Watershed boundary, land use, and storm volume estimation

Key points: The RWSM is an integral component of the method and used to generate land use and storm runoff volume information for each watershed.

GIS boundary information for the watershed area upstream from each sampling point was obtained from the San Mateo and Santa Clara County Stormwater program staff and abstracted from the GIS database of watershed boundaries within the RWSM (SFEI, 2018). The RWSM watershed boundaries are for full watersheds draining to the Bay. Subwatersheds upstream of sampling points were delineated using storm drain maps and best professional judgement for areas between storm drain lines. As described by McKee et al. (2019), for each watershed area of interest, the RWSM was then used to estimate the proportion of each land use within each watershed of interest. The RWSM includes a calibrated watershed model (Wu et al., 2017) that was used to estimate the annual average runoff coefficient for each watershed of interest that was then combined with storm rainfall to estimate storm volume (McKee et al., 2019).

Uncertainties associated with the interpretive techniques

There are a number of sources of uncertainty with any analytical scheme. In this section, we will remind the reader who is less familiar with the storm-event loads and yields methodology of the errors and uncertainties associated with the method.

Uncertainty of storm rainfall extrapolation

Key points: There are uncertainties associated with extrapolation of rainfall information from the few sites to the many stormwater sites; these errors are relatively small but could be improved by using a greater density of rain gauges with additional quality assurance effort.

As mentioned above, rainfall was estimated from the existing rain gauge network. In the pilot application of the methodology (McKee et al. 2019), the largest distance between a gauge location and a sampling site was 9.1 km (mean = 4.25 km) with a maximum rainfall uncertainty estimated to be +/- 11% and a mean uncertainty of +/-5.0%. In this extended application for 137 watersheds, the average distance from a sampled site to the nearest rain gauge was 6.2 km and we were able to obtain rainfall data for 80% of the sites within 9.5 km but still worse than the pilot application. So average errors have increased to +/-7.3% with a maximum estimated

Rain gauge	Timestep	Latitude	Longitude	Source
Alamitos	15 min	37.247222	-121.870556	SCVWD Alert Precip Gauge
Buchanan Field Airport	Hourly	37.992	-122.055	NOAA
City of San Jose	15 min	37.349444	-121.904444	SCVWD Alert Precip Gauge
J3 Pump station	15 min	37.583691	-122.080551	pers. communication, Alameda County
Mountain View	15 min	37.394167	-122.059722	SCVWD Alert Precip Gauge
OFS #29 at 66th Ave.	15 min	37.759937	-122.196481	pers. communication, Alameda County
Palo Alto	15 min	37.455556	-122.100556	SCVWD Alert Precip Gauge
Richmond City Hall	15 min	37.936900	-122.342700	California Data Exchange Center
Rodeo Fire Stn	15 min	38.035000	-122.270000	California Data Exchange Center
San Leandro Bay	15 min	37.700000	-122.217000	California Data Exchange Center
San Mateo WWTP	15 min	37.568466	-122.295695	pers. comm. San Mateo County
San Mateo WWTP	Hourly	37.568466	-122.295695	pers. comm. San Mateo County
SFO	Hourly	37.6197	-122.3647	NOAA
Sunnyvale WTP	15 min	37.355278	-122.059167	SCVWD Alert Precip Gauge
West Yard	15 min	37.308056	-121.994444	SCVWD Alert Precip Gauge

Table 1. Rainfall gauge locations used in the analysis and the associated source information.

error of 22% for Kirker Ck at Pittsburg due to the nearest gauge being at Buchanan Field Airport 18.7 km away. These uncertainties, although still acceptable, could be improved if rain gauges closer to the sampling sites could be quality assured (for example weather underground data).

Uncertainty of storm runoff estimation

Key points: The uncertainty in storm runoff estimation is large due to the original uncertainties in the calibration of the RWSM and use of annual scale runoff coefficients that do not capture intra-storm variability. Improvements could be possible through either a recalibration of the RWSM or the use of a new RMP hydrology model that has more advanced data inputs and algorithms for estimation of storm rainfall-runoff processes.

Rainfall measured or estimated for each storm at each sampling site was combined with runoff coefficients as an output from the RWSM for each watershed or subwatershed of interest (Wu et al., 2017) to estimate storm volume. Despite the many strengths of the RWSM, the main weakness is a lack of accountability in the known variability of the ratio between rainfall to runoff

between storms due to variations in storm size, intensity, and antecedent moisture conditions. McKee et al. (2019) explored these challenges and found that for smaller impervious watersheds there did not appear to be a seasonal bias but estimated a +/- 42% mean error for this technique. McKee et al. (2019) also noted some potential over prediction bias for smaller watersheds with highly impervious cover associated with the RWSM calibration. During this extended application of the methods, no improvements were made in runoff estimation. There are two avenues for future improvements. The RWSM will be recalibrated in 2022 using soon to be updated PRISM rainfall data for the period 1991-2020, a period more representative of current conditions than the 1981-2010 period that was used for the previous calibration. Alternatively, the RMP is funding the development of a regional Watershed Dynamic Model (WDM) using Loading Simulation Program in C++ (LSPC), a watershed model that was developed from Hydrologic Simulation Program Fortran (HSPF) and uses the same algorithms for simulating hydrology (Zi et al., 2021). The outputs from this new model could be explored and may have advantages over the RWSM given the more spatially and temporally resolved data inputs and the algorithms within LSPC to estimate storm rainfall-runoff processes that consider seasonal variability associated with soil moisture, surface storage, groundwater variability, and surface water-groundwater interactions.

Sum of all the uncertainties

Key points: The cumulative uncertainties associated with estimating storm-event loads and yields are large but of a similar magnitude to the 95% confidence interval around the mean PCBs EMC for Pulgas Creek Pump Station South (one of these more polluted and well sampled watersheds). Based on duplicate samples, the biases for storm-event loads and yields appear to be slightly smaller than for EMCs, and EPCs.

As with any exercise in data interpretation, there is uncertainty and bias associated with all the steps from field measurement, laboratory analysis, and interpretational techniques. Yet, one of the weaknesses of ranking based on EMCs in water or EPCs is the lack of any recognition of uncertainty in the ranking process, despite the data having all the normal uncertainties of environmental chemical data, and despite the data set being generated from storms of differing intensity, duration, antecedent rainfall conditions, and varying PCBs source-release-transport characteristics between watersheds. All these factors cause large uncertainties and biases that make interpretation of the data challenging.

The three primary water quality indicators gathered or computed for each site are:

- Event mean concentrations (EMCs)
- Estimated particle concentrations (EPCs)
- Standard storm-event yields (see above for details)

Although all of these indicators have uncertainties, because EMC data are generated directly from analysis of water samples, of the three indicators, EMC data have the least accumulated error (sampling, handling and laboratory uncertainties only) and are deemed the most certain with the exception of EMCs <1,000 pg/L, where detection limit issues of some of the individual congeners that comprise the sum of 40 congeners reported by the RMP become concerning.

