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An Approach to Industrial Stormwater Benchmarks: Establishing and Using Site-Specific Threshold Criteria at Lawrence Livermore National Laboratory

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Current regulatory schemes use generic or industrial sector specific benchmarks to evaluate the quality of industrial stormwater discharges. While benchmarks can be a useful tool for facility stormwater managers in evaluating the quality stormwater runoff, benchmarks typically do not take into account site-specific conditions, such as: soil chemistry, atmospheric deposition, seasonal changes in water source, and upstream land use. Failing to account for these factors may lead to unnecessary costs to trace a source of natural variation, or potentially missing a significant local water quality problem. Site-specific water quality thresholds, established upon the statistical evaluation of historic data take into account these factors, are a better tool for the direct evaluation of runoff quality, and a more cost-effective trigger to investigate anomalous results.

Lawrence Livermore National Laboratory (LLNL), a federal facility, established stormwater monitoring programs to comply with the requirements of the industrial stormwater permit and Department of Energy orders, which require the evaluation of the impact of effluent discharges on the environment. LLNL recognized the need to create a tool to evaluate and manage stormwater quality that would allow analysts to identify trends in stormwater quality and recognize anomalous results so that trace-back and corrective actions could be initiated.

LLNL created the site-specific water quality threshold tool to better understand the nature of the stormwater influent and effluent, to establish a technical basis for determining when facility operations might be impacting the quality of stormwater discharges, and to provide “action levels” to initiate follow-up to analytical results. The threshold criteria were based on a statistical analysis of the historic stormwater monitoring data and a review of relevant water quality objectives.

The site-specific thresholds were established using statistical analyses of historic stormwater data and were compared to relevant water quality objectives (WQOs). The procedure includes quality checks of data; calculation of the 95% statistical confidence limits; comparison of the upper confidence limits (UCL) with applicable WQOs; re-examination of the UCL exceedence frequency; and periodic readjustment and recalculation of the confidence intervals. The procedure for calculating the specific thresholds includes the following five steps:

1. Perform a quality check of the available data;
2. Calculate statistical confidence intervals;
3. Compare the upper confidence interval to available benchmarks;
4. Examine the frequency of exceedence in your data for the upper confidence limit;
5. Adjust the exceedence probability and recalculate step 2 if step 4 is not satisfactory.

In the first step, data is plotted over time to identify any major trends or large discontinuities that may indicate a change in analytical technique, laboratory, or discharge process. Control charts are developed by plotting data that have been standardized by subtracting the mean and dividing by the standard deviation. Control charts have a mean of zero and the variability around the mean is standardized by the standard deviation. Therefore, the value 2.0 on the Y-axis corresponds to two standard deviations. Values that are many standard deviations above or below zero need to be examined because they may be outliers and a decision should be made whether to keep these values in the analysis. The trend plots and control charts are a fast way to quality check large amounts of data.

Step two involves calculating the confidence intervals for a given probability level for a select group of water quality parameters. As environmental data are often not normally distributed, this may require a correction to normalize the data (if possible). If not possible, alternative calculations developed for other distributions (e.g., Chi-squared distribution) need to be used. After normalization, the standard deviation is multiplied by the test statistic (for a normal or *t*-distribution) for the desired confidence interval (e.g., 95, 97, or 99 percent) and added to the mean value. For LLNL's site-specific thresholds, a value exceeds the threshold if it is greater than the 95 percent confidence interval (usually about two standard deviations) computed for the historical mean value for a specific parameter.

The purpose of steps three and four is to determine if the value for the UCL calculated is acceptable to use at your site. This is determined by comparing the UCL value to published regulatory reference values, such as ambient water quality goals, basin plan objectives, or drinking water maximum contaminant levels. If the calculated UCL values exceed regulatory reference values, the reasons and background information should be documented. Another validation of the UCL value is to see how often it would trigger further investigation. If this value is used as an "action level", but is exceeded once a year (or more), the exceedence probability may be set too low. It is important not to set the action level so low that it triggers a "chicken little" response. These two approaches basically determine if the UCL value calculated is too high or too low to be an effective action level. If it is not a useful value, then return to step two and increase the probability to 97 percent to see if a better value is returned.

