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Determination of Study Reporting Limits for Pesticide Constituent Data for the California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project, 2004–2018—Part 1: National Water Quality Laboratory Schedules 2003, 2032, or 2033, and 2060

Scientific Investigations Report 2019–5107

U.S. Department of the Interior
U.S. Geological Survey

Cover: Closeup of a sample bottle; photograph taken by Zeno Levy, December 2019.

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Conversion Factors

Multiply	By	To obtain
	Length	
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
meter (m)	1.094	yard (yd)
	Volume	
liter (L)	33.81402	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)

Supplemental Information

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter (µg/L).

Abbreviations

BQS	Branch of Quality Systems
DQI	data-quality indicator
DLBLK	method detection limit determined from blanks
DLBLK-FB	method detection limit determined from field blanks
DLBLK-LSB	method detection limit determined from laboratory set blanks
EPA	U.S. Environmental Protection Agency
GAMA-PBP	Groundwater Ambient Monitoring and Assessment Program Priority Basin Project
GCMS	gas chromatography mass spectrometry
IRL	interim reporting level
LCMS	liquid chromatography electrospray ionization-mass spectrometry
LRL	laboratory reporting level
LSB	laboratory set blank
LT-MDL	long-term method detection limit
MCL	maximum contaminant level
MDL	method detection limit
MDL_{max}	maximum method detection limit
ML	minimum level
NAWQA	National Water-Quality Assessment
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
NWQP	National Water Quality Program
OBSP	Organic Blind Sample Project
SWRCB	State Water Resources Control Board
USGS	U.S. Geological Survey
VOC	volatile organic compound

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By Miranda S. Fram and Sylvia V. Stork

Abstract

The California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP) is a long-term cooperative project designed to assess the quality of groundwater resources used for public and domestic drinking water supplies in the State of California, to monitor and evaluate changes to that quality, to investigate the human and natural factors controlling water quality, and to improve the availability of comprehensive groundwater quality data and information. Between May 18, 2004, and May 3, 2018, the GAMA-PBP collected 3001 groundwater samples for analysis of pesticide constituents by the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) (note that 'pesticide constituents' includes parent compounds and degradates). Of these samples, 2994 were analyzed for pesticide constituents on schedules 2003, 2032, or 2033 (65 to 84 constituents), and 840 were analyzed for pesticide constituents on schedule 2060 (58 constituents). The original dataset reported by the NWQL to the USGS National Water Information System (NWIS) database contained a total of 2,688 detections of 78 pesticide constituents and 253,825 non-detections. In this original dataset, 33 percent of the 3,001 samples analyzed had reported detections of one or more pesticide constituents.

This report describes the GAMA-PBP data-quality objectives for pesticide data, the procedures used to establish study reporting limits, and use of those reporting limits to censor the data from the NWQL so that the final data published by the GAMA-PBP meet these data-quality objectives. The final GAMA-PBP dataset for samples collected from May 2004 to May 2018, after censoring, had a total of 1,632 detections of 37 pesticide constituents. In the final GAMA-PBP dataset, 25 percent of the 3,001 samples analyzed had detections of one or more pesticide constituents.

The presence of pesticides in groundwater is commonly evaluated by calculating detection frequencies. Detection frequencies for pesticides are sensitive to detection limits and method performance for concentrations near those limits; therefore, the two primary data quality issues addressed in the GAMA-PBP data-quality objectives for pesticides are (1) establishing criteria for classifying data from the laboratory as detections or non-detections for the purpose of data reporting by the project and (2) accounting for changes in analytical methods or method performance over time. The GAMA-PBP addresses these issues by developing study reporting limits that are used as the boundary between detections and non-detections for the reporting of GAMA-PBP results. These reporting limits are defined from method detection limits (MDLs) provided by the NWQL, unless examination of results from laboratory set blanks (LSBs) and GAMA-PBP field blanks indicates that a higher concentration censoring limit is warranted. The GAMA-PBP selected the MDL as the primary choice for defining study reporting limits for consistency with U.S. Environmental Protection Agency (EPA) guidelines for reporting detections of pesticides and other organic constituents.

A five-step procedure is used to develop study reporting limits and censor the GAMA-PBP dataset accordingly. The effect of the censoring at each step is described to provide information about the relative effect of each step on the overall censoring of the dataset. Steps 1 and 2 can be implemented at the time the data are received, whereas steps 3−5 require information accumulated over an extended period.

- Step 1: Reject results that were most likely the result of specific contamination instances attributable to unusual field or laboratory conditions during sample collection or processing. Two such instances were identified, leading to rejection of 25 detections, which were assigned a data-quality indicator code of "Q" for "reviewed and rejected" in the NWIS database.

- Step 2: Use the NWQL MDLs in effect at the time each sample was analyzed as the reporting limit. A total of 506 detections were censored on this basis.
- Step 3: Use the maximum MDL established by the NWQL during July 2004–August 2018 (MDL_{max}) as the reporting limit. The rationale for using the MDL_{max} as the reporting limit is based primarily on the observation that the concentrations of MDLs generally increased over time. A total of 438 detections were censored on this basis.
- Step 4: Use the LSBs to identify periods of greater potential laboratory contamination bias and define raised reporting limits to be used during those periods. These periods were defined by using a moving average detection frequency approach. For consistency with the NWQL procedures for defining raised reporting limits on the basis of detections in LSBs, the raised reporting limits were defined as equal to three times the highest concentration measured in an LSB during the period. A total of 25 detections in groundwater samples analyzed during periods of increased laboratory contamination bias were censored.
- Step 5: Use the LSBs and field blanks to identify potential contamination bias from field or laboratory processes outside of the time periods identified in step 4. The NWQL protocols were used to define the MDLs from blanks analyzed outside of the periods identified in step 4. If an MDL defined from blanks was greater than the MDL_{max}, the MDL defined from blanks was used to censor the data. One constituent had a study reporting limit defined on this basis, and a total of 62 detections in groundwater samples were censored.

As of 2019, the USGS NWIS database does not have the capability to store both the original value reported by the NWQL and the final value published by the GAMA-PBP that reflects application of the quality-control censoring described in this report. In the interim, while this capability is developed, the 1,031 results censored in steps 2−5 are blocked from public release in NWIS, and the GAMA-PBP has published the original and final values in a USGS data release accompanying this report. The entire GAMA-PBP final dataset for pesticide constituents on schedules 2003, 2032, or 2033, or on schedule 2060 is publicly available in that USGS data release, through the USGS GAMA-PBP public web portal, and through the California State Water Resources Control Board GAMA public groundwater information system.

Introduction

The California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP) is part of the California State Water Resources Control Board (SWRCB) GAMA Program and is being implemented as a cooperative project between the SWRCB and the U.S. Geological Survey (USGS). The purposes of the GAMA-PBP are to (1) assess water quality in groundwater resources used for public and domestic drinking water supplies statewide at the basin scale, (2) monitor and evaluate changes in the quality of these resources, (3) evaluate the natural processes and human activities that may control the presence and concentrations of constituents of concern, (4) improve the availability of information about groundwater quality to the State of California.

The GAMA-PBP includes analysis of organic constituents (volatile organic compounds, pesticides and pesticide degradates, and pharmaceuticals) using laboratory methods that have lower detection limits than are required for regulatory sampling. These laboratory methods were developed by the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, which analyzes samples for the GAMA-PBP, the USGS National Water-Quality Assessment (NAWQA) Project, and other USGS projects. The detection limits used by the NWQL are commonly much less than the concentrations of drinking-water-quality benchmarks such as U.S. Environmental Protection Agency (EPA) and SWRCB Division of Drinking Water maximum contaminant levels (MCLs), indicating that the analytical methods can detect concentrations relevant to human health. At these very low concentrations, organic constituents can be useful as sensitive tracers of the influence of human activities on groundwater. In addition, because much is unknown about the effects of pesticides on human health, the presence of even low concentrations may be of concern to State and local agencies. For example, under the Pesticide Contamination Prevention Act, the California Department of Pesticide Regulation is required to investigate detections of pesticides at any concentration in groundwater (California Department of Pesticide Regulation, 2017).

The reporting of pesticide data is an interpretive process, requiring development of criteria for deciding if the signal at the detector on the analytical instrument is indeed due to the constituent of interest and of criteria for classifying confirmed identifications on the instrument as reported detections or non-detections. The criteria for deciding if the signal at the detector is indeed due to the constituent of interest are developed by the laboratory and generally are codified as part of the analytical method (Zaugg and others, 1995; Lindley and others, 1996; Furlong and others, 2001; Sandstrom and others, 2001, 2015; Madsen and others, 2003). The criteria for classifying a confirmed detection as a reported detection or non-detection are developed from a combination of the laboratory's and the project's data-quality objectives.

Data produced by the NWQL and stored in the USGS National Water Information System (NWIS) database are intended to be used by many projects ranging from research projects to projects driven by regulatory needs. Data-quality objectives can differ among these different types of projects. To serve all types of projects, it is USGS policy to store original data produced by the laboratory in NWIS without applying any censoring based on project-specific data-quality objectives (U.S. Geological Survey, 2017a).

Data-quality objectives for different projects often differ in the level of acceptable risk for Type I and Type II errors. A Type I error is reporting a constituent as present in a sample when it is not truly present, also called a "false positive" detection. A Type II error is reporting a constituent as not present in a sample when it is truly present, also called a "false negative" non-detection. The GAMA-PBP uses more stringent criteria for limiting the risk of false positive detections than do some other USGS projects. False positive detections can increase the difficulty of using pesticide constituents as environmental tracers, potentially leading to erroneous conclusions, and may trigger unnecessary (and costly) regulatory investigations. For example, because pesticides are human-manufactured constituents, their presence in a groundwater sample indicates at least some of the groundwater tapped by the well must be modern recharge. Thus, a false positive detection of a pesticide in a sample from a well could lead to erroneous conclusions about groundwater flow paths in the aquifer system, the vulnerability of the well to contamination from processes at the land surface, and the concentration of pesticides in modern recharge. As the risk of false positive detections decreases, however, the risk of false negative non-detections increases. False negative non-detections can increase the chance that the presence of pesticide constituents in the environment could be missed.

The USGS policy has led to considerable confusion for some public users of the GAMA-PBP data. The practice of serving the laboratory results on NWIS Web, without censoring in response to project data-quality objectives, means that the version of the data available from NWIS Web may differ from the version available from other public Web portals. In particular, data retrieved from NWIS Web (https://waterdata.usgs.gov/nwis) have more detections of pesticide constituents than data for the same samples retrieved from the SWRCB's GAMA Groundwater Information System (http://geotracker.waterboards.ca.gov/gama/gamamap/public) and the GAMA-PBP data viewer (https://ca.water.usgs.gov/projects/gama/water-quality-results/). Such discrepancies have led to numerous questions from public users of the data.

To assure that the data available to the public from NWIS and other portals are the final data published by the GAMA-PBP after application of censoring to meet project data-quality objectives, while still preserving the original data from the NWQL in NWIS, changes to NWIS are needed to enable the capability to store both values. Pending modernization of the NWIS database to add this capability, the GAMA-PBP has blocked from public NWIS-Web retrieval results reported as detections in the original data from NWQL but as non-detections in the final data published by the GAMA-PBP. The original and final data are reported together in a USGS data release (Lor and others, 2019), and the final data are also released on the SWRCB GAMA Groundwater Information System and the GAMA-PBP public data viewer.

During the last decade, the GAMA-PBP has published a series of reports and papers describing the project's data-quality objectives for groups of water-quality constituents and the evaluation and censoring procedures to meet these objectives (Olsen and others, 2010; Fram and Belitz, 2011; Fram and others, 2012; Davis and others, 2014). This report is the first of two publications about data-quality objectives and censoring procedures for the GAMA-PBP pesticide data; a subsequent publication is planned to present data-quality objectives and censoring procedures for GAMA-PBP data for pesticide constituents on NWQL Schedule 2437. The GAMA-PBP has used these procedures to ensure that data published under the auspices of the GAMA-PBP fully meet the project's data-quality objectives.

The purpose of this report is to describe the GAMA-PBP data-quality objectives and data evaluation, censoring, and reporting procedures for pesticide constituents on NWQL schedules 2003, 2032, or 2033, or on schedule 2060. The NWQL uses laboratory "schedules" to define a subset of the constituents determined by an analytical method. Schedules 2003, 2032, and 2033 use the same analytical method, but schedule 2003 includes quantification of 65 of the available analytes, schedule 2032 includes quantification of 69 of the available analytes, and schedule 2033 includes quantification of 84 of the available analytes. The 84 pesticide constituents on schedules 2003, 2032, or 2033 are analyzed by a solid-phase extraction, gas chromatography mass spectrometry (GCMS) method (Zaugg and others, 1995; Lindley and others, 1996; Sandstrom and others, 2001; Madsen and others, 2003). Schedule 2060 includes 58 polar pesticide and pesticide degradate constituents that are analyzed by a solid-phase extraction, high-performance liquid chromatography electrospray ionization-mass spectrometry method (LCMS; Furlong and others, 2001). Caffeine also is analyzed as part of schedule 2060, but because caffeine is not a pesticide constituent, it is not included in this report. A total of 2,994 groundwater samples collected by the GAMA-PBP between May 2004 and May 2018 were analyzed for pesticide constituents on schedules 2003, 2032, or 2033, and 840 groundwater samples collected by the GAMA-PBP between May 2004 and February 2011 were analyzed for pesticide constituents on schedule 2060.

National Water Quality Laboratory Data Reporting Conventions

The NWQL reporting conventions for organic constituents are discussed in detail in other publications (Childress and others, 1999; Medalie and others, 2019; U.S. Geological Survey, 2015); only a summary is presented here. Organic constituents generally have a long-term method detection limit (LT-MDL) and a laboratory reporting level (LRL). An interim reporting level (IRL) and interim MDL may be used before sufficient data have been compiled to determine an LT-MDL and LRL. For convenience, this report generally refers to interim MDLs and LT-MDLs as MDLs.