EPCs incorporate the same uncertainties of EMCs but uncertainties are compounded since EPCs are derived from both PCBs and SSC EMCs. So, although we still have very high confidence in the EPCs, errors can increase when SSCs are low and PCBs EMCs are medium to high; such situations can cause highly elevated and questionable EPCs (McKee et al., 2019). Standard storm-event yields are derived from EMC data but combine a number of additional uncertainties associated with the use of the RWSM (Wu et al., 2017; SFEI, 2018) estimating storm volume, adjusting the resulting load estimate to a standard storm size, and normalizing the loads by land area (McKee et al., 2019). Thus, standard storm yields are the least certain of the indicators and there can be spurious results especially when older industrial land use is only a smaller portion of the watershed.

Field measurement of storm EMCs in small urban watersheds and loads computation using the turbidity surrogate technique has an estimated uncertainty of between +/- 14-72% (Gilbreath et al., 2012). So, it should not be surprising that the modeled estimates of storm-event loads and yields presented here would have even larger uncertainty given the cumulative uncertainties of every step from the field and laboratory measurement of EMC, estimation of rainfall by extrapolation from a local gauge, estimation of the runoff coefficient using the RWSM, adjustment of the measured storm load to a standard storm, and the generation of yields based on land use and source area mapping that is also uncertain.

McKee et al. (2019) reported cumulative errors of 60-290% and commented that although these seem large, they are similar in size to the 95% confidence interval around the mean PCBs EMC for Pulgas Creek PS South data which is 155%. They argued that the comparison of errors between sampling sites may help to prioritize further sampling at sites that are predicted to have both a high rank for storm-event yields and a larger uncertainty. The cumulative uncertainty associated with all the steps applied in this expanded analysis of 137 watersheds is similar to those discussed in detail previously (McKee et al., 2019). Due to the adjustment to a standard size storm, theoretically the biases associated with comparing samples from various storm sizes between watersheds should have been reduced. We are encouraged to see that the mean differences between duplicate samples for storm-event loads and yields are less than those of duplicate EMCs and EPC's (n=15) indicating that the method has helped to reduce those biases but that biases have not been completely removed. In the future, it may be possible to improve the method through the use of either flow data generated from a recalibration of the RWSM or the new WDM currently being developed by the RMP (Zi et al., 2021).

Systematic step-by-step method for generating the results database

Key points: The step-by-step methods described here when followed can be used to add further data to the database as more watershed sites are sampled, sites are resampled, or as more rainfall data are identified for use with the 23 sites that were not considered in the present version of the database.

In this section we summarize the step-by-step methods we used to generate the database and complete the comparative analysis. The column headers color coded to help the user easily identify data which are either:

- Measured, recorded, or known information (Green)
- Information obtained from GIS or the RWSM (Grey)
- Estimated using a formula or relationship (Yellow)
- The final results (Blue).

Step 1: Collate PCBs data (pg/L and ng/g) for each watershed sampling site Enter the name of the sampling sites in a new row at the bottom of the database. Enter important identifying information such as any alternative sites names, the county where the site is located, who completed the sampling, and the geographic coordinates of the sampling location (the database uses the WGS 84 coordinate system). Then enter the PCBs event mean concentration (EMC) (ng/L) and SSC data for each field site. If the estimated particle concentration (EPC) was generated by some other means, enter that directly, otherwise compute it as the ratio of PCBs concentration (pg/L) divided by SSC (mg/L). Since these data were generated by laboratory analysis of field collected water samples the columns in the database that contain these data are color coded green. For sites that have been sampled more than once, enter both samples but add an indication in the "duplicate sample" column that it's one of a duplicate. We used the notation D for duplicate, the sequential number 1 to x to indicate the number of sites with duplicates, and the letter lowercase "a" for the lower concentration sample and "b" for the higher concentration sample. In the next column titled "Which duplicate to use?" we entered the label "use this one" for the sample in the duplicate with the highest PCBs concentration (pg/L). But a user may have a different reason for that choice. In a later step you will see that in the comparative analysis we filtered the database to only show the duplicate with the higher PCBs concentration (pg/L). But a user can also filter the database to compare duplicates only.

Step 2: Watershed boundary data and site characteristics

Obtain watershed boundary data from any source deemed reliable. Possible sources include the Oakland Museum of California storm drain mapping project, county or city databases of storm drain infrastructure or topographic maps or a combination of these. Using a geographic information system (GIS) (we used ESRI ArcGIS but there are other options), generate an estimate of watershed area. If there is interest, other ancillary data could be obtained such as an estimate of impervious cover (we used NLCD).

Step 3: Generate land use information

In the methods section above we discuss how we used the RWSM as the basis for much of the GIS work and for generation of the land use information. As long as the information is available for every watershed in the database (so that a comparative analysis can be done between watersheds), a user can make their own decisions about how to define the area in a watershed that is of interest (that is, likely producing the majority of PCBs mass). In the database, we used the definitions described by McKee et al. (2019) where a potentially PCBs contaminated area was assumed to be equivalent to the area of RWSM "dirty" land uses and source areas (Old Industrial and Source Areas plus Old Commercial and Old Transportation. Two columns in the database have this designation (one for area in (km²) and the other for the % area in relation to

the total watershed area. The rest of the watershed area is designated "RWSM clean". These were computed by adding up the data from other columns of land use information that is otherwise ancillary data (also designated step 3). These other data types may be useful for some users.

Step 4: Estimate the runoff coefficient for each watershed

The runoff coefficient is the amount of rainfall that ends up as stormwater runoff. This is obtained as an output from the RWSM for each watershed designated by a watershed boundary that was entered as input data into the RWSM. This could be generated by another means as long as it can be done so consistently across all watersheds. Enter this information in the column titled "RWSM Avg Annual Runoff Coefficient (Wu et al., 2017)". The data are entered as a decimal fraction and will likely be in the range of 0.15-0.8. Data outside this range should be checked and confirmed. Other annual average runoff information for each watershed and for each land use within the watershed can also be obtained from the RWSM. This has also been retained in the database.

Step 5: Classify watershed nesting

In this case the term nesting refers to subwatersheds that are part of other larger watersheds in the same database. This information may be helpful later when comparing the results from one watershed to another. It will give the user a reminder to consider this issue when thinking about how to use the information for management purposes. For watersheds that are nested, we entered the parent watershed into the appropriate cell.

Step 6: Rank each site by EMC and EPC and SSC

The rank is the number designation from highest (Rank 1) to lowest. If there were 200 sites in the database, this would be a number designation from 1 to 200. If 25 sites were sampled twice, then the ranks would number 1 to 225. Determine the ranks for each site based on PCBs concentration (pg/L), estimated particle ratio (EPC (ng/g)) and SSC (see columns titled "Rank (EMC)", "Rank (EPC)", and "Rank (SSC)". The SSC rank will help the user to gain a little more familiarity with how SSC varies between sites and how it influences both the EMC and EPC data. The Excel database uses a formula in each ranking column to compute the ranks. If more data is added to the database, the formula will need to be modified in the rank columns to include the extra rows of data added. Consult the Excel help tool if you are unfamiliar with how to modify the formula.

Step 7: Determine the nearest rain gauge

Locate the nearest suitable rain gauge with data recorded on a 1-hour interval or less. Determine the distance between the rain gauge and the sampling location and enter the name of the rain gauge and the distance into the Excel database.