After this fine-tuning of the UCL value, it can be used as a threshold criteria to identify out-of-the-ordinary data that should be investigated further to determine if concentrations of that parameter are increasing in the stormwater runoff.

As an example, presented here is the process of data analysis and decision points using more than 10 years of copper data from the LLNL Livermore site. Quality assurance procedures are well established and in place at LLNL and quality control samples, including sample duplicates, were examined. In plotting the data we noticed that the detection limits provided by the analytical laboratory for copper analyses changed from 0.050 mg/L to 0.01 mg/L in the mid 1990s and changed again to 0.002 mg/L in 2001 (**Figure 1**). The data presented in **Figure 1** are for the effluent stormwater sampling location along the Arroyo Las Positas called WPDC. All values listed as less than the limits of detection were removed from the calculation of confidence intervals. The change in detection limits creates the appearance of a false trend in the data as more low values were measured in recent years.

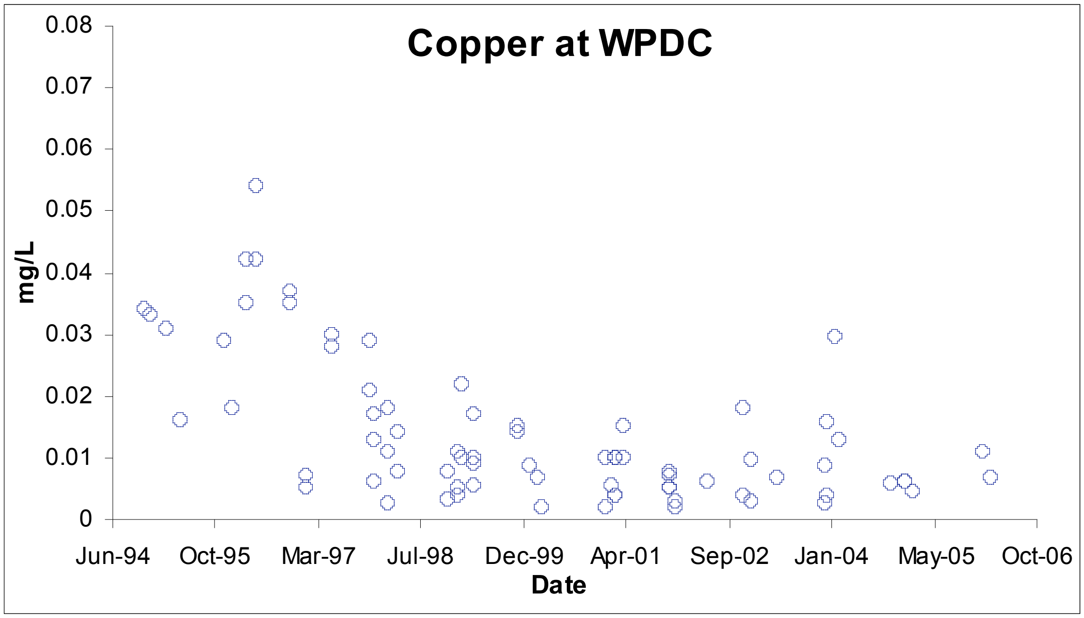

Figure 1. Historical copper concentrations measured in stormwater samples collected from effluent location WPDC along the Arroyo Las Positas at the LLNL Livermore Site.

A control chart, values normalized by subtracting the mean and dividing by the standard deviation, is shown in **Figure 2**. These charts are helpful for looking for data outliers that exceed two or three standard deviations. There were some elevated points in our copper data; however, they appear not to be isolated values and it was decided not to remove any outliers.

Prior to the calculation of confidence intervals, tests were performed to examine if the data were normally distributed. There was a slight non-normality to the data so a transformation was attempted. In addition, we attempted to remove the trend in the data prior to calculating the upper confidence limit. Neither of these approaches significantly altered the upper confidence limit, so a simple confidence interval calculation was used.