The MDL is the minimum concentration of a constituent that can be reported as a detection with 99 percent confidence that the concentration in the sample is greater than that in a blank (U.S. Environmental Protection Agency, 2016a). The LT-MDLs are determined using about 24 low-level spikes analyzed during a 6–12-month period, whereas interim MDLs can be determined using 7 low-level spikes analyzed during a much shorter time (Childress and others, 1999; U.S. Geological Survey, 2015; U.S. Environmental Protection Agency, 2016a). Interim MDLs and LT-MDLs are calculated from the following relation (Childress and others, 1999; fig. 1*A*):

$$C_{1-\alpha} = s \times t_{(n-1,1-\alpha)} \quad (1)$$

where

- n is number of replicate low-level spikes,
- s is standard deviation of the measured concentrations of the n low-level spikes,
- α is level of significance,
- t is critical value of Student's test statistic for n−1 degrees of freedom and α level of significance, and
- $C_{1-\alpha}$ is concentration threshold (equal to MDL when α is 0.01).

The NWQL collects data for reagent spikes and laboratory blanks continually and re-evaluates the MDL at least annually. If there has been a change, the NWQL generally implements the new MDL and LRL at the start of the following Federal fiscal year (October 1) (Childress and others, 1999; U.S. Geological Survey, 2015). The procedure for determining the MDL relies on the assumption that standard deviation of multiple measurements of the low-level spike is the same as the standard deviation of multiple hypothetical measurements of a blank. If this assumption is true, then equation 1 yields the concentration threshold above which a sample reported as containing that concentration of the constituent has less than a 1 percent probability of having been drawn from the blank-water population—a false positive. If the assumption of constant standard deviation is true, the concentration threshold above which a sample truly containing that concentration of the constituent has less than a 1 percent probability of being reported as having been drawn from the blank-water population—a false negative—is equal to twice the MDL (Childress and others, 1999; fig. 1*A*). The LRL is generally set at twice the MDL for this reason. Note that the LRL may be set at a higher concentration if there are other factors affecting the probability of false negative non-detections, such as variability in analytical instrument sensitivity. The NWQL reports non-detections as less than ("<") the LRL concentration (<LRL).

The relation described in equation 1 can also be used to illustrate the relation between the concentration threshold ($C_{1-\alpha}$) and the probabilities of false positive detections and false negative non-detections. In figure 1*A*, the frequencies of detected concentrations in populations of samples with true concentrations of zero and the LRL are represented by normal distributions centered on zero and the LRL, respectively. One percent of the area of the distribution centered on zero has a concentration greater than the MDL, corresponding to a 1 percent probability of a false positive detection in a sample with a true concentration of zero. One percent of the distribution centered on the LRL has a concentration less than the MDL, corresponding to a 1 percent probability of a false negative non-detection in a sample with a true concentration at the LRL (modified from Childress and others, 1999). Figure 1*B* shows the probabilities of false positive detections (reported concentration greater than the MDL when the true concentration is less than the MDL) and false negative non-detections (reported concentration less than the MDL when the true concentration is greater than the MDL) as a function of the true concentration of a population of samples. The frequencies of detection concentrations are assumed to be normal distributions with the same standard deviations centered on the true concentrations. The probabilities of false positive detections and false negative non-detections increase as the true concentration decreases: the probability that a reported detection at a concentration equal to one-quarter of the MDL is a false positive detection is 27 percent, and the probability that a sample with a true concentration equal to one-quarter of the MDL is reported as a non-detection is 96 percent. The probability that a reported detection at a concentration equal to the LRL is a false positive detection is 0.002 percent, and the probability that a sample with a true concentration equal to the LRL is reported as a non-detection is 1 percent.

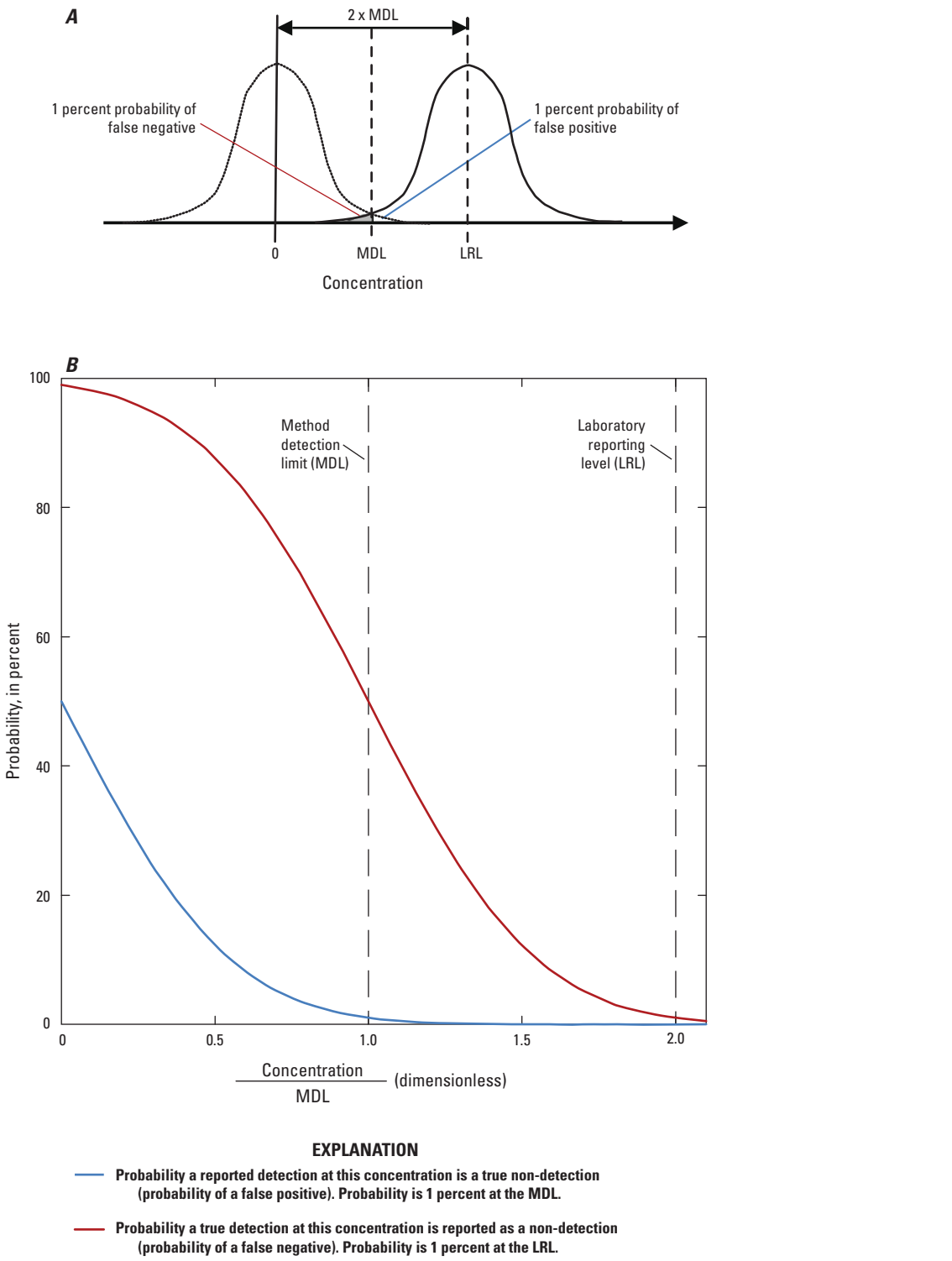

Figure 1. Probability of false positive detections and false negative non-detections as a function of concentration. *A*, The frequencies of detected concentrations in populations of samples with true concentrations of zero and the laboratory reporting level (LRL) are represented by normal distributions centered on zero and the LRL, respectively (modified from Childress and others 1999). *B*, The probabilities of false positive detections and false negative non-detections as a function of the true concentration of a population of samples.

The NWQL reporting conventions for organic constituents analyzed by "information-rich" methods permit reporting of detections at concentrations less than the MDL in effect at the time the sample was analyzed (Childress and others, 1999; U.S. Geological Survey, 2010, 2015). Gas chromatography and liquid chromatography methods that use mass spectrometric detection (GCMS and LCMS) methods are considered information rich because constituents are identified by chromatographic retention time, presence of qualifying ions, and acceptable quantification-to-qualifying ratios that need to be met to confirm identification of the analyte. These extra levels of information enhance qualitative identification and confirmation that the constituent is indeed detected. The EPA procedure (U.S. Environmental Protection Agency, 2016a) and other procedures for calculating the MDL by estimating the probability distribution of the blank signal do not have these enhanced identification capabilities. Reporting detections at concentrations less than the MDL reduces the probability of false negative non-detections (fig. 1).

Although the GCMS and LCMS laboratory methods provide enhanced qualitative identification capabilities, a confirmed identification does not distinguish between analytes present in the groundwater sample and analytes added by contamination during sample collection, processing, or analysis. Detections at concentrations less than the MDL have greater than a 1 percent probability of being false positive detections (fig. 1). The methods used to calculate the MDL are based on the assumption that analysis of a hypothetical population of true blanks produces a normal distribution of concentrations centered on a concentration of zero that has a standard deviation equal to the standard deviation of multiple analyses of a low-level spike (Childress and others, 1999; U.S. Environmental Protection Agency, 2016a). For such a distribution, the probability that a true blank yields a detection increases to 50 percent as the threshold for defining a result as a detection approaches a concentration of zero (fig. 1*B*). These detections in true blanks may be due to unintended low-level contamination of the blanks during laboratory analysis or to low-level noise inherent in the analytical instrumentation used for detection. In addition, the ability to detect constituents at concentrations less than the MDL may vary with instrument conditions, sample matrix, laboratory analyst, and other factors, which can result in variable effective detection limits for different samples.

Detections at concentrations less than the LRL or MDL were reported by the NWQL with either an "E" remark code (before October 1, 2010) or with "n" and "t" result-level value-qualifier codes, respectively (starting October 1, 2010; U.S. Geological Survey, 2010, 2015). The E remark code and the n and t result-level value-qualifier codes assigned by the NWQL do not affect the evaluations described in this report.

GAMA Priority Basin Project Data Quality Objectives for Pesticide Constituents

The GAMA-PBP established data-quality objectives by using the EPA Data Quality Objective Process (U.S. Environmental Protection Agency, 2006). The data censoring protocols developed and implemented in this report are part of the sixth step of that process, "Specify performance or acceptance criteria"; however, to provide an explanation for why those protocols were developed, the results of preceding steps also are described in this report. The USGS Laboratory Evaluation Policy describes requirements for projects to develop data-quality objectives and evaluate the performance of analytical laboratories relative to those data-quality objectives (U.S. Geological Survey, 2014). These evaluations are reviewed by USGS specialists (in 2019, reviews are by a USGS Water Science Center Water Quality Specialist in the Water Science Center with which the project's principal investigator is associated) and must be approved by the relevant USGS executive (in 2019, approval is by the Director of the Water Science Center with which the project's principal investigator is associated) before the project can publish data produced by the laboratory. The NWQL and laboratories contracted by the NWQL generally are considered exempt from this evaluation, review, and approval process because they already comply with USGS-approved quality-assurance practices (U.S. Geological Survey, 2014). Because the data-quality objectives of the GAMA-PBP differ from those of many other USGS projects, the GAMA-PBP applies the evaluation processes outlined in the USGS Laboratory Evaluation Policy to all laboratories producing data for the project, including the NWQL.

Agencies charged with managing groundwater resources used for drinking water supplies or regulating or planning for safe drinking water supplies need information about the presence of pesticide constituents in groundwater resources used for drinking water supplies. Examples of how this information may be used include (1) identifying which constituents are found in groundwater so that informed decisions can be made about which constituents may require monitoring; (2) evaluating effectiveness of, or potential need for, regulations intended to protect drinking water supplies from contamination; and (3) deciding where to allocate attention and resources, or estimating whether attention and resources may be needed in the future, to ensure availability of resources for providing clean drinking water or remediation of affected groundwater resources. Sampling done for regulatory compliance purposes provides information about whether the few pesticide constituents with regulatory benchmarks are present at concentrations above those benchmarks. Many more pesticides and pesticide degradates have non-regulatory benchmarks, such as EPA human-health benchmarks for pesticides (U.S. Environmental Protection Agency, 2017) and USGS health-based screening levels (Norman and others, 2018). The presence of pesticide constituents at low concentrations in the environment can be a sensitive tracer of the existence of contamination pathways and may provide an early warning of future water-quality problems (for example, Belitz and others, 2003; Gilliom and others, 2006).

The GAMA-PBP developed a study design to meet these information needs (Belitz and others, 2003; California State Water Resources Control Board, 2003). The GAMA-PBP uses a stratified random design to ensure that samples are spatially distributed and statistically representative of the groundwater resources used for drinking water supplies, either public or domestic depending on the study area (Belitz and others, 2010). Networks of wells are defined to represent study areas at various spatial scales. The GAMA-PBP collects samples from wells in these networks for analysis of as many pesticide constituents as feasible to determine which are present in groundwater, how the presence of pesticide constituents differs among areas of the State, how the presence of pesticide constituents or their concentrations change with time, and what human activities and natural processes may be controlling those patterns. The design of the GAMA-PBP is similar to that of the groundwater components of the USGS NAWQA project (Hirsch and others, 1988; Rosen and Lapham, 2008). The GAMA-PBP began collecting samples in 2004, assessing baseline groundwater-quality conditions in the entire area of the State used for drinking water supplies (for example, Belitz and others, 2015), and monitoring through time to assess changes in those conditions (for example, Kent and Landon, 2016). The GAMA-PBP submits samples to the NWQL for analysis of pesticide constituents because the NWQL methods include a large number of constituents and can detect those constituents at very low concentrations.

The GAMA-PBP data-quality objectives for pesticide constituents address two primary data-quality issues. First, the project establishes criteria for classifying laboratory results as detections or non-detections. These criteria are based on defining acceptable risk for false positive detections. Second, the project establishes criteria for accounting for changes in analytical methods or method performance through time.

The concentrations of pesticide constituents detected in California groundwater resources used for drinking water supplies tend to be low, rarely as high as even one-tenth of the concentration of drinking-water quality benchmarks (Belitz and others, 2015). Therefore, the GAMA-PBP has primarily evaluated the presence of pesticide constituents by detection frequencies, with differences in presence of pesticide constituents among study areas identified by comparison of detection frequencies (for example, Bennett, 2018; Burton and Wright, 2018). For many public users of the GAMA-PBP data in California, as long as the concentrations are lower than benchmark concentrations, the primary interest has been detection frequency—is the pesticide constituent detected or not—rather than concentrations. Thus, data-quality objectives associated with detection frequencies are the focus of this report. A subsequent publication is planned to address GAMA-PBP data-quality objectives for comparison of pesticide concentrations in samples analyzed at different times by the same or different analytical methods.