Step 8: Collate rainfall data

Collate data on the total storm rainfall for the nearest gauge to each sampling site. First identify the storm period that will be used as the "Storm Start" and "Storm End". A storm is defined as starting two hours prior to the start time of the composite sample to the end time of the

composite sample. Use gauges that record rainfall at least hourly but ideally more frequently. Check the reliability of the collated rainfall data by comparing it to other nearby gauges. If the nearest gauge has data quality issues for the storm of interest, add a note to the Excel database indicating why you had to choose a gauge further distant.

Step 9: Collate rainfall extrapolation data

Collate NOAA 14 2-hour, 1-year return storm depth for the sampling site and for the chosen nearest rain gauge site. To do this, go to the NOAA 14 Atlas website (https://hdsc.nws.noaa.gov/hdsc/pfds/pfds_map_cont.html?bkmrk=ne) (note we are using the default settings of precipitation depth, English units (in), and partial duration). Cut and paste in the GIS coordinates of each site (firstly for the sampling site) being careful to use the compatible coordinate system. Enter the data into the database column titled "NOAA 14 2-hr, 1-year return storm depth for the sampling site (in)". Then repeat the exercise for the chosen rain gauge and place the data in the column titled "NOAA 14 2-hr, 1-year return storm depth for the nearest 15 min recording rain gauge (in)". For the majority of sites and rain gauges in the Bay area, the 2-hour, 1-year return storm depth will be between 0.4-0.8 inches. Double check data that fall outside this range.

Step 10: Adjust rainfall data

Have the database compute the adjusted rainfall data for each site using the formula found in the column titled "Estimated (adjusted) storm rainfall for the sampling location (in)". It is simply the measured total storm rainfall from the chosen nearest rainfall gauge adjusted up or down by the ratio of the 2-hour, 1-year return storm depth for the sampling site and for the chosen nearest rain gauge site. If the sampling site has a lower 2-hour, 1-year return storm depth than does the rain gauge, then the adjustment is downward and vice-versa.

Step 11: Compute the storm volume

Have the database compute the storm volume (cubic meters (m^3)) for each site by multiplying the RWSM runoff coefficient by the adjusted storm rainfall and the watershed total area and doing units conversion. The formula to do this is found in the column titled "Estimated storm volume for the sampled storm (m^3) ".

Step 12: Compute the storm load of PCBs

Have the database compute the storm load for the entire watershed (grams (g)) for each site by multiplying the storm volume (m³) generated in the last step by the PCBs EMC (pg/L) and doing units conversion. The formula to do this is found in the column titled "Estimated storm load for the sampled storm".

Step 13: Adjustment factor for standard storm loads

There is a relationship (described by a power function) between the size of a storm and the load transported within a watershed. This relationship can be estimated from the slope of the power function (which we call an "adjustment factor") for adjusting the storm load generated in Step 12 to a load that would be transported in a standard-sized storm. The average slope of the power function between storm size and load for the Bay Area well-sampled watersheds is 1.25. This

value is used to represent a standardized adjustment factor. This factor is found in the columns in the database titled "Factor to adjust estimated storm load to standard storm load (average slope factor (1.25))". In the future, if evidence is found that supports the generation of a watershed specific factor based on land use or some other causative variable, this could be modified. But in the meantime, a slope of 1.25 is used.

Step 14: Analyze rainfall data – Determine maximum 2-hour rainfall intensity This is the first of two steps in the interpretation and use of the rainfall data for estimating standardized storm loads. We found that for the watersheds in the Bay Area that were monitored over multiple storms, the maximum rainfall intensity during the storm measured over a 2-hour period was the best predictor of total storm load. So, in this step, we use the small time-interval data (1-hour or less) to determine the maximum 2-hour rainfall intensity at the rain gauge site for the storm of interest. Place that information in the database in the column titled "Max 2-hr intensity at rain gauge site (in)". By definition, unless the storm was only 2 hours long, the data in this column should be less than the data in the column titled "Rain gauge site Total Storm Rainfall (in)".

Step 15: Determine return frequency of the sampled storm

For each rain gauge used in the analysis there is a unique equation for estimating the return frequency. This equation is based on information obtained from the NOAA 14 Atlas⁴. There are separate tabs in the database that show how these formulas were generated. If a new sampling location uses an existing rain gauge site, just copy the unique return frequency formula for that rain gauge into the cell in the column titled "Return frequency of maximum rainfall intensity (inches/2 hr.) based on NOAA 14 Atlas (years)". In the future, if a new rain gauge site is used, a user will need to generate a new formula. To do this go to the NOAA 14 Atlas⁵ and enter the GIS coordinates of the rain gauge. We are interested in the data in the row labeled "2-hr" for the columns labeled "Average recurrence interval (years)" for 1, 2, 5, 10, 25, and 50 years. Copy and paste the data out of the NOAA 14 Atlas table into a new tab and then reformat it (transpose it) into two columns, one containing the return frequency and one containing the depth of rainfall associated with that return frequency (note we are using the default settings of precipitation depth, English units (in), and partial duration). Then graph the data using a semi log approach (log on the y axis) and generate the formula. Figure 2 presents an example of the graphical analysis used to generate an equation to describe the relationship between rainfall depth and return frequency for the sampling location "SlindenAveSD291". In this example, the formula shown is used in the database for the sampling location "SLindenAveSD291" to convert the rainfall depth for the measured storm to an estimated return frequency.

⁴ This approach assumes that Atlas 14, which is based on averages that are long term rainfall measurements, is a good estimate of return frequency. This might not be true as climate changes. Should this method be further developed in the future for other pollutants, later versions of NOAA 14 or some other tool for estimating return frequency should be considered (Jon Butcher, personal communication, January 2022).

⁵ <u>https://hdsc.nws.noaa.gov/hdsc/pfds/pfds_map_cont.html?bkmrk=ne</u>



Figure 2. Relationship between rainfall depth and return frequency based on data published in the NOAA 14 Atlas. This example is for the SFO rain gauge. This is the nearest rain gauge to the SLindenAveSD291 sampling site.

Step 16: Compute the adjusted storm load for a standard sized storm

This is a simple step since the formula is in the Excel database found in the column titled "Estimated storm load for the sampled storm adjusted to 0.3 yr. return using a slope of 1.25 (g)". The formula takes the storm load generated in step 12 and adjusts it up or down using the standardized slope adjustment factor of 1.25 (Step 13) by an amount that is proportional to the return frequency of the measured storm to the median return frequency of the entire data set. In the pilot analysis, the median return frequency was 0.5 years and in the current application, it is 0.3 years (the median of the data in the column titled "Return frequency of maximum rainfall intensity (inches/2 hr.) based on NOAA 14 Atlas (years)" (Step 15). To minimize the overall adjustment, we recommend as new data are added, that this median be recalculated to try to maintain maximum accuracy of the adjustment. Quality check the result by comparing the adjusted storm load for a standard sized storm to the measured storm load. The adjusted storm load for a standard sized storm to the measured storm load. The adjusted storm load for a standard sized storm to the measured storm load. The adjusted storm load for a standard sized storm to the measured storm load. The adjusted storm load for a standard sized storm to the measured storm load.