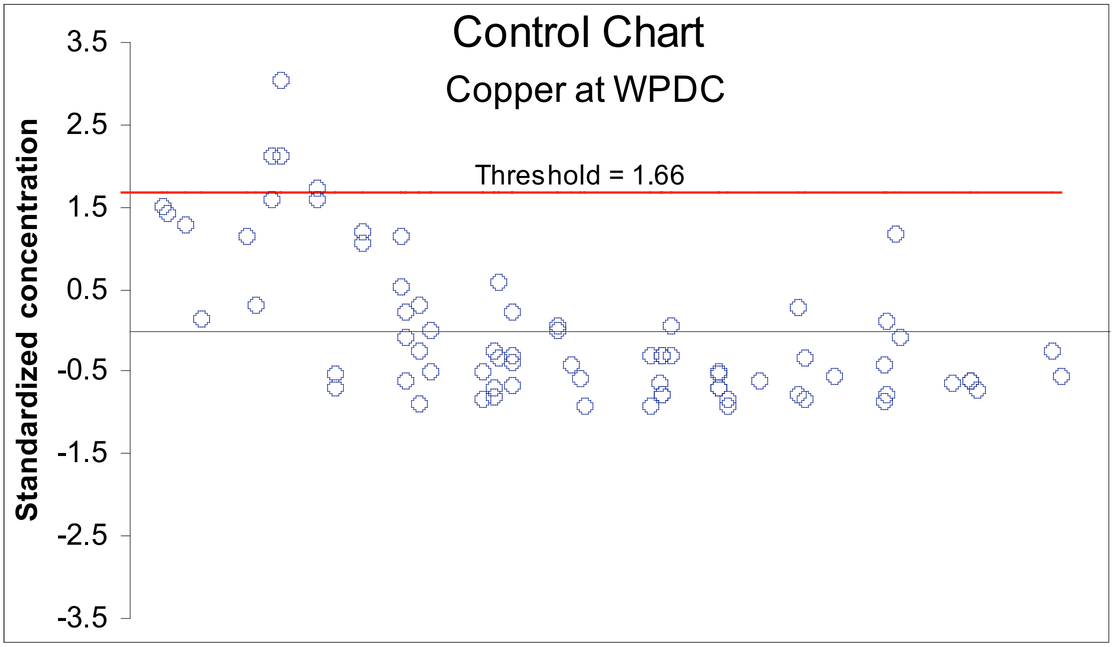

Figure 2. Control chart of copper concentrations measured in storm water samples collected from effluent location WPDC along the Arroyo Las Positas at the Livermore Site of LLNL.

The upper confidence limits was:

Mean + t-statistic * standard deviation.

The t-statistic was taken from a standard textbook for a 95 percent confidence for 100 degrees of freedom (number of samples -1) (Daniel, 1995). The resulting value was 1.66, so the mean 0.0143 mg/L added to the standard deviation 0.0131 mg/L multiplied by 1.66, resulted in a threshold value of 0.036 mg/L. The threshold value is higher than the USEPA ambient water quality criteria for copper of 0.013 mg/L; however, it is lower than mean values reported in Stenstrom and Lee (2005) for Los Angeles County, Sacramento County, and the State of Connecticut (1.01 mg/L, 0.18 mg/L, and 0.13 mg/L, respectively).

The test statistic is plotted in **Figure 2** and the threshold value is plotted in **Figure 3**. Also shown in **Figure 3** are the historical copper data for stormwater samples from the channels of the Arroyo Las Positas that flow onto the Livermore site (influents). LLNL decided to use the threshold value calculated for the effluent location (WPDC) on the arroyo as a more conservative action level. As seen in **Figure 3**, the copper concentrations in samples collected at influent locations (ALPO, GRNE, and ALPE) are often higher than corresponding results from effluent location WPDC. Therefore, we made the decision to use the threshold calculated for WDPC for all monitoring locations on site. In this way LLNL can also capture and report values of copper that are entering the site at higher concentrations than those leaving the site in stormwater runoff. The potential frequency of exceeding this threshold at location WPDC is low and has occurred on the order of four times in our historical record. However, exceedence of the threshold at influent locations, particularly ALPO and ALPE is more common. This is acceptable as it documents water quality in the background water quality in Arroyo Las Positas.