The GAMA-PBP follows EPA guidelines for reporting detections of organic constituents including pesticide constituents. The EPA defines an MDL as follows: “The MDL is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.” (U.S. Environmental Protection Agency, 2016a). Many EPA-approved methods for organic constituents state that the reporting of laboratory results can be linked to the MDL:

> Unless specified otherwise by a regulatory authority or in a discharge permit, results for analytes that meet the identification criteria are reported down to the concentration of the ML (minimum level) established by the laboratory through calibration of the instrument. …. The term “minimum level” refers to either the sample concentration equivalent to the lowest calibration point in a method or a multiple of the method detection limit (MDL), whichever is higher. (U.S. Environmental Protection Agency, 2016b, 2016c).

Thus, for consistency with EPA data reporting conventions, the GAMA-PBP classifies results at concentrations greater than or equal to the ML as detections and results at concentrations less than the ML as non-detections.

For NWQL methods, the lowest calibration standard is always lower than the LRL, but is not always lower than the MDL. Therefore, the ML is equal to the MDL for some pesticide constituents, but is equal to the lowest calibration standard (a higher concentration than the MDL) for other pesticide constituents. The concentration of the lowest calibration standard for the calibration curve associated with each result is not easily accessible to the public, however, whereas the LRL and MDL are readily available. For that reason, the GAMA-PBP defined the ML as the MDL. Note that for pesticide constituents for which the ML should be the lowest calibration standard, the effect of using the MDL as the ML is to expand the range of reported concentrations classified as detections.

The GAMA-PBP implements classification of results as detections or non-detections using study reporting limits. In practice, these reporting limits commonly are the same concentration as MDLs provided by the NWQL. The primary effect of censoring data with the GAMA-PBP study reporting limits is to classify confirmed identifications reported by the NWQL at concentrations less than the MDL as non-detections for the purpose of data reporting.

Other projects do not use the same data-quality objectives as the GAMA-PBP. For some projects, a benefit of reporting detections below the MDL is to help characterize the potential presence of environmental contaminants, including pesticide residues, in water resources that might be bioactive or have water-quality benchmarks at trace (part-per-trillion or lower) levels. Part of the USGS mission is to be at the leading edge of water-quality research in the Nation. For pesticides, this includes identifying "first sightings" of trace constituents in the environment and developing new analytical methods with ever lower MDLs for those constituents. In this scientific research context, a false negative error may represent an important loss of information, and there may be a greater tolerance for risk of false positive errors in exchange for reduction in risk of false negative errors. For these reasons, the results that were originally reported by the laboratory have been preserved in NWIS for use by other researchers. Note that reporting conventions, like the NWQL's, that allow for reporting of detections at concentrations less than the MDL are used by some other research laboratories (for example, Austin and others, 2016).

The GAMA-PBP also uses the study censoring limit approach to create greater consistency in data reporting over time. For a project like the GAMA-PBP that spans many years, the NWQL's practice of re-evaluating MDLs on an annual basis results in a dataset with multiple detection limits and laboratory reporting levels. The presence of pesticide constituents in groundwater across different areas or times can be evaluated by comparing detection frequencies calculated relative to a single common reporting limit for each constituent. The MDL for a constituent may change over time for many reasons, such as changes in method performance over time, changes in procedures used to calculate MDLs, or a change to using a new analytical method. In addition, there may be raised reporting levels applied to individual samples for various reasons. There are advanced statistical methods designed to accommodate datasets with multiple censoring limits (for example, Helsel, 2005), however, the GAMA-PBP rarely uses such statistical methods, and in general, attempts to maintain uniform detection limits.

For example, Fram and Belitz (2011) evaluated laboratory blanks analyzed during 2004−11 for 14 pharmaceutical compounds (NWQL schedule 9003/2080) and used the maximum of the 5 MDLs determined by the NWQL for each compound during 2004−11 as the study reporting limit. Results reported as detections by the NWQL with concentrations less than study reporting limits were reported by the GAMA-PBP as non-detections. Fram and others (2012) used several different methods to establish study reporting limits for volatile organic compounds (VOCs) on NWQL schedule 2020, based on evaluation of field blanks and MDLs. Study reporting limits were established for 10 of the 18 VOCs detected in at least 1 GAMA-PBP field blank collected during 2004−11 and were applied to all GAMA-PBP samples collected during this period.

Censoring a dataset originally reported with multiple reporting levels to a single reporting limit, however, results in loss of information in two ways. First, detections with concentrations between the selected censoring limit and any lower censoring limits that were in effect at the time the samples were analyzed are re-classified as non-detections, thereby potentially increasing the number of false negative non-detections in the dataset—samples reported to have a non-detection of a constituent when it is actually present. This may result in failure to identify the presence of a constituent in the environment. Second, results that are non-detections relative to a censoring limit that is higher than the selected censoring limit must be considered as "not analyzed" when calculating a detection frequency relative to the selected censoring limit, thereby reducing the effective size of the dataset. The GAMA-PBP study design is based on sampling a set of wells that is spatially representative of the groundwater resource tapped by the population of wells in a study area, and classifying some samples as not analyzed may potentially introduce spatial bias into what was originally a spatially representative dataset. The convenience of having a dataset with a uniform censoring limit must be balanced with the potential consequences of these losses of information. It is important that the original value reported by the NWQL be retained in NWIS so that evaluations of false negatives can be made if data-quality objectives change or if the data are to be used for other studies with different data-quality objectives.

Review and Censoring of the GAMA Priority Basin Project Dataset

A total of 2,994 groundwater samples collected by the GAMA-PBP between May 2004 and May 2018 were analyzed for pesticide constituents on schedules 2003, 2032, or 2033 (fig. 2*A*; table 1). Schedule 2003 included 65 pesticide constituents and was less expensive than schedule 2032 (69 constituents) or schedule 2033 (83 constituents). The 64 pesticide constituents common to the three schedules each were analyzed in 2,994 groundwater samples. During 2004–13, the most commonly used schedule was 2003.

Schedule 2032 is schedule 2003 without fonofos oxon (discontinued in 2005 before schedule 2032 began), but with *cis*-propiconazole, *trans*-propiconazole, λ-cyhalothrin, molinate, carbofuran, propanil, and thiobencarb added. Most of the added pesticide constituents were commonly used on rice fields in California (Orlando and Kuivila, 2004). Samples collected in the three GAMA-PBP Sacramento Valley public-supply aquifer assessment study units (Bennett and others, 2011) were analyzed for pesticide constituents on schedule 2032 because rice is a dominant crop in the Sacramento Valley. Pesticide constituents on schedule 2032 but not on schedule 2003 were analyzed in 1,241 samples (table 1).

Schedule 2033 is schedule 2032 plus cyanazine, α-endosulfan, endosulfan sulfate, oxyfluorfen, tefluthrin, 3,5-dichloroaniline, disulfoton, disulfoton sulfone, tebuconazole, EPTC, ethoprop, and propargite. Samples collected in the GAMA-PBP public-supply aquifer assessment study units in the Kern Basin, southeastern San Joaquin Valley, western San Joaquin Valley, Madera-Chowchilla basins of the San Joaquin Valley, the upper Santa Ana watersheds basins, the Northern Coast Ranges basins, the central Sierra Nevada, and the Bear Valley and Lake Arrowhead area were analyzed for pesticide constituents on schedule 2033. Many of these study units have extensive areas of current or legacy agricultural land use; however, other study units with extensive areas of current or legacy agricultural land use were analyzed for pesticide constituents on schedule 2003 instead of schedules 2032 or 2033. The GAMA-PBP began establishing a groundwater-quality trends monitoring network in 2007; all samples collected in 2007–18 from wells on the growing trends network were analyzed using schedule 2033. Pesticide constituents on schedule 2033, but not on schedule 2032, were analyzed in 1,000 samples (table 1).

The number of samples analyzed for pesticide constituents on schedules 2003, 2032, or 2033 in 2014–18 was less than in the previous years (fig. 2*A*) because the GAMA-PBP only used schedule 2033 for samples for trends network wells; samples from new study units during those years were analyzed for pesticide constituents on the NWQL's new schedule 2437 (Sandstrom and others, 2015).

A total of 840 groundwater samples collected by the GAMA-PBP between May 2004 and February 2011 were analyzed for pesticide constituents on schedule 2060 (fig. 2*B*; table 1). All but 7 of the samples analyzed for pesticide constituents on schedule 2060 also were analyzed for pesticide constituents on schedule 2003, 2032, or 2033. Nearly all samples collected in 8 GAMA-PBP study units, 15 to 60 percent of the samples collected in 12 study units, and none of the samples collected in the remaining 15 study units were analyzed for pesticide constituents on schedule 2060. Most study units in which the average land use within 500 meters (m) of wells sampled by the GAMA-PBP was greater than one-third agricultural had at least some samples analyzed for pesticide constituents on schedule 2060, and most study units in which the average land use within 500 m of wells sampled by the GAMA-PBP was less than one-third agricultural had no samples analyzed for pesticide constituents on schedule 2060. The number of samples for each constituent varied from 840 to 803 for all but 3 constituents. Atrazine (39632), tebuthiuron (82670), and deethylatrazine (04040) are common to schedule 2060 and schedules 2003, 2032, or 2033. Schedule 2003, 2032, or 2033 is the preferred method for those constituents, so if a sample is analyzed for pesticide constituents on both schedules 2003, 2032, or 2033 and schedule 2060, only the result from schedules 2003, 2032, or 2033 is recorded in NWIS.

Not all samples sent to the NWQL could be analyzed for all constituents because of various sample preparation and analysis problems; therefore, the number of samples with results for some constituents was less than the 2,994, 1,241, or 1,000 samples analyzed for pesticide constituents on schedules 2003, 2032, or 2033, respectively (table 1). For example, of the 64 constituents common to all 3 schedules, 45 had analytical results reported for 2,994 samples, whereas the other 19 had analytical results reported for 2,489 to 2,993 samples.

The original data for the groundwater samples reported by the NWQL to the NWIS database contained a total of 2,688 detections of 78 pesticide constituents and 253,825 non-detections. In this original dataset, 33 percent of the 3,001 samples analyzed had reported detections of one or more pesticide constituents.

The GAMA-PBP reviewed and censored data for pesticide constituents on schedules 2003, 2032, or 2033, or on schedule 2060 in five steps (fig. 3). This section is divided into five parts, corresponding to the five steps. Each part includes an explanation of the purpose of the step, the methods developed and used for the step, and the results of the censoring implemented by the step.

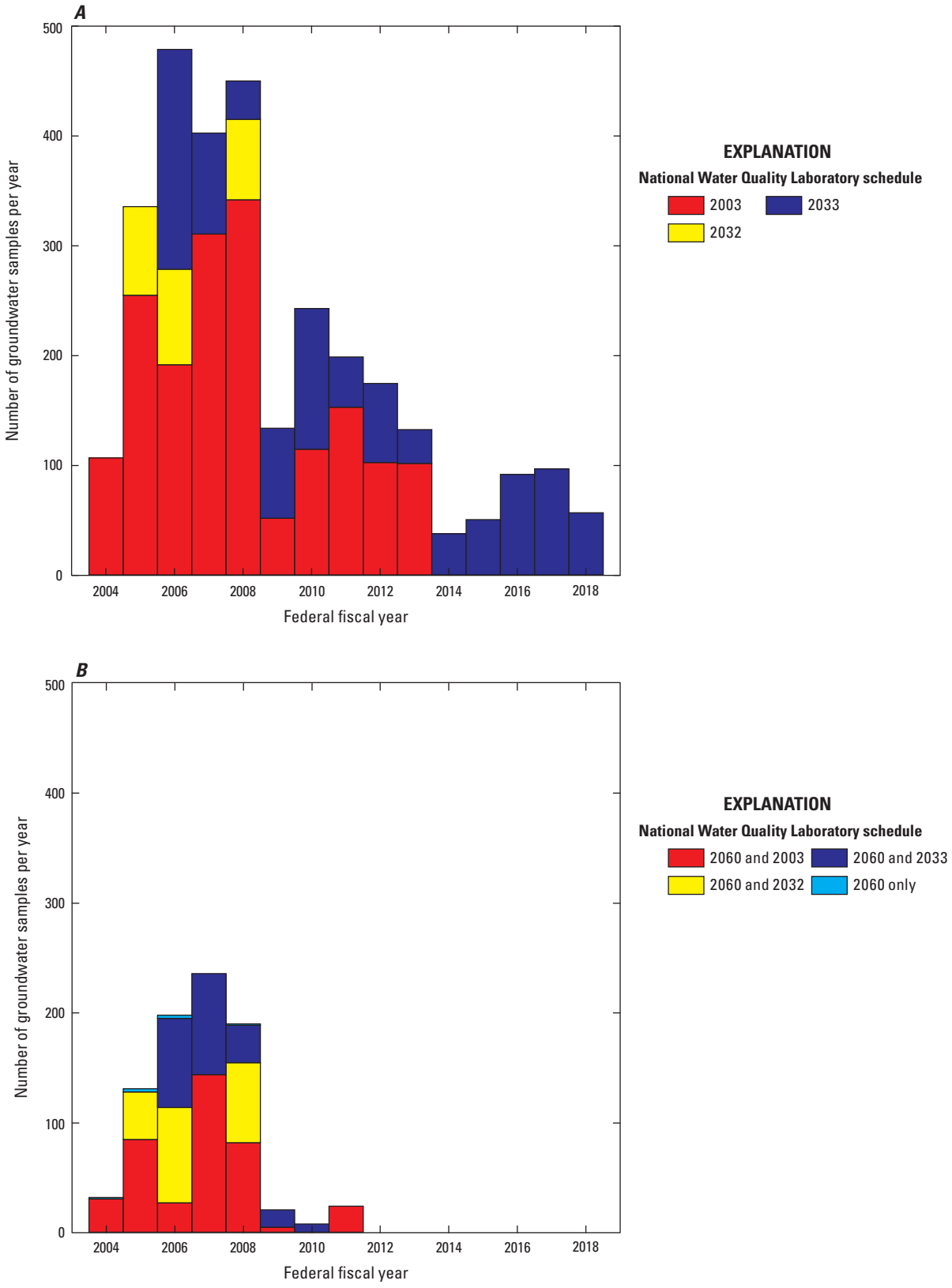

Figure 2. Numbers of California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP) samples analyzed each Federal fiscal year for pesticide constituents on *A*, U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) schedules 2003, 2032, or 2033, and *B*, NWQL schedule 2060; samples are further divided by whether they were also analyzed for pesticide constituents on NWQL schedules 2003, 2032, or 2033.