Step 17: Compute the adjusted storm-event yield

This is the final and easy step. This is simply the adjusted storm load for a standard sized storm divided by the area of interest in each watershed. In the database, it was done for the whole watershed area (see the column titled "Adjusted load using 1.25 slope (0.3 year return) normalized to whole watershed area (g/km2)") and for the small area deemed to be more likely generating the majority of PCB mass (see the column titled "Adjusted load using 1.25 slope (0.3 year return) normalized to RWSM old industrial and source areas plus RWSM old commercial and old transportation"). For watersheds with a large proportion of their area in older industrial, commercial, and transportation land uses, these will be very similar yields. For other watersheds (particularly the larger ones with mixed land uses), these estimated storm-event yields will be quite different. This difference is a large part of the power of this database for supporting management decisions. Yield computed using just the portion of the watershed that is likely

producing the majority of the PCBs mass allows the direct comparison of PCB source areas one to another rather than whole watersheds one to another.

Step 18: Collate the PCBs congener data for each storm sample

Sometimes databases of PCBs data will only report 40 congeners following the traditional RMP protocol and other times databases may contain PCB concentrations for all 209 congeners analyzed. To generate consistent percent contribution data for each Aroclor, the method uses data standardized to the "RMP 40" congeners common to all samples⁶. Collate all the congener data into a worksheet.

Step 19: Compute the percent contribution of each congener to the sum

Compute the proportion of the sum of PCBs that is associated with each congener by dividing the concentration (pg/L) for that congener by the sum of 40 congeners. For congeners whose concentration is at or less than the reporting limit, assume the concentration is zero.

Step 20: Compute the contribution of the indicator congeners for each Aroclor Per the detailed methods found in Davis and Gilbreath (2019), the Aroclor 1242 indicators are PCBs 18, 28, 31, and 33, the Aroclor 1248 indicators are PCBs 44, 49, 66, and 70, the 1254 indicators are PCBs 87, 101, 110, 118, and the 1260 indicators are PCBs 149, 170, 180, 187.

Step 21: Standardize the indices for each Aroclor

To standardize the indices for each Aroclor, they were expressed as a percentage of the sum of the indices for the four major Aroclors (1242, 1248, 1254, and 1260)

Step 22: Categorize (classify) the indices

To aid in interpretation the data for the Aroclor indices were binned into categories and described as a primary contributor to the observed concentration, a secondary contributor, or a minor contributor, in the following manner:

- A. Greater than or equal to 40% of the sum of the four Aroclor indices (primary contributor);
- B. Greater than or equal to 20% and less than 40% of the sum of the four Aroclor indices (secondary contributor); and
- C. Less than 20% of the sum of the four Aroclor indices (minor contributor)

How to review and use the database

The database is organized in relation to the steps used to generate it. For ease, the columns are given titles referred to in the previous section that describes the systematic steps for generating the results database. The step number (Step 1-22) is also in the column headers and the user should note that some steps lead to multiple columns of data and when this occurs, you will see, for example, the entry of "Step 1" or "Step 7" at the top of multiple columns. The database was published with formulas intact to enable future expansion or modification

⁶ The RMP 40: PCBs 8, 18, 28, 31, 33, 44, 49, 52, 56, 60, 66, 70, 74, 87, 95, 97, 99, 101, 105, 110, 118, 128, 132, 138, 141, 149, 151, 153, 156, 158, 170, 174, 177, 180, 183, 187, 194, 195, 201, and 203.

when new data and information becomes available. Users should (upon download), make a new copy of the database with a local file name and keep the original for reference.

Results

In this section, we summarize the information found in the project database that is provided for download in Excel format along with this report. Although the method does provide an individual ranking, given the uncertainties and biases inherent in this type of data interpretation, it is recommended that the ranks by any of the indicators (storm-event EMC, EPC, load or yield) not be treated literally but rather used to organize the watersheds into general groups of higher, medium, and lower priority categories for management consideration. At this time there are no strict boundaries between high and medium and medium and low so this type of classification needs to be considered conceptual.

Watershed characteristics

Key points: The data set we now have for this comparative analysis is large and very diverse in terms of watershed characteristics and water quality.

A total of 137 watersheds were available for this comparative analysis. These watersheds and subwatersheds range in size from 0.016-232 km2 (a ~15,000-fold variation), impervious cover ranges from 2-91%, and the land use distributions in these areas range from 3-100% potentially PCBs contaminated, RWSM "dirty" land uses and source areas (Old Industrial and source areas plus Old Commercial and Old Transportation). The median for the data set was 61% with only 33% of the watersheds having less than 50% potentially PCBs contaminated area (under this definition). SSC and PCBs EMCs ranged from 3.2-2,626 mg/L (a ~820-fold variation) and 106-307,579 pg/L (a ~2,900-fold variation) respectively, whereas EPCs ranged from 4.0-9,343 ng/g (a ~2,350-fold variation). The variability between watersheds far exceeds the likely variability between storm specific EMCs and EPCs for a given watershed (usually <90-fold) making it very possible to rank watersheds one against the other to separate out a group of about 20% of the watersheds that are of potentially higher management interest (Gilbreath and McKee, 2021). But as will be seen, the estimation of standardized storm-event loads and yields reveals a starkly contrasting set of ranks to help managers with decisions.

Standardized storm loads

Key points: Watershed size has a strong influence on watershed load. However, watersheds of similar size do emit a very wide range of loads in relation to land use and source characteristics. The impacts to downstream Bay margin areas may also vary depending on the biological and physical characteristics of these areas.

Based on the steps outlined in the methods overview section, estimated loads for the sampled storms adjusted to a 0.3-year return storm (the median storm return frequency in the data set)

ranged from 0.000017-2.8 g (guoted to 2 significant figures) (a ~165.000-fold variation). The much greater variation for loads in relation to EMCs and EPCs was expected since it reflects the combination of all the sources of variability between sampling sites (EMC, climate, land use as it impacts runoff characteristics and contaminant sources, and watershed area). However, one should always remember that ranking in this manner is strongly influenced by watershed size (Figure 3). But as the figure also shows, for a given watershed size, there is a large variation in watershed load that occurs given the large variation in land uses and source areas releasing PCBs into stormwater. The ranking of the watersheds by load provides an indicator of the local magnitude of mass that would dilute out as it discharges into the Bay at the margin. There are a number of factors that influence the sensitivity of the Bay margin areas downstream from a watershed including the types of resident species (both prey and predator), and the geometry, flushing times, and wind influences on resuspension (Yee et al., 2017). Bay margin areas that have a shorter flushing time that are adjacent to larger watersheds and watersheds carrying larger loads may be able to disperse loads out into the open Bay. In this case there would be larger local impacts from net deposition causing increased exposure rates and slower recovery times (e.g. Yee et al., 2017).



Figure 3. Relationship between watershed area and watershed load indicates two aspects of the results; both the influence of watershed area on loads and the large scatter that is the result of large differences in load for a given watershed size.

Standardized storm-event yields

Storm-event yields based on normalizing loads to whole watershed area

Key points: The yields (mass per unit area of the watershed per storm) appear to be generally reasonable in comparison to those generated from our well-sampled watersheds and yields reported from studies in other parts of the world.