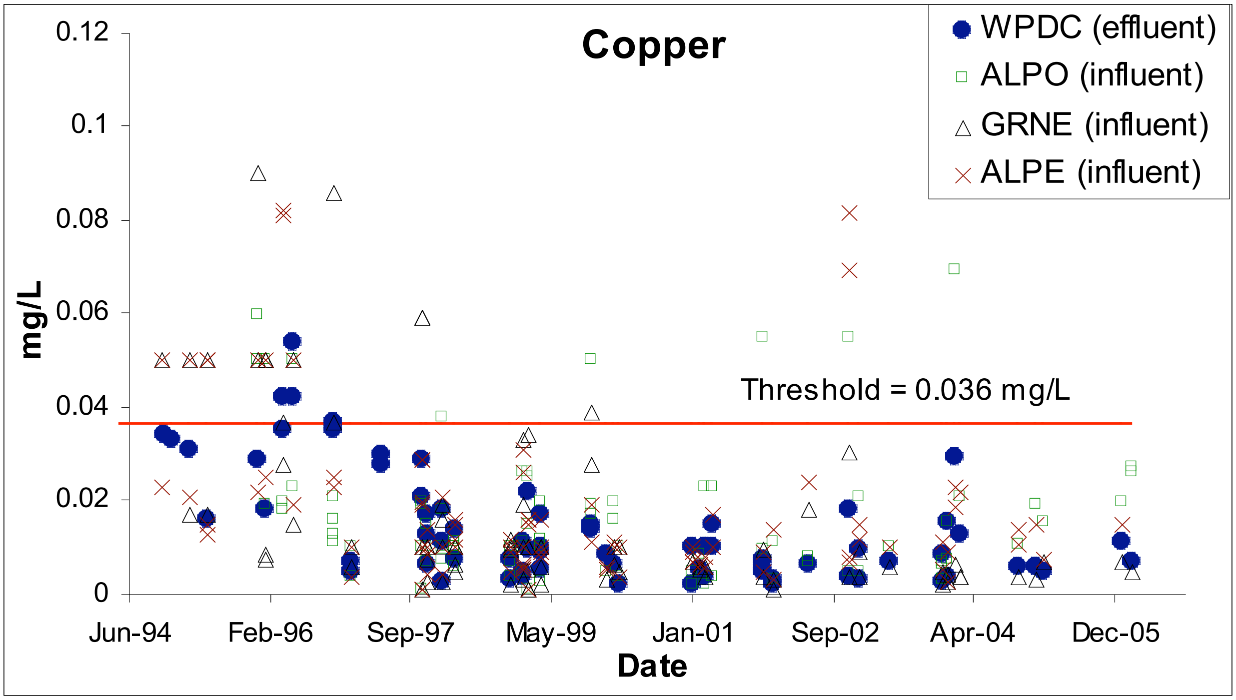

Figure 3. Historical copper concentrations measured in stormwater samples collected from effluent (WPDC) and influent (ALPO, GRNE, and ALPE) sampling locations along the Arroyo Las Positas at the LLNL Livermore Site.

Once the site-specific thresholds are established, LLNL's stormwater analysts use them to evaluate stormwater effluent quality and to help identify upset conditions caused by industrial activities. Effluent data are compared with the thresholds. If the effluent concentrations exceed any of the thresholds, the effluent values are compared with corresponding influent concentrations. If effluent concentrations are lower than influent concentrations, it is assumed that the sources are upstream or naturally occurring and no further action is required. When effluent concentrations exceed influent concentrations an investigation is initiated.

The standardized evaluation, which forms the basis for objective management decisions, includes the following three key steps that are further elaborated upon in **Figure 4**.

1. Compare stormwater effluent concentrations with the above LLNL site-specific threshold criteria.
2. If effluent concentrations exceed any criterion, compare effluent values with corresponding influent concentrations.
3. If effluent concentrations are lower than influent concentrations, assume that the sources are upstream or naturally occurring and take no further action.