Table 1. Numbers of groundwater samples analyzed for pesticide constituents on U.S. Geological Survey (USGS) National Water Quality (NWQL) schedules 2003, 2032, or 2033 or on schedule 2060 during May 2004 through May 2018 for the California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP), numbers of detections in the original and final datasets, numbers of detections rejected or censored at each of the five sequential review and censoring steps, and the GAMA-PBP study reporting limit established by these five steps.

[The constituent identification code is the concatenation of the 5-digit numeric USGS parameter code that identifies a constituent or property and the 5-digit alphanumeric USGS method code that indicates the analytical method used to measure it. NWQL schedule 2003, 2032 and 2033 use method codes GCM35, GCM39, GCM14, GCM29, and GCM40; NWQL schedule 2060 uses method code LCM29. Censoring steps (see text for discussion): Step 1, reject results inferred to be the result of contamination during sample collection or processing; Step 2, censor results for concentrations less than the MDL in effect at the time the sample was analyzed; Step 3, censor results for concentrations less than the highest MDL established by the NWQL during July 2004–August 2018; Step 4, censor results analyzed during a period of more frequent laboratory contamination and concentrations less than three times the highest LSB during that period; Step 5, censor results with concentrations less than the MDL determined from field blanks or LSBs analyzed outside of a period of more frequent laboratory contamination. **Constituent**: CIAT, 2-Chloro-4-isopropylamino-6-amino-*s*-triazine; CEAT, 2-Chloro-6-ethylamino-4-amino-*s*-triazine; OIET, 2-Hydroxy-4-isopropylamino-6-ethylamino-*s*-triazine. **Other abbreviations**: GAMA-PBP, Groundwater Ambient Monitoring and Assessment Program Priority Basin Project; LSB, laboratory set blank; MDL, method detection limit; NWQL, National Water Quality Laboratory; USGS, U.S. Geological Survey; —, none; µg/L, microgram per liter]

Constituent identification code	Constituent name	Number of samples with analytical results	Number of detections in original dataset	Number of detections rejected or censored at each step of the review process					Number of detections in final dataset	Study reporting limit (µg/L)[1]	Maximum raised censoring limit applied during step 4 (µg/L)[2]
				Step 1	Step 2	Step 3	Step 4	Step 5			
	Total detections		2,688	25	506	438	25	62	1,632		
	Number of constituents having detections		78	18	55	44	6	1	37		
	Constituents on NWQL schedule 2003, 2032, or 2033										
49260GCM33	Acetochlor	2,994	4	—	1	—	—	—	3	0.005	—
46342GCM35	Alachlor	2,994	2	—	—	1	—	—	1	0.004	—
39632GCM35	Atrazine	2,994	461	—	28	—	6	62	365	0.005	0.009
82686GCM35	Azinphos-methyl	2,994	—	—	—	—	—	—	—	0.06	—
61635GCM39	Azinphos-methyl oxon	2,974	—	—	—	—	—	—	—	0.021	—
82673GCM35	Benfluralin	2,994	7	1	5	1	—	—	—	0.007	0.0558
82680GCM35	Carbaryl	2,994	3	—	3	—	—	—	—	0.1	—
82674GCM35	Carbofuran	1,241	—	—	—	—	—	—	—	0.03	—
61618GCM39	2-Chloro-2’,6’-diethylacetanilide	2,994	—	—	—	—	—	—	—	0.005	—
61633GCM39	4-Chloro-2-methylphenol	2,994	—	—	—	—	—	—	—	0.004	—
38933GCM35	Chlorpyrifos	2,994	4	1	—	1	—	—	2	0.005	—
61636GCM39	Chlorpyrifos oxon	2,978	1	—	1	—	—	—	—	0.04	—
04041GCM35	Cyanazine	1,000	—	—	—	—	—	—	—	0.02	—
61585GCM39	Cyfluthrin	2,994	—	—	—	—	—	—	—	0.026	—
61595GCM39	λ-Cyhalothrin	1,241	1	—	—	1	—	—	—	0.0071	—
61586GCM39	Cypermethrin	2,994	1	1	—	—	—	—	—	0.023	—
82682GCM35	DCPA (Dacthal)	2,994	12	1	5	2	4	—	—	0.0038	0.0126
04040GCM35	Deethylatrazine (CIAT)	2,994	605	—	138	153	—	—	314	0.007	—
62170GCM29	Desulfinylfipronil	2,994	19	1	15	—	—	—	3	0.006	0.018
62169GCM29	Desulfinylfipronil amide	2,994	2	—	2	—	—	—	—	0.015	—

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Constituent identification code	Constituent name	Number of samples with analytical results	Number of detections in original dataset	Number of detections rejected or censored at each step of the review process					Number of detections in final dataset	Study reporting limit (µg/L)[1]	Maximum raised censoring limit applied during step 4 (µg/L)[2]
				Step 1	Step 2	Step 3	Step 4	Step 5			
Constituents on NWQL schedule 2003, 2032, or 2033—Continued											
39572GCM35	Diazinon	2,994	3	1	—	—	—	—	2	0.003	—
61638GCM14	Diazinon oxon	2,993	—	—	—	—	—	—	—	0.006	—
61625GCM39	3,4-Dichloroaniline	2,986	139	—	9	11	—	—	119	0.003	—
61627GCM39	3,5-Dichloroaniline	1,000	6	—	1	5	—	—	—	0.006	0.015
38775GCM39	Dichlorvos	2,993	1	—	—	1	—	—	—	0.02	—
38454GCM39	Dicrotophos	2,984	1	—	—	1	—	—	—	0.04	—
39381GCM35	Dieldrin	2,994	14	1	5	3	2	—	3	0.006	0.0207
82660GCM35	2,6-Diethylaniline	2,994	5	—	1	—	—	—	4	0.003	0.006
82662GCM40	Dimethoate	2,994	1	—	—	1	—	—	—	0.005	—
82677GCM35	Disulfoton	964	—	—	—	—	—	—	—	0.02	—
61640GCM39	Disulfoton sulfone	1,000	—	—	—	—	—	—	—	0.007	—
34362GCM39	α-Endosulfan	1,000	—	—	—	—	—	—	—	0.0055	0.0195
61590GCM39	Endosulfan sulfate	1,000	—	—	—	—	—	—	—	0.011	—
82668GCM35	EPTC	1,000	19	—	—	5	—	—	14	0.0028	—
82346GCM40	Ethion	2,994	1	1	—	—	—	—	—	0.0082	—
61644GCM39	Ethion monoxon	2,916	—	—	—	—	—	—	—	0.011	—
82672GCM35	Ethoprop	1,000	—	—	—	—	—	—	—	0.008	—
61620GCM39	2-Ethyl-6-methylaniline	2,994	1	—	1	—	—	—	—	0.005	—
61591GCM39	Fenamiphos	2,959	—	—	—	—	—	—	—	0.015	—
61645GCM39	Fenamiphos sulfone	2,993	—	—	—	—	—	—	—	0.027	—
61646GCM39	Fenamiphos sulfoxide	2,934	—	—	—	—	—	—	—	0.1	—
62166GCM29	Fipronil	2,994	12	1	8	2	—	—	1	0.02	—

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				Step 1	Step 2	Step 3	Step 4	Step 5			
Constituents on NWQL schedule 2003, 2032, or 2033—Continued											
62167GCM29	Fipronil sulfide	2,994	18	1	8	6	—	—	3	0.008	0.0111
62168GCM29	Fipronil sulfone	2,994	9	1	8	—	—	—	—	0.012	—
04095GCM35	Fonofos	2,994	—	—	—	—	—	—	—	0.005	—
61649GCM39	Fonofos oxon	180	—	—	—	—	—	—	—	0.0008	—
04025GCM39	Hexazinone	2,994	66	—	11	26	—	—	29	0.013	—
61593GCM39	Iprodione	2,992	—	—	—	—	—	—	—	0.269	—
61594GCM39	Isofenphos	2,994	2	1	—	1	—	—	—	0.007	—
61652GCM39	Malaoxon	2,994	—	—	—	—	—	—	—	0.04	0.072
39532GCM35	Malathion	2,994	—	—	—	—	—	—	—	0.014	—
61596GCM39	Metalaxyl	2,994	22	—	—	10	—	—	12	0.007	0.0153
61598GCM39	Methidathion	2,994	—	—	—	—	—	—	—	0.006	—
61664GCM39	Methyl paraoxon	2,994	—	—	—	—	—	—	—	0.01	—
82667GCM35	Methyl parathion	2,994	—	—	—	—	—	—	—	0.008	—
39415GCM35	Metolachlor	2,994	50	1	6	28	1	—	14	0.01	0.0312
82630GCM35	Metribuzin	2,994	3	—	—	2	—	—	1	0.014	—
82671GCM35	Molinate	1,241	9	—	—	—	—	—	9	0.004	0.108
61599GCM39	Myclobutanil	2,987	4	—	—	3	—	—	1	0.017	—
49295GCM39	1-Naphthol	2,994	4	—	4	—	—	—	—	0.0363	0.009
61600GCM39	Oxyfluorfen	1,000	1	—	1	—	—	—	—	0.0085	0.021
82683GCM35	Pendimethalin	2,994	2	—	—	—	—	—	2	0.011	—
82687GCM35	*cis*-Permethrin	2,994	1	1	—	—	—	—	—	0.007	—
82664GCM35	Phorate	2,994	1	—	1	—	—	—	—	0.027	—

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				Step 1	Step 2	Step 3	Step 4	Step 5			
Constituents on NWQL schedule 2003, 2032, or 2033—Continued											
61666GCM39	Phorate oxon	2,958	—	—	—	—	—	—	—	0.013	—
61601GCM39	Phosmet	2,649	—	—	—	—	—	—	—	0.1	—
61668GCM39	Phosmet oxon	2,504	—	—	—	—	—	—	—	0.0079	—
04037GCM35	Prometon	2,986	104	—	14	17	—	—	73	0.006	0.0093
04036GCM39	Prometryn	2,994	10	1	1	—	—	—	8	0.005	—
82679GCM35	Propanil	1,241	2	—	—	1	—	—	1	0.007	—
82685GCM35	Propargite	1,000	—	—	—	—	—	—	—	0.02	—
79846GCM40	*cis*-Propiconazole	1,241	1	—	1	—	—	—	—	0.0064	—
79847GCM40	*trans*-Propiconazole	1,241	1	—	1	—	—	—	—	0.017	—
82676GCM35	Propyzamide	2,993	—	—	—	—	—	—	—	0.004	—
04035GCM35	Simazine	2,994	578	—	4	87	2	—	485	0.005	0.027
62852GCM14	Tebuconazole	1,000	—	—	—	—	—	—	—	0.01	—
82670GCM35	Tebuthiuron	2,994	64	—	11	10	—	—	43	0.014	—
61606GCM39	Tefluthrin	1,000	6	—	6	—	—	—	—	0.007	0.0186
82675GCM35	Terbufos	2,958	—	—	—	—	—	—	—	0.009	—
61674GCM39	Terbufos oxon sulfone	2,994	—	—	—	—	—	—	—	0.022	—
04022GCM39	Terbuthylazine	2,994	3	—	—	1	—	—	2	0.0045	—
82681GCM35	Thiobencarb	1,241	2	—	2	—	—	—	—	0.008	—
61610GCM39	Tribufos	2,489	1	1	—	—	—	—	—	0.018	—
82661GCM35	Trifluralin	2,994	12	1	8	3	—	—	—	0.009	0.0324

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[The constituent identification code is the concatenation of the 5-digit numeric USGS parameter code that identifies a constituent or property and the 5-digit alphanumeric USGS method code that indicates the analytical method used to measure it. NWQL schedule 2003, 2032 and 2033 use method codes GCM35, GCM39, GCM14, GCM29, and GCM40; NWQL schedule 2060 uses method code LCM29. Censoring steps (see text for discussion): Step 1, reject results inferred to be the result of contamination during sample collection or processing; Step 2, censor results for concentrations less than the MDL in effect at the time the sample was analyzed; Step 3, censor results for concentrations less than the highest MDL established by the NWQL during July 2004–August 2018; Step 4, censor results analyzed during a period of more frequent laboratory contamination and concentrations less than three times the highest LSB during that period; Step 5, censor results with concentrations less than the MDL determined from field blanks or LSBs analyzed outside of a period of more frequent laboratory contamination. **Constituent**: CIAT, 2-Chloro-4-isopropylamino-6-amino-*s*-triazine; CEAT, 2-Chloro-6-ethylamino-4-amino-*s*-triazine; OIET, 2-Hydroxy-4-isopropylamino-6-ethylamino-*s*-triazine. **Other abbreviations**: GAMA-PBP, Groundwater Ambient Monitoring and Assessment Program Priority Basin Project; LSB, laboratory set blank; MDL, method detection limit; NWQL, National Water Quality Laboratory; USGS, U.S. Geological Survey; —, none; µg/L, microgram per liter]