Standardized loads were normalized to the whole watershed area to generate standardized storm yields as a means for removing the impacts of watershed size on comparisons of relative

loading rates between watersheds. Yields computed this way ranged from 0.00018-1.4 g/km² (a variation of ~8,100-fold). Normalization of annual average loads to the whole watershed area has proven very useful in the past for easy comparisons to data from other parts of the world (Gilbreath et al., 2015; McKee et al., 2017) since consistent land use descriptions are seldom reported. Although the method was never designed to estimate annual average loads and vields, it is possible to scale the estimated storm loads to the annual average runoff volume for each watershed using linear scaling to derive annual yields that ranged between 0.02-80 g/km² with a median of 1.2 g/km². Although, linear scaling likely caused an underestimate of the annual loads and yields⁷, these results compare closely in magnitude with watershed scale annual average yields reported in other parts of the world (McKee et al., 2017: 0.05-13 g/km²) and in our well measured local watersheds (Table 2), thus providing general confidence that the mean tendency of our results are in range of what may be expected for urban watersheds. Of interest, with caution, yields scaled in this manner could also be generally compared to the TMDL loads⁸. However, as a reminder, it is noted again that normalizing to whole watershed area is less sensitive as a metric for local level watershed pollutant specific inter-comparisons since it does not adjust for the dilution of stormwater EMCs by water and sediment derived from "cleaner" areas of the watershed, in this case less PCBs-contaminated land uses. For 33% of the watersheds in this analysis, this dilution area is at least 50% of the watershed area. But with these caveats, as stated previously, we have general confidence in the mean tendency of our results.

Storm-event yields based on RWSM "dirty" land uses and source areas

Key points: Normalizing loads to the area of the watershed that is estimated to be producing the majority of the mass allows direct comparison between PCBs source areas rather than whole watersheds. A number of watersheds that rank lower for storm-event EMC or EPC have source areas that rank high for storm-event yields.

The portion of RWSM "dirty" land uses and source areas (Old Industrial and source areas plus Old Commercial and Old Transportation) in each of our watersheds were used to normalize the standard storm-event loads to generate storm-event yields. Standardized storm yields generated in this manner allow the direct comparison and rank of old industrial PCBs source areas one to another rather than whole watersheds (a key weakness with ranking based on concentrations in stormwater or on suspended sediment). Standardized storm yields ranged between 0.00069-1.45 g/km² (a variation of ~2,100-fold). Many watersheds that rank in the

⁷ The relationship between rainfall and runoff and annual loads typically follows a power function (Load = a constant (A) multiplied by rainfall (or runoff) to the power of X where A is a function of the source characteristics of the contaminant of interest and X is a function of the erosive or transporting energy provided by the rainfall or runoff. Mean annual loads are therefore biased towards higher energy storms and mean annual runoff typically transports less than the mean annual load (McKee et al., 2017). ⁸ The PCB TMDL for San Francisco Bay calls for implementation of control measures to reduce stormwater PCB loads from 20 kg to 2 kg by 2030. In simple terms, a 2 kg PCB load allocation translates to a mean annual yield of 0.31 g/km² for the free-flowing areas downstream from reservoirs (6,650 km²) (McKee et al., 2015). If uncertainties are negated, ~25% of the 137 watersheds being described in this report are estimated to have yields less than this amount. However, it should be noted that there are large uncertainties since methods used here were never designed for scaling and averaging at annual scale.

Table 2. Estimated annual average watershed yields (g/km²) based on whole watershed area for well-sampled watersheds in the Bay Area based on multiple storm samples over multiple years (McKee et al., 2015).

Location Name	Watershed Area downstream from Reservoirs (km ²)	% Impervious Cover	Mean Annual PCBs Load (g)	Mean Annual PCBs Yield (g/km²)	Confidence in the estimate
This study	0.016-232	2-91	-	0.01-50	Low
Pulgas Pump Station-South	1	87%	49	85	Medium
Sunnyvale East Channel	15	59%	128	9.0	Medium
Guadalupe R. at Hwy. 101	233	39%	1,336	5.7	High
San Lorenzo Creek	63	13%	324	5.1	Low
North Richmond Pump Station	2	62%	9	4.7	High
Coyote Creek	319	21%	1,291	4.0	Low
Zone 4 Line A	4	68%	15	3.5	High
San Leandro Creek	9	38%	30	3.4	Medium
Walnut Creek	232	15%	464	2.0	Low
Guadalupe R. at Almaden Expy.	107	22%	69	0.64	Medium
Lower Marsh Ck	84	10%	40	0.47	High
Sac. Riv. At Mallard Island	80,080	5%	7,900	0.099	High

upper 50 for yields estimated in this manner also rank highly for EMC (40) and EPC (35). Thus, in many cases, the estimation of storm-event yields just added further weight of evidence for management decision making. But as an example of how storm-event yield-based ranking might change perception of contamination in a watershed, in 18 cases, watersheds ranked >50 for either EMC or EPC (roughly in the lower two thirds of the database) were ranked between 1-50 for storm-event yield (roughly in the upper third of the database). These results provide managers with new insights on potential sources of interest in these 18 watersheds that may have been otherwise overlooked.

So how reliable and useful is this information? Based on the RWSM outputs, on average, 64% of PCBs annual loads were estimated to be derived from Old Industrial and Source Areas, and a further 32% is estimated to come from Old Commercial and Old Transportation areas; together these account for a total of 96% of the loads (Wu et al., 2017); at a sub-regional scale, the RAA

Phase I report for Santa Clara Basin shows similar results (89%: SCVURPPP, 2020b). Thus, we chose the portion of RWSM "dirty" land uses and source areas (Old Industrial and source areas plus Old Commercial and Old Transportation) in each of our watersheds to normalize the loads to generate yields. By making this choice we do not suggest that land uses are uniform within or between watersheds or that they are consistently or accurately mapped (leading to the potential for interpretive inconsistencies between watersheds). In addition, some areas that were occupied by these land uses but have now been redeveloped yet may still have some residual contamination are not captured by this normalization procedure neither is past or ongoing dumping outside of these land uses (Jon Butcher, personal communication, January 2022)⁹. However, we do know that the alternative of normalizing loads to the whole watershed area has the issue of inconsistent treatment of dilution between watersheds that also makes it an insensitive indicator (discussed in the previous section). So although not perfect, these land uses represent a best estimate of the relative portion of the watershed area that may be producing the majority of the PCBs mass. So, although there are challenges within interpretative methodology, the estimation of storm-event yields using the portion of RWSM "dirty" land uses and source areas provides new insights for managers to consider for a number of watersheds and importantly, allows the direct comparison of PCBs source areas one to another rather than whole watershed-based EMCs or EPCs (the main weakness of the previous ranking methods).

Sites with two storm samples

Key points: The sample with the highest EMC was retained in the ranking database since it is most likely indicative of the greatest number of source areas contributing to the mass transport processes during a storm. But information from the other sample can be used to understand variability and uncertainties.

Within the current data set of 137 locations, 15 sites have been resampled during a second storm so far. Resampling occurred for two main reasons:

- 1. If the first storm that was sampled was very small, it was deemed likely that little or no transport of PCBs or soil erosion from source areas occurred lending to a low EMC, or
- 2. Even if the storm size for the first sample was reasonable, given the watershed characteristics (the large proportion of older industrial area), the low EMC or EPC that was measured was so surprising that stakeholders felt there was a reasonable chance of a false negative in this case it is thought that for a reason other than rainfall characteristics, sources possibly remained disconnected from the sampling location during the sampled storm.