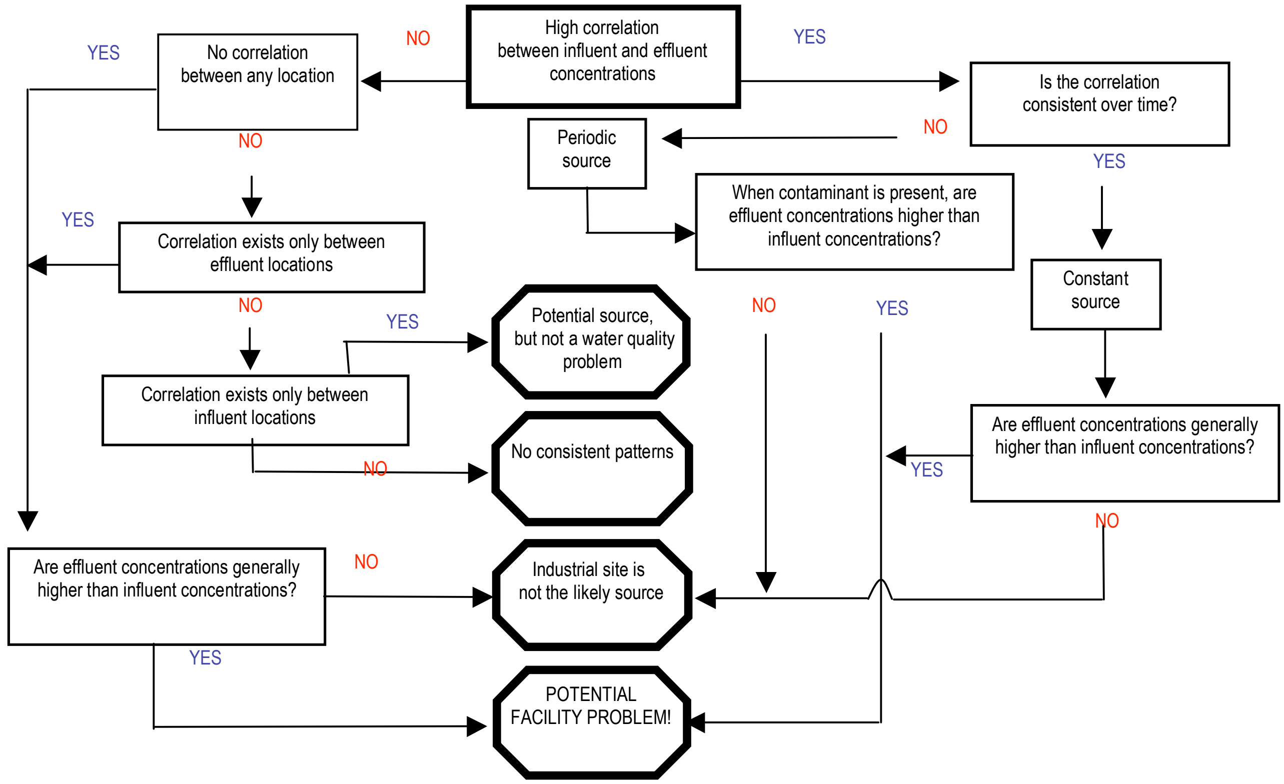

Figure 4. LLNL's Stormwater quality evaluation decision tree. (Source Campbell et al., 2004).

Using this methodology LLNL has established site-specific threshold concentrations for 16 parameters routinely monitored and detected in stormwater (**Table 1**). The parameters range from the basic parameters required of all industrial permit monitoring programs, to those expected in LLNL site stormwater including metals, pesticides, and radioactive parameters. LLNL developed threshold criteria for:

1. Constituents that were seen routinely in stormwater runoff, as in the case of copper and zinc;
2. Constituents that we wanted to pay special attention to, such as mercury;
3. Constituents that were subject to a source investigation, such as tritium and diuron.