Constituent identification code	Constituent name	Number of samples with analytical results	Number of detections in original dataset	Number of detections rejected or censored at each step of the review process					Number of detections in final dataset	Study reporting limit (µg/L)[1]	Maximum raised censoring limit applied during step 4 (µg/L)[2]
				Step 1	Step 2	Step 3	Step 4	Step 5			
Constituents on NWQL schedule 2060											
49315LCM29	Acifluorfen	826	—	—	—	—	—	—	—	0.04	—
49312LCM29	Aldicarb	822	—	—	—	—	—	—	—	0.15	—
49313LCM29	Aldicarb sulfone	822	—	—	—	—	—	—	—	0.04	0.012
49314LCM29	Aldicarb sulfoxide	822	—	—	—	—	—	—	—	0.051	—
39632LCM29	Atrazine	7	2	—	1	1	—	—	—	0.04	—
50299LCM29	Bendiocarb	822	—	—	—	—	—	—	—	0.042	—
50300LCM29	Benomyl	840	2	—	2	—	—	—	—	0.03	—
61693LCM29	Bensulfuron-methyl	840	1	—	—	1	—	—	—	0.03	—
38711LCM29	Bentazon	840	49	—	6	10	—	—	33	0.03	0.009
04029LCM29	Bromacil	840	51	—	20	10	—	—	21	0.03	—
49311LCM29	Bromoxynil	826	7	—	7	—	—	—	—	0.06	—
49310LCM29	Carbaryl	822	—	—	—	—	—	—	—	0.02	0.0027
49309LCM29	Carbofuran	822	—	—	—	—	—	—	—	0.03	—
04038LCM29	CEAT	840	84	—	57	2	—	—	25	0.04	—
61188LCM29	Chloramben methyl ester	834	—	—	—	—	—	—	—	0.1	—
50306LCM29	Chlorimuron-ethyl	826	1	—	1	—	—	—	—	0.04	0.03
61692LCM29	*N*-(4-Chlorophenyl)-*N*'-methylurea	840	9	—	8	1	—	—	—	0.06	0.0027
49305LCM29	Clopyralid	833	—	—	—	—	—	—	—	0.07	—
04031LCM29	Cycloate	840	—	—	—	—	—	—	—	0.03	—
39732LCM29	2,4-D	840	3	—	2	1	—	—	—	0.03	—
50470LCM29	2,4-D methyl ester	841	—	—	—	—	—	—	—	0.2	—

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Constituent identification code	Constituent name	Number of samples with analytical results	Number of detections in original dataset	Number of detections rejected or censored at each step of the review process					Number of detections in final dataset	Study reporting limit (µg/L)[1]	Maximum raised censoring limit applied during step 4 (µg/L)[2]
				Step 1	Step 2	Step 3	Step 4	Step 5			
Constituents on NWQL schedule 2060—Continued											
38746LCM29	2,4-DB	840	—	—	—	—	—	—	—	0.01	—
49304LCM29	Dacthal (DCPA) monoacid	840	—	—	—	—	—	—	—	0.02	—
04040LCM29	Deethylatrazine (CIAT)	7	2	—	1	1	—	—	—	0.03	—
38442LCM29	Dicamba	833	—	—	—	—	—	—	—	0.05	—
49302LCM29	Dichlorprop	840	—	—	—	—	—	—	—	0.02	—
49301LCM29	Dinoseb	840	10	—	8	—	—	—	2	0.03	0.0018
04033LCM29	Diphenamid	826	29	—	21	7	—	—	1	0.02	—
49300LCM29	Diuron	840	66	—	23	5	10	—	28	0.02	0.084
49297LCM29	Fenuron	840	4	—	1	2	—	—	1	0.1	0.0315
61694LCM29	Flumetsulam	832	—	—	—	—	—	—	—	0.04	0.609
38811LCM29	Fluometuron	840	—	—	—	—	—	—	—	0.02	—
49308LCM29	3-Hydroxy carbofuran	822	—	—	—	—	—	—	—	0.03	—
50356LCM29	Imazaquin	826	2	—	2	—	—	—	—	0.07	0.015
50407LCM29	Imazethapyr	840	9	—	6	1	—	—	2	0.04	0.003
61695LCM29	Imidacloprid	840	1	—	1	—	—	—	—	0.04	—
38478LCM29	Linuron	840	—	—	—	—	—	—	—	0.02	—
38482LCM29	MCPA	836	1	—	1	—	—	—	—	0.033	—
38487LCM29	MCPB	840	—	—	—	—	—	—	—	0.2	—
50359LCM29	Metalaxyl	840	7	—	5	2	—	—	—	0.02	—
38501LCM29	Methiocarb	822	—	—	—	—	—	—	—	0.02	—
49296LCM29	Methomyl	810	—	—	—	—	—	—	—	0.06	—

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Constituent identification code	Constituent name	Number of samples with analytical results	Number of detections in original dataset	Number of detections rejected or censored at each step of the review process					Number of detections in final dataset	Study reporting limit (µg/L)[1]	Maximum raised censoring limit applied during step 4 (µg/L)[2]
				Step 1	Step 2	Step 3	Step 4	Step 5			
Constituents on NWQL schedule 2060—Continued											
61697LCM29	Metsulfuron-methyl	810	1	—	1	—	—	—	—	0.07	0.0243
49294LCM29	Neburon	840	—	—	—	—	—	—	—	0.01	—
50364LCM29	Nicosulfuron	836	—	—	—	—	—	—	—	0.16	—
49293LCM29	Norflurazon	840	8	—	2	3	—	—	3	0.02	—
50355LCM29	OIET	809	12	—	6	5	—	—	1	0.04	—
49292LCM29	Oryzalin	840	—	—	—	—	—	—	—	0.02	—
38866LCM29	Oxamyl	804	9	8	—	1	—	—	—	0.06	—
49291LCM29	Picloram	803	—	—	—	—	—	—	—	0.06	—
49236LCM29	Propham	840	—	—	—	—	—	—	—	0.03	—
50471LCM29	Propiconazole	840	—	—	—	—	—	—	—	0.03	—
38538LCM29	Propoxur	822	—	—	—	—	—	—	—	0.03	—
38548LCM29	Siduron	840	13	—	13	—	—	—	—	0.02	0.054
50337LCM29	Sulfometuron-methyl	826	3	—	1	2	—	—	—	0.09	0.042
82670LCM29	Tebuthiuron	7	—	—	—	—	—	—	—	0.03	0.0024
04032LCM29	Terbacil	840	—	—	—	—	—	—	—	0.023	—
49235LCM29	Triclopyr	815	1	—	—	—	—	—	1	0.04	—

[1]Study reporting limits for all constituents are the maximum method detection limit (MDL_{max}) established by the NWQL during July 2004–August 2018 (table 2), except for Atrazine (39632GCM35), for which the study reporting limit is the detection limit determined from GAMA-PBP field blanks (DLBLK-FB) (table 4).

[2]Maximum raised censoring reporting limit defined during identified periods of more frequent laboratory contamination occurring during July 2004–May 2016 (table 3). Raised censoring reporting limits are applied to samples analyzed during the identified periods.

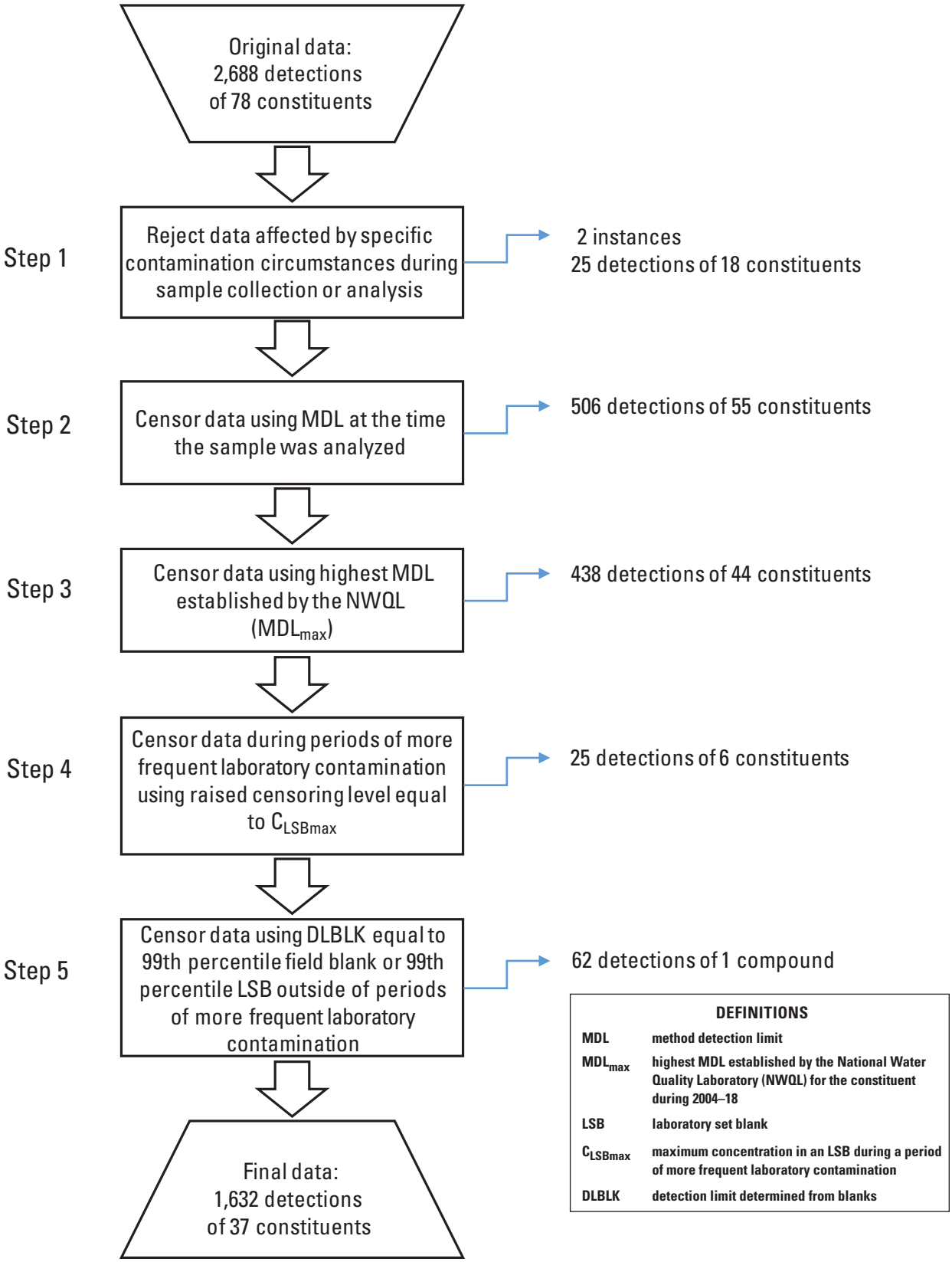


Figure 3. Order for reviewing data and establishing and implementing censoring protocols by the California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP) for pesticide constituents on U.S. Geological Survey National Water Quality Laboratory (NWQL) schedules 2003, 2032, or 2033, or on schedule 2060 for samples collected during 2004–18.

Step 1: Rejecting Results on the Basis of Unusual, Specific Instances of Contamination or Other Problems During Collection or Processing of Samples

The first step of data review was to identify results or samples that should be rejected entirely. The GAMA-PBP rejects data by changing the data-quality indicator (DQI) code in NWIS to "Q" for "reviewed and rejected" and adding an explanation to the result-level field comment field. Rejected results are not reported to the public on NWIS Web. The effect of rejecting results on subsequent data analysis is the same as if the sample had not been analyzed at all (in other words, there are no data for that sample for that constituent). At the time of publication of this report (2019), projects such as the GAMA-PBP are permitted to reject results entirely by applying a DQI code of Q, but are not permitted to change laboratory-reported results in the NWIS database in response to data-quality issues (U.S. Geological Survey, 2017a).

The GAMA-PBP uses rejection of results only in the rare cases in which there is strong evidence that a specific instance or circumstance during collection or processing of the sample seriously compromised the sample. Expert judgement is required to identify these specific instances to avoid unwarranted rejection of data. It is not possible to describe procedures for identifying all possible causes; several examples are given to illustrate the thought processes used and some of the limitations.

The following discussion includes three examples of specific instances of contamination during collection of samples. The first example is a hypothetical case involving detection of a constituent present in personal care products or pharmaceuticals. Examination of field-blank results found that all environmental samples and field blanks collected by a particular person had detections of a constituent, and that constituent was not detected in environmental samples or field blanks collected by any other personnel. The number of samples collected was large enough that the correlation between the sample collector and the detections was highly unlikely to be coincidental. Detections of the constituent in samples collected by the person would be rejected. Note that the key to establishing the causal relation between the person and the detections was that the constituent was never detected in samples not collected by the person inferred to be the source of the contamination during sample collection or processing.

The second and third examples are from the GAMA-PBP assessment of contamination of VOC samples during collection and processing of samples (Fram and others, 2012). Evaluation of data for the VOC 1,2,4-trimethylbenzene in about 2,000 groundwater samples and about 200 field blanks collected over an 8-year period by the GAMA-PBP concluded that solo detections of 1,2,4-trimethylbenzene in groundwater samples, field blanks, and source-solution blanks were due to contamination during sample collection. The field vehicles had become contaminated with 1,2,4-trimethylbenzene from the equipment used to collected radon-222 samples. In this case, because a number of samples were affected (up to 40 percent in study units for which radon-222 samples were collected at every site) and the concentrations resulting from the contamination were low, the affected data were censored (reported as less than a statistically determined study reporting limit) rather than rejected. Note that identifying the solo 1,2,4-trimethylbenzene detections as due to contamination during sample collection required extensive quality-control data and metadata about the project's field sample collection activities. The GAMA-PBP assessment of contamination of VOC samples during collection and processing of samples also found that rare detections of acetone, tetrahydrofuran, and methyl ethyl ketone at concentrations up to several hundred micrograms per liter in groundwater samples with no other detections of VOCs were due to contamination by volatilization of polyvinyl chloride (PVC) cement from newly constructed wellhead plumbing (Fram and others, 2012). Affected data for those three VOC constituents were rejected in NWIS. Identifying this cause of contamination was facilitated by the thorough descriptions of the field sites recorded by the field crews.

An alternative to the extensive data and metadata analysis required to reject results might have been to resample sites with suspicious detections. Resampling of sites may not be possible for logistical reasons, however (for example, well owners may not give permission for a field crew to return to the site, or the project may not have funds to do resampling) or may not be appropriate for scientific reasons (for example, the study design includes sampling during a particular season or hydrologic event). In addition, the decision to reject data from one sample may require evaluation of data from a larger population of samples, which could impose a long delay between the original sampling of the site and the proposed resampling of the site.

Examination of the GAMA-PBP data for pesticide constituents on schedules 2003, 2032, or 2033, or on schedule 2060 found 2 cases of specific contamination instances during sample collection and processing: false positive detections of oxamyl in 8 samples most likely due to use of contaminated field sample collection equipment and false positive detections of 25 pesticide constituents in 1 sample for unknown reasons.