⁹ There is of course a generalized background due to atmospheric deposition and source areas that apply to electronic transmission lines in older developed areas as well as PCB uses in caulks and other products. The normalization as designed did not take these issues into account either. A further development could be to design some kind of weighted fraction of residential and commercial development age prior to the general ban on commercial uses of PCBs. This would address the blanket assumption that it is always old industrial, commercial, and transportation that provides the bulk of the loads whereas sometimes it was the disposal of wastes into nearby undeveloped areas (that are old) that was also a problem (Jon Butcher, personal communication, January 2022).

When two storms were sampled there were large variations in EMCs between samples at each site. This was expected and has been observed in many watersheds around the Bay Area previously (McKee et al., 2015). Duplicate samples of EMC ranged between 1.14-fold variation between samples (given sampling and laboratory uncertainties, essentially identical) to 25-fold with a median variation between samples of 4.1-fold. As previously discussed (McKee et al., 2012), due to a correlation between EMC and SSC, EPC variation between samples at a given sampling site tends to be less (1.04 to 9.2-fold, median = 1.5-fold). And given the lack of independence between EMC and flow and variable dilution of the mass in transport between storms of differing character, the estimated loads and yields computed for each storm and for each site also varied less than the EMCs (1.1 to 24-fold variation, median =3.5-fold).

But with all this variation, which sample out of the two for each site is the most valid for ranking watersheds? We argue that the sample with the highest EMC is most likely indicative of the greatest number of source areas contributing to the mass transport processes during a storm. Or in different terms, for that watershed, it is the sample with the highest EMC that represents the best balance between the transport of mass from the PCB source areas and the dilution of that mass by storm flow volume from the watershed as a whole that results in the EMC.

So how does that play out for our 15 sites with two storm samples? In 14 out of 15 sites, the sample with the greatest EMC also exhibited the greatest EPC (Rodeo Creek at Seacliff Court Pedestrian Bridge was the exception). At all but three sites (Kirker Creek at Pittsburg Antioch Highway, SMBUR164A, 100CTC400A), the sample with the greatest EMC also exhibited the greatest SSC. And at all but three sites (100CTC500A, Meeker Slough, Kirker Creek at Pittsburg Antioch Highway), the sample with the greatest EMC also exhibited the greatest estimated storm-event yield.

As a standard protocol, the sample for a site with the greatest EMC was used for site classification. In the majority of cases, this biased the classification towards an increased indication of elevated pollutant sources. Data from the second sample can be used to check if there was anything missed, to understand variability between storms, and uncertainties associated with the estimate of storm-event yields. We found that on average, the variability between storm-event yields from duplicate samples was slightly lower than the variability between EMCs and EPCs, helping to suggest that the storm-event yield method is robust. As mentioned previously, better estimates of storm runoff either from a recalibrated version of the RWSM (in the RMP 2022 work plan) or from the new WDM currency being developed by the RMP (Zi et al., 2021) could help to improve the storm-event yields estimates in the future.

Aroclor indicators

Key points: Aroclors were used for a wide variety of applications and thus are not perfect indicators of specific source areas upstream. However, specific Aroclors did have some unique applications and the presence of two or three at a site can also be indicative of potential source areas to consider.

As described in the Methods section, congener data were used to estimate the contributions of Aroclors in each sample. Suitable data to estimate the proportional presence for Aroclors (1242, 1248, 1254, and 1260) were available for 74 of the 137 watershed sites. Just one site (Rodeo Creek at Seacliff Court Pedestrian Bridge) showed Aroclor 1242 as a primary component of the sample (>40%). At this site, Aroclor 1248 showed up as a secondary contribution (20-40% of the sample). Aroclor 1242 was also a secondary component of the sample taken at Line3AM1 at Industrial Pump Station watershed. Aroclor 1248 showed up as a primary component of the sample in the Meeker West watershed with Aroclor 1254 as a secondary component there. Aroclor 1248 was found to be a secondary component of the samples in a total of 10 watersheds. Aroclor 1254 was by far the dominant Aroclor showing up as a primary component in 46 of the 74 watersheds and a secondary component in a further 27 of the 74 watersheds. In just one watershed (Outfall to Colma Creek), Aroclor 1254 was present as just 14% of the sample and in this case, Aroclor 1260 was the primary component accounting for an estimated 80% of the sample. Aroclor 1260 was generally more common at the sites than 1242 and 1248, being a primary component at 16 sites and a secondary component at 46 sites.

During the development of the methodology, Davis and Gilbreath (2019) explored Aroclor variability in 25 Guadalupe River storm samples. They found that contributions of Aroclors 1254 and 1260 varied within fairly restricted ranges: 23-62 and 20-65%, respectively helping to support the use of Aroclor indicators as a suggestion for upstream sources. So, although environmental samples are subject to differential weathering that tends to move their composition away from original Aroclors (Jon Butcher, personal communication, January 2022), the similarity between samples collected during several or many storms does suggest that differential weathering has not obscured the samples and that Aroclors may provide some useful information for management purposes. At seven of the 15 sites included in our data base, congener data were available for computation of Aroclor indicators for both duplicate samples. At five of the seven sites, the Aroclor indicators were similar between storm samples, suggesting that Aroclor contributions are a reasonably consistent indicator of the PCBs export from these watersheds; a similar outcome to Davis and Gilbreath (2019).

Since each Aroclor was used for a wide variety of applications (Erickson and Kaley, 2011), Aroclors are not perfect indicators of source types or source areas for each of these watersheds, but there are some useful suggestions that can arise from the Aroclor indicators (Table 3). For example, Rodeo Creek at Seacliff Court Pedestrian Bridge showed Aroclor 1242 as a major component of the PCBs mass in the sample. This may indicate unique 1242 sources upstream from the sample site that include capacitors and carbonless copy paper. In contrast, Aroclor 1254 had several unique uses including caulk and joint sealants, cutting oils, and inks, and insulation and other building materials (Table 3). Although Aroclor 1254 had many nonunique uses (for example all the Aroclors were used in hydraulic fluids and other lubricants), at the many sites where Aroclor 1254 was dominant, these unique sources might be considered when doing property inspections. For the 16 watersheds where Aroclor 1260 was dominant, extra vigilance during property inspections could be placed on searching out past use or presently damaged and leaking transformers which, if the use of Aroclor 1254 is included, accounted for 27% of the US sales. In the 16 watersheds where Aroclor 1260 was dominant, 13 had estimated contributions to the total concentration of PCBs that were 50% or greater. This differed from Aroclor 1254 where just 21 of the 46 watersheds where this Aroclor dominated had contributions 50% or greater. In contrast, Aroclor 1248 had no historical unique major uses (Table 3) thus the presence of Aroclor 1248 in a sample may have little use for management purposes, unless soil or sediment data indicate a source area or areas with a profile dominated by 1248. For example, Davis and Gilbreath (2019) explored Aroclor profiles in soil samples collected in the Guadalupe River watershed and found a three-block area within the watershed that had very high soil concentrations and Aroclors 1254 and 1260 present. They suggested that management of this area could reduce concentrations and loads but suggested there must be other sources (Davis and Gilbreath, 2019).