Thresholds are re-evaluated periodically as new data is added to the dataset, and thresholds for additional constituents are developed based on review of the data annually.

Table 1. LLNL site-specific threshold criteria.

Parameter	Livermore site
Total suspended solids (TSS)	750 mg/L[a]
Chemical oxygen demand (COD)	200 mg/L[a]
pH	<6.0, >8.5[a]
Nitrate (as NO_3)	10 mg/L[a]
Orthophosphate	2.5 mg/L[a]
Beryllium	1.6 µg/L[a]
Chromium (VI)	15 µg/L[a]
Copper	36 µg/L[a]
Lead	15 µg/L[b]
Zinc	350 µg/L[a]
Mercury	Above RL[c]
Diuron	14 µg/L[a]
Oil and grease	9 mg/L[a]
Tritium	36 Bq/L[a]
Gross alpha radioactivity	0.34 Bq/L[a]
Gross beta radioactivity	0.48 Bq/L[a]

[a] Site-specific value calculated from historical data and studies. These values are lower than the other regulatory reference values except for Cu, Zn, TSS, and COD.

[b] California and EPA drinking water action level.

[c] RL = analytical reporting limit = 0.0002 mg/L for mercury.

LLNL stormwater analysts review the analytic results from the storm water monitoring as compared with the threshold values. **Table 2** presents a typical comparison table for two water years. All data exceeding thresholds are included, whether influent or effluent. Color shading highlights the watershed paths. Locations ALPO, ALPE, GRNE are influent locations that correspond to the WPDC effluent location on the Arroyo Las Positas watershed. ASS2 is the influent location that corresponds to the ASW effluent location on the Arroyo Seco watershed. Boldfaced values are those that exceed the threshold at an effluent point.

Table 2. Summary of constituents in stormwater found to be greater than the LLNL specific threshold comparison criteria for two typical water years.

Parameter	Date	Location	Influent or Effluent	Result	Threshold criteria[a]
Water Year 2000–2001					
Copper	02/12/01	ASS2	Influent	0.018	0.013
Copper	04/06/01	ALPE	Influent	0.017	0.013
Copper	04/06/01	ALPO	Influent	0.023	0.013
Copper	04/06/01	WPDC	Effluent	0.015	0.013
Diuron	02/12/01	GRNE	Influent	0.079	0.014
Diuron	02/12/01	ALPO	Influent	0.080	0.014
Diuron	03/02/01	ALPO	Influent	0.093	0.014
Diuron	03/02/01	GRNE	Influent	0.036	0.014
Diuron	03/02/01	WPDC	Effluent	0.013	0.014
Diuron	04/06/01	ALPO	Influent	0.018	0.014
Lead	02/12/01	ASS2	Influent	0.015	0.015
Oil and grease	**01/08/01**	**WPDC**	**Effluent**	**14**	**9**
Zinc	01/10/01	ASS2	Influent	0.25	0.117
Zinc	01/08/01	ASW	Effluent	0.20	0.117
Zinc	02/12/01	ASS2	Influent	0.39	0.117
Zinc	**03/02/01**	**WPDC**	**Effluent**	**0.12**	**0.117**