Case 1: Oxamyl in Nine Samples

Oxamyl is a pesticide constituent on NWQL schedule 2060 and was originally reported as detected in groundwater from nine sites sampled in 2005 (table 1) and in the field blank collected at one of those sites. Eight of the sites were monitoring wells sampled between March 29, 2005, and April 18, 2005, near the city of Sacramento, California (GAMA_IDs SSV-QPCFP-01 and -02, NAM-06, and NAMFP-05, -06, -07, -09, and -10; Dawson and others, 2008). The field blank collected with the monitoring well equipment at site SSV-QPCFP-01 and the replicate collected at site NAMFP-06 also had detections of oxamyl. The final site was a monitoring well near the city of Fresno, California (GAMA_ID: KINGFP-08; Burton and Belitz, 2008), that was sampled on November 2, 2005, using the same equipment as used to sample the Sacramento monitoring wells. Oxamyl was not detected in the replicate sample collected at this site, nor was it detected in the field blank collected with the same equipment 2 days earlier. Oxamyl was not detected in any other GAMA-PBP groundwater samples during 2004–18. The fact that oxamyl was only detected in 9 groundwater samples and a field blank collected with the same equipment over a relatively short time, and not detected in any of the other 831 samples analyzed for pesticide constituents on schedule 2060 during 2004–18, was considered suspicious and triggered further investigation. This investigation of the oxamyl results was initiated in 2017 in response to questions about the data from the California Department of Pesticide Regulation. The investigation was more than a decade after the wells were sampled, and re-sampling the wells to verify the detections was not possible.

Oxamyl degrades rapidly in surface-water and soil environments (U.S. Environmental Protection Agency, 2004), and its absence from the California Pesticide Contamination Prevention Act Groundwater Protection List (California Department of Pesticide Regulation, 2018a) indicates that it is considered unlikely to be detected in groundwater because of its physical properties. The eight Sacramento monitoring wells ranged in depth from 64 to 326 m below land surface (median 145 m) and yielded groundwater with an estimated age of 2,000 to 40,000 years before present (Bennett and others, 2011). Based on tritium mass balance (data from Dawson and others, 2008), some of the groundwater samples could be mixtures of groundwater with a range of ages, including a maximum of 10 percent by volume of water recharged since oxamyl was first registered for use in 1974. The oxamyl concentrations reported in the samples from the eight Sacramento monitoring wells ranged from 0.006 to 0.081 microgram per liter (µg/L). In order for the groundwater samples to have those concentrations, the concentration in the fraction of the water recharged since 1974 would have to have been greater than 0.06 to 0.8 µg/L. However, results in NWIS Web for all surface-water samples collected at sites in California and analyzed for oxamyl (677 samples collected from 1993 through 2014) show a detection frequency of 0.3 percent and a maximum concentration of 0.031 µg/L, indicating oxamyl was unlikely to be present in groundwater recharge.

Oxamyl is an insecticide and nematicide. The monitoring well sites are in Sacramento County, near the boundaries with Yolo or Placer County. There were 524 registered applications of oxamyl in Yolo and Sacramento Counties in 1991–2016, two-thirds of which were for research use or use in greenhouse and outdoor locations used for growing plants in containers or seedlings for transplanting (California Department of Pesticide Regulation, 2018b). Most of the research and greenhouse and outdoor locations for container and transplant plants were reported at the county level, with no finer details such as street address or Public Land Survey section. Oxamyl applications to field crops were reported at the level of Public Land Survey section. There were nine registered applications to field crops (tomatoes and pumpkins) within 5 kilometers (km) of the monitoring well sites; all nine applications were on the opposite side of the Sacramento River from the monitoring well sites. Because lateral groundwater-flow directions generally are toward the Sacramento River (Faunt, 2009), it is unlikely that recharge from the fields where oxamyl was applied would have reached the monitoring wells.

On the basis of the suspicious pattern of detections, oxamyl's chemical properties, the depth of the wells, the age of the groundwater, and the absence of oxamyl use in the vicinity of the wells, the oxamyl detections in the eight Sacramento monitoring wells were considered highly unlikely to reflect true presence of oxamyl in the groundwater. The oxamyl detections were inferred to be the result of contamination from the monitoring well sampling equipment used to collect all of the samples and the field blank. On that basis, the eight detections of oxamyl in groundwater samples from the monitoring wells sampled between March 29 and April 18, 2005, in the Sacramento area were rejected. The GAMA-PBP report that originally reported these detections of oxamyl was reissued, and an erratum was published (Dawson and others, 2008). The rejected data also are listed and identified as "rejected" in the USGS data release published concurrently with this report (Lor and others, 2019).

The way the monitoring well sampling equipment, or the field crew operating the equipment during the weeks that the samples were collected, became contaminated with oxamyl is unknown. Most of field crew members using the equipment were based in the USGS Sacramento office, and two of the Sacramento-based crew members used the equipment during 3 of the 4 weeks during which there were detections in groundwater samples. Although there were no documented uses of oxamyl near the well sites, oxamyl was used in Sacramento County; therefore, exposure of field personnel to oxamyl cannot be ruled out.

A separate oxamyl detection in the sample collected on November 2, 2005, near Fresno was rejected for a different reason than the Sacramento samples. The monitoring well sampling equipment had not been used during the 7-month period between the Sacramento and Fresno sampling events, the field crew members were not the same as those using the equipment for the Sacramento monitoring wells, and the field blank collected with the monitoring well sampling equipment 2 days before the sample was collected did not have a detection. Thus, there was no direct evidence that the monitoring well sampling equipment was still the source of the oxamyl contamination. This detection of oxamyl was at a concentration lower than the MDL at the time the sample was analyzed and was therefore censored in step 2 (see discussion in section on step 2). After full quality-control assessment of the project data, there were zero detections of oxamyl in groundwater samples collected by the GAMA-PBP in 2004−18.

Case 2: Unusually Large Number of Constituents an a Single Sample

Original results for a groundwater sample collected from a domestic well on April 25, 2013 (GAMA_ID S-MS-P06), and analyzed for pesticide constituents on schedule 2003, 2032, or 2033 showed detections of 17 pesticide constituents (Goldrath and others, 2015). Among the 1,018 GAMA-PBP samples with an original reported detection of at least 1 pesticide constituent, the median number of constituents detected was 2, the 95th percentile was 7 detections, the second highest number was 9 detections, and the maximum was 17 detections (this sample). Because of the large number of detections, the results were considered suspicious, and further investigation was undertaken. Permission to re-sample the well to verify the detections could not be obtained.

The combination of pesticide constituents detected in S-MS-P06 was unusual. The study unit included 100 domestic wells in an area of California that has intensive agricultural land use (Goldrath and others, 2015; Burton and Wright, 2018). Of the 17 detected pesticide constituents, 16 had no detections in any other samples from the study unit, and 4 of the constituents (schedule 2003, 2032, or 2033 constituents cypermethrin, tribufos, ethion, and *cis*-permethrin) were not detected in any other GAMA-PBP samples during 2004−18 (table 1). The four most commonly detected pesticide constituents in GAMA-PBP samples are the herbicides simazine and atrazine and the herbicide degradates deethylatrazine and 3,4-dichloroaniline (table 1): 94 percent of GAMA-PBP samples for which there were two or more reported detections of pesticide constituents in the original data from the NWQL included detections of at least one of those four constituents. Of the 161 GAMA-PBP samples with detections of 5 or more pesticide constituents, S-MS-P06 was the only sample that did not have a detection of simazine, atrazine, deethylatrazine, or 3,4-dichloroaniline. Of the 17 constituents detected in S-MS-P06, 11 were insecticides or insecticide degradates. In the rest of the GAMA-PBP 2004–18 dataset, the maximum number of insecticides or insecticide degradates detected in a single sample was five. The combination of pesticide constituents detected in S-MS-P06 did not resemble the combinations of pesticide constituents detected in any of the other 3,000 groundwater samples collected by the GAMA-PBP during 2004−18.

Other information about S-MS-P06 also indicates detection of a large number of pesticide constituents is unlikely to reflect the composition of the groundwater. Groundwater age-dating results indicate that the sample may be composed entirely of pre-modern groundwater, and land use within 500 m of the well was classified as 67 percent natural and 32 percent agricultural (Burton and Wright, 2018). Field notes and photographs did not show evidence of storage of pesticides near the site. Of the 14 pesticide parent compounds detected, 8 had no registered uses in the zip code areas (95019, 95039, and 95076) within an 8-km radius of the well (benfluralin, dacthal, dieldrin, ethion, fipronil, isofenphos, metolachlor, and tribufos) (California Department of Pesticide Regulation, 2018b). The three pesticide degradates detected are degradates of fipronil.

Because of these results, the pesticide detections reported in S-MS-P06 were considered highly unlikely to reflect the actual presence of pesticide constituents in the groundwater. No direct evidence was found to explain how the sample may have been contaminated during collection or analysis, however. Two hypotheses for a source of contamination are an inadvertent switch with a spiked sample or contamination with a spike solution or an unusual carryover during laboratory processing of the sample.

Evidence indicates that the detections in S-MS-P06 were unlikely to have been the result of a switch with a spiked sample or inadvertent spiking. The concentrations of pesticide constituents originally reported as detected in S-MS-P06 ranged from 0.0012 to 0.019 µg/L. The concentrations of pesticide constituents in GAMA-PBP matrix spike samples commonly are approximately 0.2 µg/L, indicating that S-MS-P06 was not likely switched with a matrix spike sample or accidentally spiked. The USGS Branch of Quality Systems (BQS) Organic Blind Sample Program (OBSP) low-level spikes generally contain 35 to 55 pesticide constituents. Examination of the 60 BQS OBSP analyzed between July 2012 and December 2013 found none of the spikes contained all 17 of the pesticide constituents detected in S-MS-P06—the maximum number was 13—and that the median concentrations of the 17 pesticide constituents in the spikes ranged from 3 to 28 times higher than the concentrations detected in S-MS-P06. This indicates that S-MS-P06 was not likely to have been switched with a BQS OBSP sample.

Highly unusual carryover contamination during laboratory processing or analysis remains a possibility. Many of the pesticide constituents detected in S-MS-P06 are among the pesticide constituents known to have greater frequencies of laboratory contamination: of the 17 pesticide constituents detected in S-MS-P06, 8 are constituents were associated with more frequent periods of laboratory contamination (see step 4 for discussion), and 7 of the 11 pesticide constituents for which there were more than 1 such period during 2001−18 were detected in S-MS-P06. Determining the reason that laboratory contamination by some pesticide constituents is more frequent than by others is beyond the scope of this report.

Despite the absence of a cause for contamination of S-MS-P06, the GAMA-PBP concluded that the preponderance of evidence indicated it was highly unlikely the 17 reported detections of pesticide constituents in S-MS-P06 were representative of conditions in the groundwater at the sampled well and rejected all of the pesticide constituent results (detections and non-detections) for the sample. The report that published the data for this study unit contains an explanation of the rejected data in a footnote on the table of pesticide results (Goldrath and others, 2015). The rejected data also are listed in the USGS data release published concurrently with this report (Lor and others, 2019).

Reporting of Rejected Results

Prior to this report, the GAMA-PBP had originally assigned the suspicious detections in S-MS-P06 and the oxamyl detections in the Sacramento monitoring wells a DQI code of "R" for "reviewed and accepted" and a remark code of "V" in NWIS. The V remark code is applied when assessment of field or laboratory blanks indicates that there is a positive bias of more than 10 percent in the concentration of a constituent due to contamination during collection, processing, or analysis of the sample (U.S. Geological Survey, 1997). In practice, interpretation of V-coded data is ambiguous: most data users interpret the V code as indicating the result is a true detection that was influenced by contamination bias rather than a detection that may have a greater probability of being a false positive detection due to contamination bias. The V code does not differentiate between a detection whose concentration has a positive bias due to contamination during sample collection, processing, or analysis and a detection that is entirely due to that contamination. Because the GAMA-PBP data-quality objectives for pesticide constituents are primarily concerned with classifying results as detections or non-detections, the GAMA-PBP no longer uses V codes. Applying a DQI code of Q to reject the data entirely removes the ambiguity associated with a V code.

In summary, review of the dataset in step 1 led to identification of two specific instances warranting rejection of data in NWIS—one involving contamination of eight samples during sample collection in the field and one of unknown origin. A total of 25 detections of 18 pesticides constituents were rejected (table 1).

Step 2: Censoring Using Method Detection Limits in Effect at the Time the Sample Was Analyzed

The original GAMA-PBP dataset includes results reported as confirmed identifications (detections) by the NWQL at concentrations less than the MDL in effect at the time each sample was analyzed. As described in the section on data-quality objectives, results at concentrations less than the MDL do not meet the GAMA-PBP criteria for a detection. Therefore, the MDL in effect at the time a sample was analyzed was used to censor the data. Results reported as detections in the original dataset at concentrations less than the MDL in effect at the time the sample was analyzed are classified by the GAMA-PBP as non-detections.

This step of censoring at the MDL in effect at the time the sample was analyzed (step 2) is a subset of step 3. In step 3, the data are censored at the highest MDL in effect during 2004–18. Step 2 was retained as a separate step because it can be applied as soon as the project receives the data, whereas many years are required to accumulate a sufficient amount of data to establish the censoring limits used in step 3. In addition, retaining step 2 as a separate step allows for assessment of the effects of step 2 and step 3 on the final dataset separately.

The GAMA-PBP publishes a USGS data release (or USGS data series report prior to 2016) upon completion of each study unit and published more than 45 such reports during 2005−18. The censoring limits defined in step 2 may be used in study unit data releases when a more comprehensive assessment of censoring limits, such as the assessments described in Olsen and others (2010), Fram and Belitz (2011), Fram and others (2012), Davis and others (2014), and this report, is not yet available for a set of constituents. The GAMA-PBP does not re-issue data series reports or data releases when censoring limits are updated or when the NWQL re-loads data in NWIS (for example, U.S. Geological Survey, 2007). The most up-to-date data are available electronically from NWIS (https://waterdata.usgs.gov/nwis), the GAMA-PBP data viewer (https://ca.water.usgs.gov/projects/gama/water-quality-results/), and the SWRCB groundwater information system (http://gamagroundwater.waterboards.ca.gov/gama/gamamap/public).