In summary, although not perfect (weathering, variability in storm samples, and a variety of applications), managers could use the presence of Aroclor indicators as further supporting evidence to decide whether or not to elevate a site to a higher level of interest or in the cases of sites with lower EMCs and EPCs, a further indication beyond low SSC and small storm size that resampling before classification would be needed (see next section for that discussion). Aroclor profiles and a knowledge of historic uses may also help managers to prioritize further investigations using soil sampling upstream.

Aroclor	1242	1248	1254	1260			
			Transformers				
Major uses (>20,000 metric t)	Capacitors (large, small, light ballasts)		Caulk and joint sealants				
	Hydraulic fluids (and other lubricants)						
Minor uses (<20,000 metric t)	Heat transfer fluids / Systems						
	Carbonless copy paper		Wire and ca	ble coatings			
			Cutting oils				
			Inks				
	Paints, varnishes, lacquers, and other coatings						
			Insulation and other building materials				

Table 3. Aroclor uses. Information adapted from Erickson and Kaley (2011).

Discussion

Bay Area municipalities are working on finding and prioritizing subwatersheds and source properties that contain elevated concentrations or mass of PCBs. They use a range of information to make decisions including use history, observations of housekeeping and soil erosion, soil sampling for PCBs analysis in adjacent public right-of-way areas, and interviews, sampling, and inspections onsite. No single piece of information by itself is completely deterministic and in some cases, the information can sometimes be conflicting. Stormwater sampling downstream of suspected sources is another tool used to support an overall weight of evidence approach and as will be discussed in the following sections, that information is also subject to weaknesses and can be conflicting.

Are there data gaps associated with storm characteristics?

Key points: There appears to be no a priori reason based on the sampled storm characteristics to reject any of the data prior to the subsequent interpretive steps.

One of the key questions before starting this kind of comparative analysis is are there any reasons to, *a priori* (based on theory from previous study and knowledge), reject any of the data. The storm characteristics during sampling is one aspect that may cause challenges with data interpretation. Based on the calibration of the Regional Watershed Spreadsheet (RWSM) model (Wu et al., 2017), antecedent rainfall exceeding 3 inches year-to-date was needed to "fill up" low points in the landscape and wet soils enough to generate runoff although this was not used as a condition for sampling in any of our field studies (e.g. Gilbreath and McKee, 2021).

Based on our experience in the field over the past 20 years, the planning work for field studies, and most recently for the reconnaissance field study (e.g. Gilbreath and McKee, 2021), 0.5 inches of rainfall in the forecast based on the 6-hour quantitative precipitation forecast (QPF) for a storm was used as a minimum threshold for staff and equipment deployment decisions to minimize "false starts". However, as noted by Gilbreath et al., this threshold was relaxed in some years due to a lack of larger storms. Rainfall intensity may also play a role in the release of PCBs from a source area and based on our 4 years of experiences sampling Zone 4 Line A in Hayward, when rain rates exceeded 0.15 in/hour, we tended to see much greater flow rates and suspended sediment transport. For example, intense storms can have lower EMCs but high EPCs if the source that is present at lower flows is overwhelmed by lower concentration sources that have low sediment erosion. This can occur when the source areas are on impervious surfaces that yield runoff in small storms. But during larger storms, runoff from pervious surfaces begins to occur, that further dilutes the PCBs but may also dilute the EPC if pervious areas are erosional (McKee et al., 2019; Gilbreath and McKee, 2021; Jon Butcher, personal communication, January 2022). These concepts make decisions about when to sample somewhat tricky but regardless of whether any of these thresholds are perfect, the data can

now be explored to look for these patterns. In particular, the stakeholders of this work wanted to know if any of these thresholds are valid for *a priori* rejection of the data¹⁰.

To test for this, scatter plots were generated between rainfall antecedence and EMC, EPC, and storm-event yield (Figure 4), storm total rainfall and EMC, EPC, and storm-event yield (Figure 5) and maximum 2-hour rainfall intensity and EMC, EPC, and storm-event yield (Figure 6). A log-log display was used to allow for easier review of the lower end of the data to visually explore these proposed thresholds. EMCs and storm yields all slightly increase in relation to antecedent rainfall (Figure 4), perhaps due to a combination of greater runoff and sediment production per unit area as saturation from below and soil erosivity increase. There are a few high data points at <3 in of antecedent rainfall. For example, site 031SCH250A in Santa Clara had an EMC, EPC, and storm-event yield of 52,717 pg/L (rank 14), 2,636 ng/g (rank 4), and 0.139 g/km2 (rank 30) respectively despite an SSC of just 20 mg/L and antecedent rainfall of 2.4 inches. At antecedent rainfall ranging between 0.79-2.64 inches EMCs ranged from 1,947-52,717 (n=5, mean = 14,385, median = 5,895). So, although we only have antecedent rainfall data for 85 out of 127 locations, based on the data, there appears to be no indication of a minimum threshold. PCBs can be transported in some watersheds during low antecedent rainfall conditions.

In contrast, only EMCs appear to slightly increase in relation to total storm rainfall (Figure 4), perhaps as a result of a combination of saturation from below and soil erosivity increasing during a storm, increasing connection between all areas of a watershed, and the storm drain network, and overtopping barriers within source areas, or filling and overflowing source containers. Similar to antecedent rainfall, the relationship between storm rainfall and all three indicators shows a number of high data points at rainfall <0.5 inches. There were 23, 22, and 22 sites where EMCs, EPCs, and storm-event yields ranked in the top third of the data set respectively despite storm total rainfall ranging from 0.06-0.48 inches for the 75 sites (much greater than half the entire data set) that had been sampled during storms smaller than 0.5 inches. For the 10 sites that were sampled during the smallest storms, median EMCs, EPCs, and storm-event yields were 9,535 pg/L, 173 ng/g, and 0.029 g/km² for total storm rainfall ranging between just 0.06-0.13 inches. EMC, EPC, and storm-event yield for the SMBUR85A watershed in San Mateo where the smallest storm was sampled were 31,108 pg/L, 334 ng/g, and 0.178 g/km² (all three in the upper third of the whole data set). Overall, there appears to be no indication of a minimum threshold for total storm rainfall. This makes sense since there are likely a mixture of PCB sources that includes both upland erosion and seepage of liquid-phase PCBs. The former have EMCs that increase with rainfall; the latter are diluted by rainfall (Jon Butcher, personal communication, January 2022). PCBs can be transported in some watersheds during low volume storms.

¹⁰ There may also be a linkage between these thresholds and incipient motion in channel sediments but this was not explored during the development phase of this method. This concept was discussed during the development of the Hydromodification Management Plans for the Bay Area. Since a portion of the PCBs and other pollutants in transport are associated with mobilization of sediment, this might be a way of defining critical thresholds (Jon Butcher, personal communication, January 2022).



Figure 4. Relationship between rainfall antecedence and event mean concentration (EMC), estimated particle concentration (EPC), and storm-event yield based on the RWSM "dirty" land uses and source areas (Old Industrial and source areas plus Old Commercial and Old Transportation).