Parameter	Date	Location	Influent or Effluent	Result	Threshold criteria[a]
Zinc	04/06/01	ASS2	Influent	0.18	0.117
Zinc	04/06/01	ASW	Effluent	0.27	0.117
Water Year 2003–2004					
Beryllium	02/02/04	ALPO	Influent	0.0018	0.0016
COD	02/02/04	ALPO	Influent	230	200
Copper	12/29/03	ALPO	Influent	0.0153	0.013
Copper	12/29/03	WPDC	Effluent	0.0156	0.013
Copper	**02/02/04**	**ASW**	**Effluent**	**0.0167**	**0.013**
Copper	02/02/04	ALPE	Influent	0.023	0.013
Copper	02/02/04	ALPO	Influent	0.0691	0.013
Copper	02/02/04	WPDC	Effluent	0.0296	0.013
Copper	02/25/04	ALPE	Influent	0.022	0.013
Copper	02/25/04	ALPO	Influent	0.021	0.013
Copper	02/25/04	WPDC	Effluent	0.013	0.013
Diuron	12/11/03	ALPO	Influent	0.58	0.014
Diuron	12/11/03	GRNE	Influent	0.18	0.014
Diuron	12/29/03	ALPO	Influent	1.20	0.014
Diuron	12/29/03	ALPE	Influent	0.073	0.014
Lead	02/02/04	ALPO	Influent	0.025	0.015
Lead	02/02/04	WPDC	Effluent	0.016	0.015
Mercury	12/29/03	ALPO	Influent	0.00041	0.0002
Nitrate (as NO_3)	12/11/03	GRNE	Influent	15	10
Nitrate (as NO_3)	12/29/03	GRNE	Influent	15	10
Oil & Grease	12/29/03	ALPO	Influent	9.2	9
Oil & Grease	12/29/03	WPDC	Effluent	10	9
TSS	02/02/04	ALPO	Influent	1900	750
Zinc	**12/11/03**	**WPDC**	**Effluent**	**0.62**	**0.35**
Zinc	**02/02/04**	**WPDC**	**Effluent**	**0.625**	**0.35**
Gross alpha (Bq/L)	12/29/03	ALPO	Influent	0.353 ± 0.15	0.34
Gross alpha (Bq/L)	02/02/04	ALPO	Influent	0.703 ± 0.26	0.34
Gross beta (Bq/L)	02/02/04	ALPO	Influent	1.17 ± 0.26	0.48

[a] Threshold criteria presented are those that were in effect during each water year evaluated. Criteria may have changed in subsequent water years.

Analysts use this type of table to quickly scan for potential water quality issues that require follow-up. High concentrations at the influent locations are documented even when there is not a corresponding high value at the effluent location during the same storm event.

In the two water years presented, three constituents were high at the effluent location without a corresponding influent explanation: copper, zinc, and oil and grease. Therefore, analysts began to evaluate and track these constituents. Source investigations at LLNL did not reveal any particular industrial process sources for these constituents. In subsequent water years, there has not been a recurrence of the oil and grease effluent threshold exceedance. Copper and zinc recur sporadically. These two constituents also frequently exceed the threshold at influent locations. As found in many municipal programs, zinc and copper are common in the urban watershed; zinc as a building material (corrugated metal pipes used for storm drains, overhead covers, security fencing) and copper from vehicle brake-pad wear.

The diuron concentrations detected in stormwater in March 2001 triggered the development of the threshold criterion for this constituent and were of enough concern to trigger a source investigation, even though the influent concentrations were higher than the effluent concentrations. The source investigation revealed that LLNL does in fact use diuron in its grounds maintenance program. However, LLNL gardeners follow established protocols; document when and where the herbicides are used, do not apply it when rain is predicted, and observe setbacks from the storm drains. None of the documented LLNL application dates coincided with the sampling events. The high concentrations at the influent points clearly indicated an upstream source. Modeling of the diuron transport and mobility indicated that the herbicide was most likely applied in accordance with its label at an upstream utility station (Campbell et al., 2004).

It became apparent from the consistent copper threshold exceedances, especially at the influent locations, that the threshold for this constituent was likely set too low. The copper data evaluation presented as an example in this paper is the re-evaluation of the historic data, which indicates that the LLNL threshold should be raised.

Since establishing the site-specific threshold criteria evaluation in Water Year 2000–2001, there have been seven separate sample results for five constituents where the site-specific threshold values were exceeded at the effluent location that were not accompanied by an exceedance at the influent location. In addition to those discussed above, the other constituents included: nitrate and diuron (one occurrence each in water year 2005–2006). The possible cause for these threshold exceedances was a stream restoration project along Arroyo Seco.

LLNL has found that the site-specific threshold criteria approach provides its stormwater analysts with a useful screening tool to identify anomalous results. The approach gives the stormwater manager information on when to deploy additional resources to investigate unusual results. The key to the usefulness of this regulatory and management tool is site-specific information that can evolve as more data is gathered and activities change.

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