Analytical data produced by the NWQL are stored in NWIS with information about the laboratory reporting level or detection limit associated with each analysis. This information is contained in the RPLEV (reporting level) and RLTYP (reporting level type) fields that can be retrieved with the data. For pesticide constituents on schedules 2003, 2032, or 2033, or on schedule 2060, the reporting level types used during July 2004–August 2018 were IRL, LRL, and MRL. The values of the reporting levels and the associated detection limits are listed in the USGS data release published concurrently with this report (Lor and others, 2019).

There were a total of 506 detections of 55 constituents at concentrations that were less than the MDL in effect at the time the sample was analyzed (table 1). This censoring step had a large effect on the number of detections in the GAMA-PBP dataset; 19 percent of the original detections reported by the NWQL were reclassified as non-detections. All detections of 20 pesticide constituents remaining after step 1 were censored in step 2 (schedule 2003, 2032, or 2033 constituents 1-napthol, 2-ethyl-6-methylaniline, carbaryl, chlorpyrifos oxon, *cis*-propiconazole, *trans*-propiconazole, desulfinylfipronil amide, fipronil sulfone, oxyfluorfen, phorate, tefluthrin, thiobencarb; schedule 2060 constituents benomyl, bromoxynil, chlorimuron-ethyl, imazaquin, imidacloprid, MCPA, metsulfuron-methyl, siduron; table 1; fig. 4).

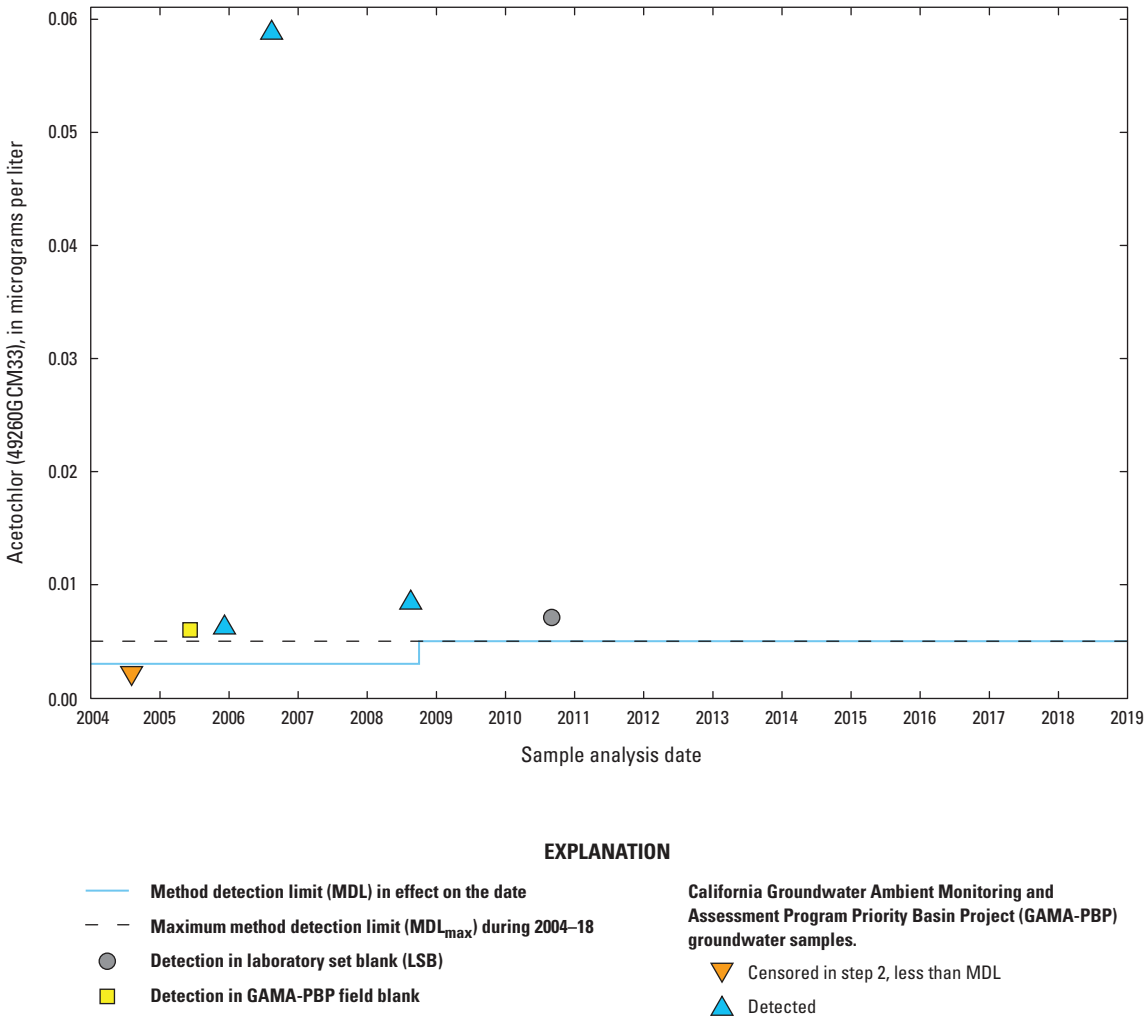
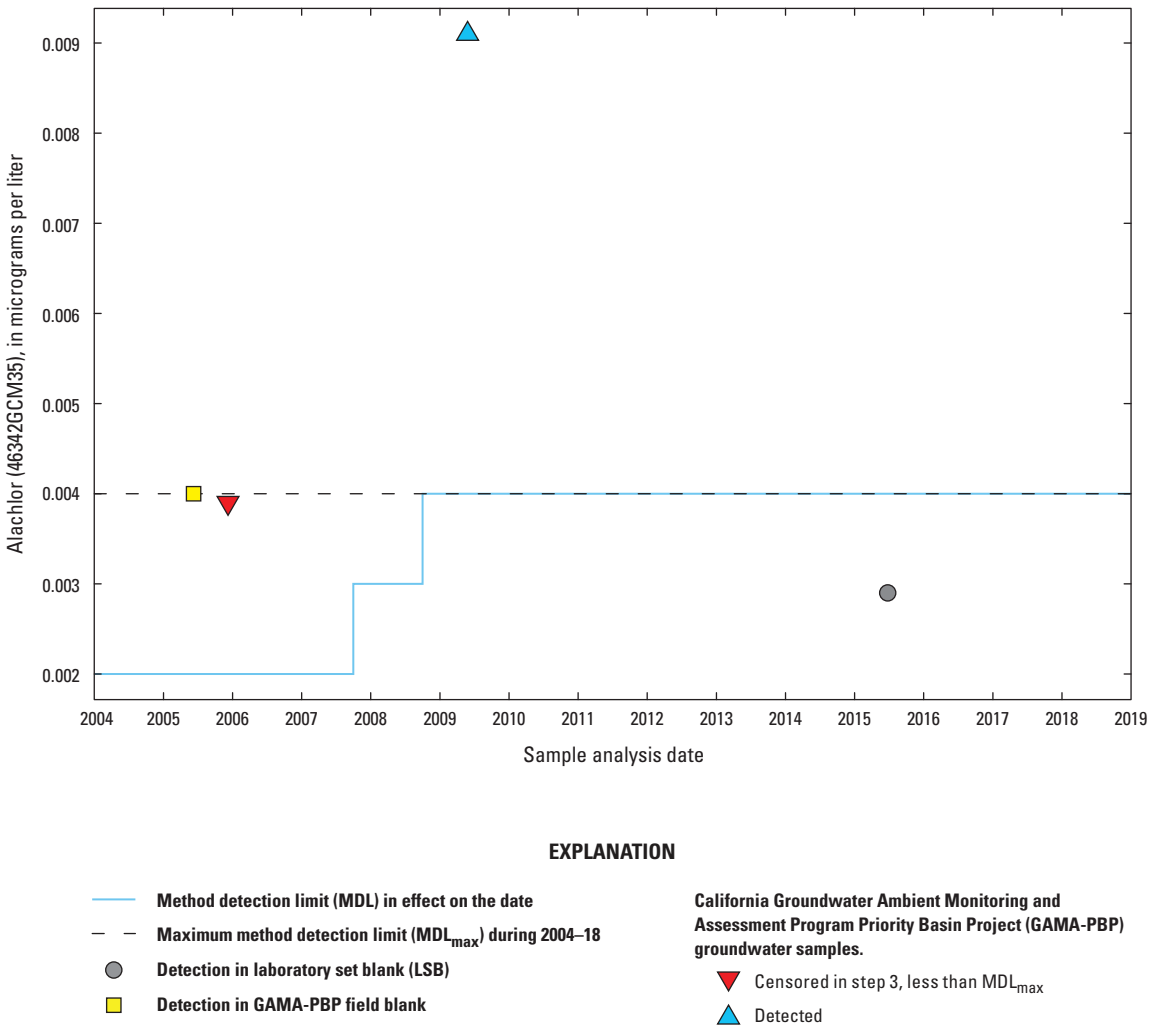


Figure 4. The concentrations of method detection limits determined by the U.S. Geological Survey National Water Quality Laboratory (NWQL), raised censoring limits used during periods of more frequent laboratory contamination (as defined in step 4 of this study), detections in laboratory set blanks (LSBs), detections in California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP) field blanks, and originally reported detections in GAMA-PBP groundwater samples for each of 78 pesticide constituents on schedules 2003, 2032, or 2033 or on schedule 2060 for which the NWQL originally reported one or more detections in samples collected by the GAMA-PBP during 2004–18. The symbols for the detections in GAMA-PBP groundwater samples indicate whether the detection was censored in steps 1–5 of this study or remains as a detection in the final dataset published by the GAMA-PBP. Constituents are identified by name and constituent identification code (see table 1).



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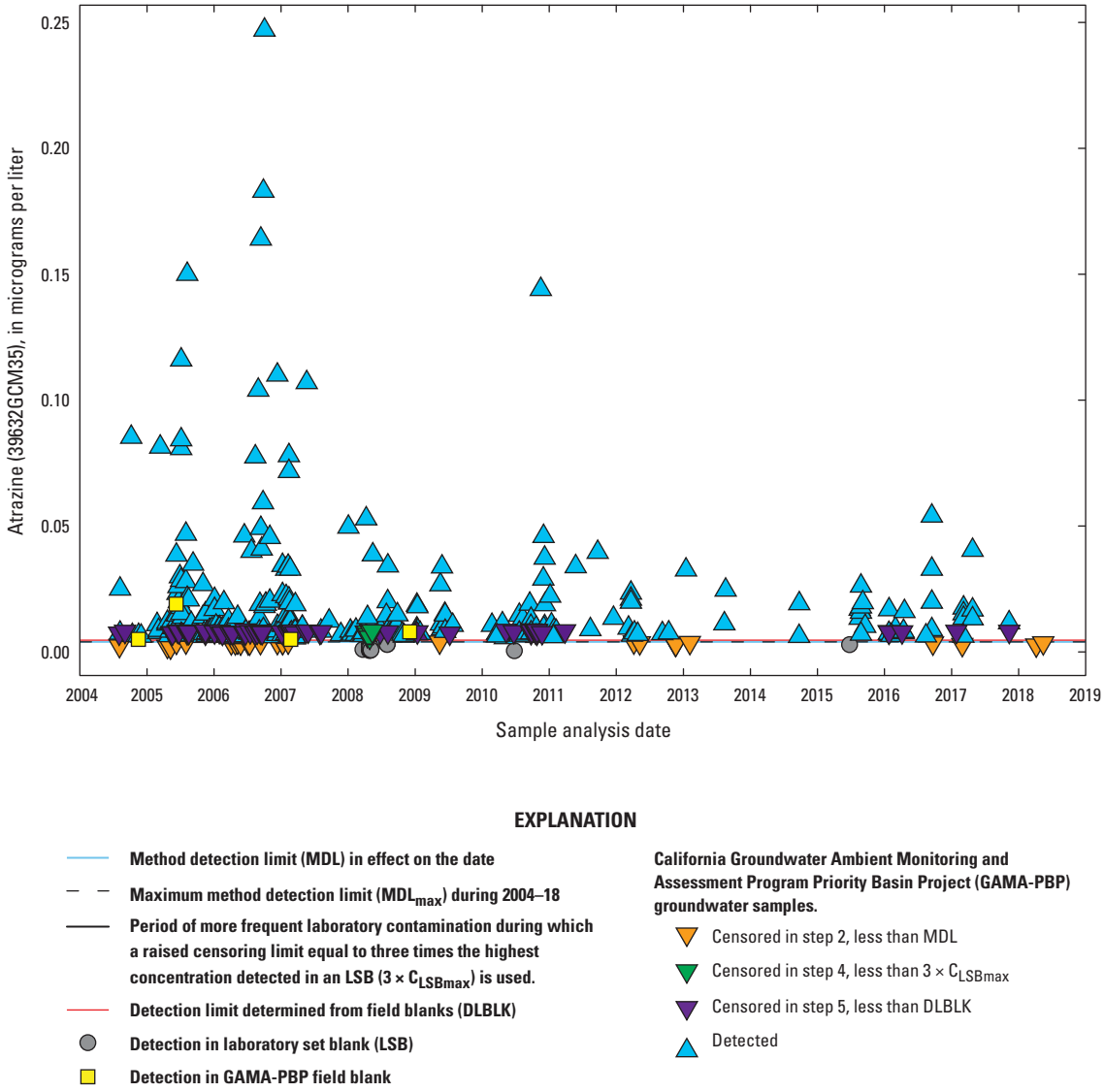