Figure 5. Relationship between storm total rainfall and event mean concentration (EMC), estimated particle concentration (EPC), and storm-event yield based on the RWSM "dirty" land uses and source areas (Old Industrial and source areas plus Old Commercial and Old Transportation).



Figure 6. Relationship between maximum 2-hour rainfall intensity and event mean concentration (EMC), estimated particle concentration (EPC), and storm-event yield based on the RWSM "dirty" land uses and source areas (Old Industrial and source areas plus Old Commercial and Old Transportation).

Similarly, only EMCs appear to slightly increase in relation to maximum 2-hour rainfall intensity (Figure 5), perhaps also as a consequence of saturation from below and soil erosivity increasing during a storm, increasing connection between all areas of a watershed and the storm drain network, and filling, overtopping or overflowing source areas. Similar to antecedent rainfall and total storm rainfall, the relationship between rainfall intensity and all three indicators shows a number of high data points at rainfall intensity <0.15 inches/hour. There were 5, 7, and 6 sites where storm-event EMCs, EPCs, and yields ranked in the top third of the data set respectively despite storm rainfall intensity ranging from 0.04-0.12 inches/hour for the 21 sites that had been sampled during storms smaller than 0.15 inches/hour. For the 10 watersheds in which the smallest storms were sampled, median storm-event EMCs, EPCs, and yields were 9,535 pg/L, 173 ng/g, and 0.029 g/km² for total storm rainfall ranging between just 0.06-0.13 inches. As with total storm rainfall, the SMBUR85A watershed in San Mateo was also sampled at the lowest rainfall intensity of any site in the data set. Overall, there appears to be no indication of a minimum threshold for storm rainfall intensity. PCBs can be transported in some watersheds during low rainfall intensity conditions.

In summary, there appears to be no *a priori* reason based on the sampled storm characteristics to reject any of the data prior to the subsequent interpretive steps since elevated storm-event EMCs, EPCs, and yields can occur at some sites regardless of climatic factors.

Evaluating data weaknesses

Key points: A decision tree for selecting sites to consider for resampling was developed based on EMC, storm-event yield, SSC, and storm characteristics. Using this decision tree, 13 sites were recommended for resampling.

As discussed in the previous section, there appears to be *no a priori* reason based on the sampled storm characteristics to reject any of the data prior to the subsequent interpretive steps since even small storms can generate medium to high EMCs, EPC, or yields. However, when storm-event EMCs, EPC, or yields were low, the samples tended to be taken during relatively small storms or the runoff from the site generated very low SSC. Therefore, to generate consistent resampling recommendations, a simple decision tree was put together (Figure 7). Since, at this time, thresholds have not been developed for classifying watersheds into high, medium or lower categories of management interest (see next section), for this exercise, the lower third of the data was used as an illustration.

As discussed in the previous section, a total storm rainfall of 0.5 in and a rainfall intensity of 0.15 in/hr. were chosen as thresholds to define a small storm. The SSC found in the resulting sample was also considered an indicator of sampling success. So what threshold for SSC might be reasonable? Based on 108 storm samples at North Richmond Pump Station and 96 samples at Pulgas Creek South Pump station, mean SSC at both of these highly urban locations was 57 mg/L (McKee et al., 2015). The median SSC across the 137 sampling sites in the current database for this application was 51 mg/L, 25% of the samples had concentrations <27 mg/L, and 16% of the samples were <20 mg/L. For this analysis we decided to set the threshold at 20



Figure 7. Decision tree for determining which sampling sites to recommend for resampling. A critical component of the decision tress is the question about SSC. If SSC is low (<20 mg/L) we assume it might have been a small storm or a low intensity storm that could have caused that. But if samples were taken during a "reasonable sized storm", we assume the SSC was low due to the watershed having relatively low sediment sources or soil erosion. As a practical check, stormwater agency staff might compare this to any field evidence they may have.

mg/L. But with relative ease, any of these thresholds could be adjusted more or less conservatively and the resulting output can be ranked based on these or any other indicator (for example, those sites that met these thresholds but have the greatest proportion of old industrial land use). Based on these criteria, there are 13 sites recommended for resampling. One additional site in Santa Clara (034BFL230A) had the lowest EMCs of any site sampled and was left on the list despite being sampled during a relatively intense storm. Table 4 was organized by county and then by land use. In the absence of any other evidence, resampling the sites with greater RWSM "dirty" land uses is one way of prioritizing resampling.

Future watershed classification

Key points: Due to a lack of well-defined thresholds to define sites of high, medium, and low management interest, classification was not possible at this time.

A decision tree to support watershed classification into high, medium or low management interest was developed but classification was not possible due to a lack of natural breaks in the data or other rationale for thresholds. The draft decision tree was provided in Appendix A so that if robust thresholds are developed in the future, the decision tree may be reconsidered. At this time, the objective to determine sites of low interest (those that could be dropped from any further consideration) was also not achieved due to data limitations. However, it is possible that many sites recommended for resampling may, in the future, be categorized as low management interest if they consistently show low EMCs, EPCs and yields after resampling.

			Rain gauge	Max 2-hr	RWSM "dirty" (old industrial and source	Adjusted load using 1.25 slope			
			site	intensity	areas plus	(0.3 year return)		PCB	
		T-4	lotal	at rain	KWSWI old	normalized to	DCDC	time-	
Watershed		TOL.	Storm	gauge	commercial and		FUES	paced	eec
watersneu/		Area		site		Idilu use area		EIVIC	55C
Catchment	County	(km2)	(in)	(in)	transportation)	(g/km2)	(ng/g)	(pg/L)	(mg/L)
SM-SSF-317A	San Mateo	0.13	0.42	0.36	98%	0.014	450	2,610	5.8
SM-SSF-1001C	San Mateo	0.056	0.11	0.070	97%	0.012	353	1,130	3.2
SM-RCY-254A	San Mateo	0.056	0.39	0.20	91%	0.010	113	1,570	14
SM-SSF-318A	San Mateo	0.28	0.42	0.36	90%	0.012	266	2,260	8.5
SM-RCY-323A	San Mateo	0.75	0.16	0.12	58%	0.0061	191	1,550	8.1
SM-MPK-71A	San Mateo	5.6	0.19	0.15	40%	0.0023	43	592	14
099GAC240B	Santa Clara	0.016	0.11	0.070	100%	0.0011	34	378	11
083GAC900E	Santa Clara	0.20	0.11	0.070	100%	0.0015	75	516	6.9
049CZC900A	Santa Clara	0.29	0.20	0.20	87%	0.0087	148	2,760	19
049CZC910A	Santa Clara	0.15	0.20	0.20	67%	0.0078	197	2,030	10
034BFL230A	Santa Clara	0.62	0.55	0.40	57%	0.0019	30	584	19
129CNC550A	Santa Clara	2.1	0.080	0.080	38%	0.0047	72	1,313	18
050GAC020D	Santa Clara	3.2	0.040	0.040	26%	0.0007	51	205	4.0
050GAC020C	Santa Clara	3.3	0.080	0.080	25%	0.0024	62	446	7.2

Table 4. Sampling sites recommended for resampling based on possible data weaknesses.

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Appendix A