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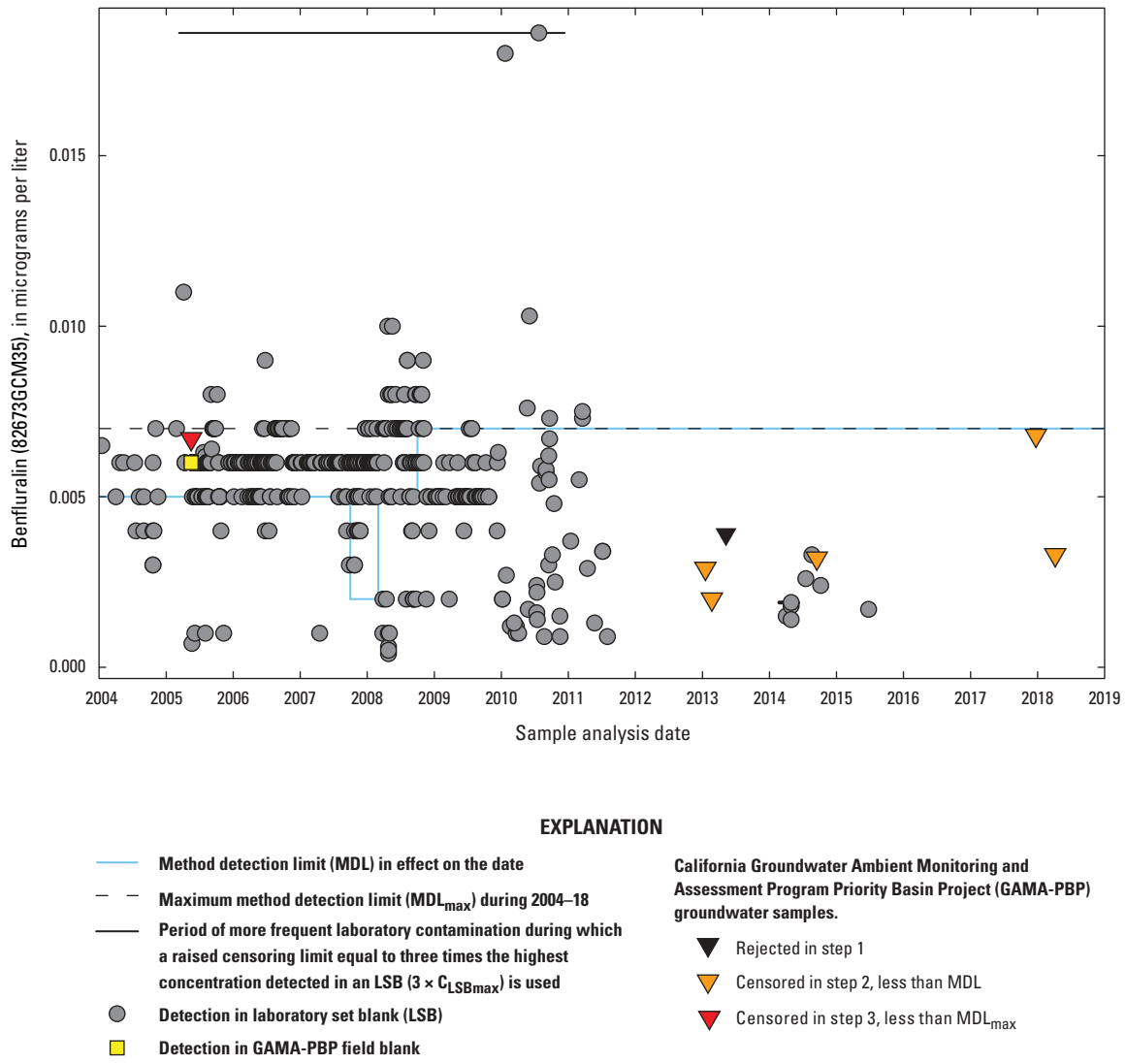

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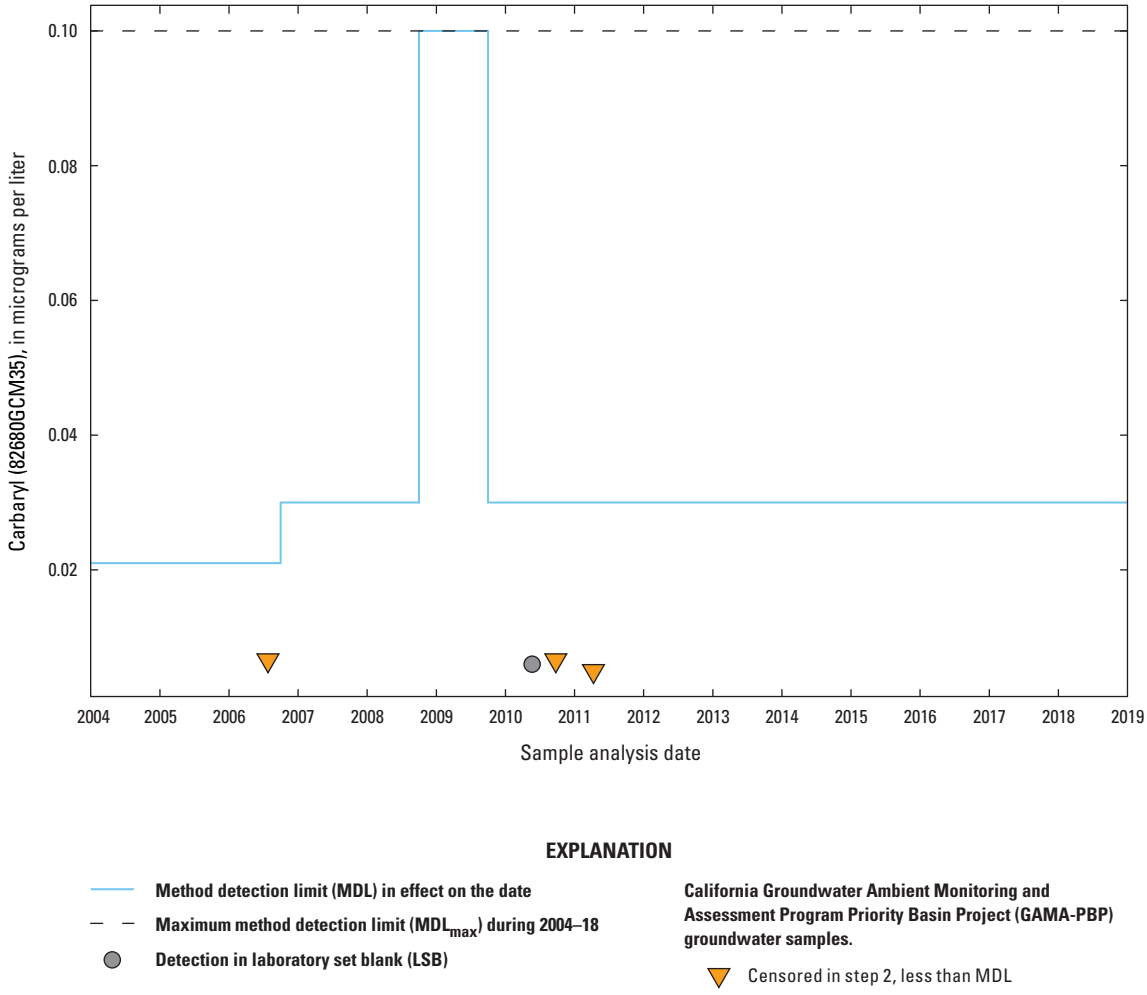

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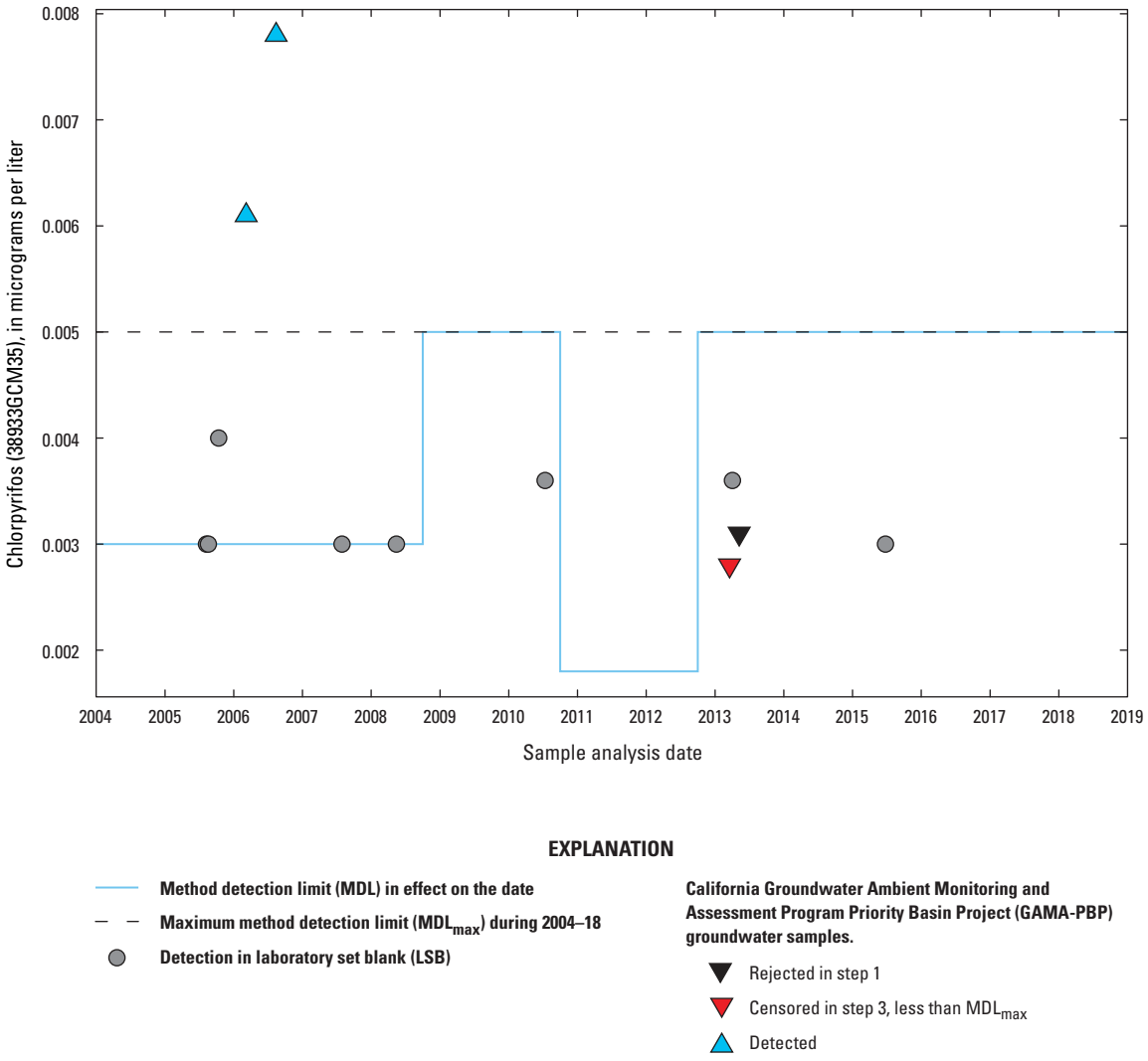

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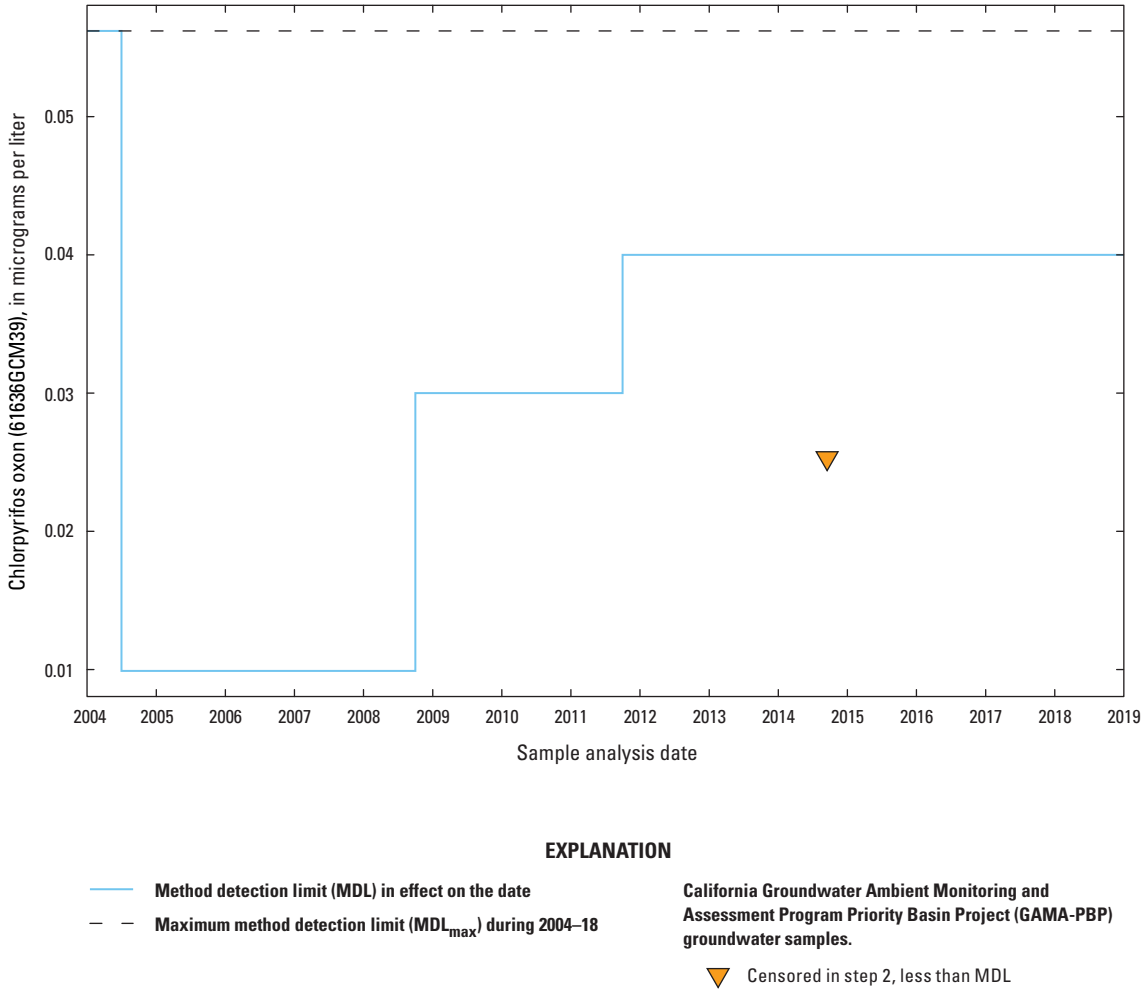

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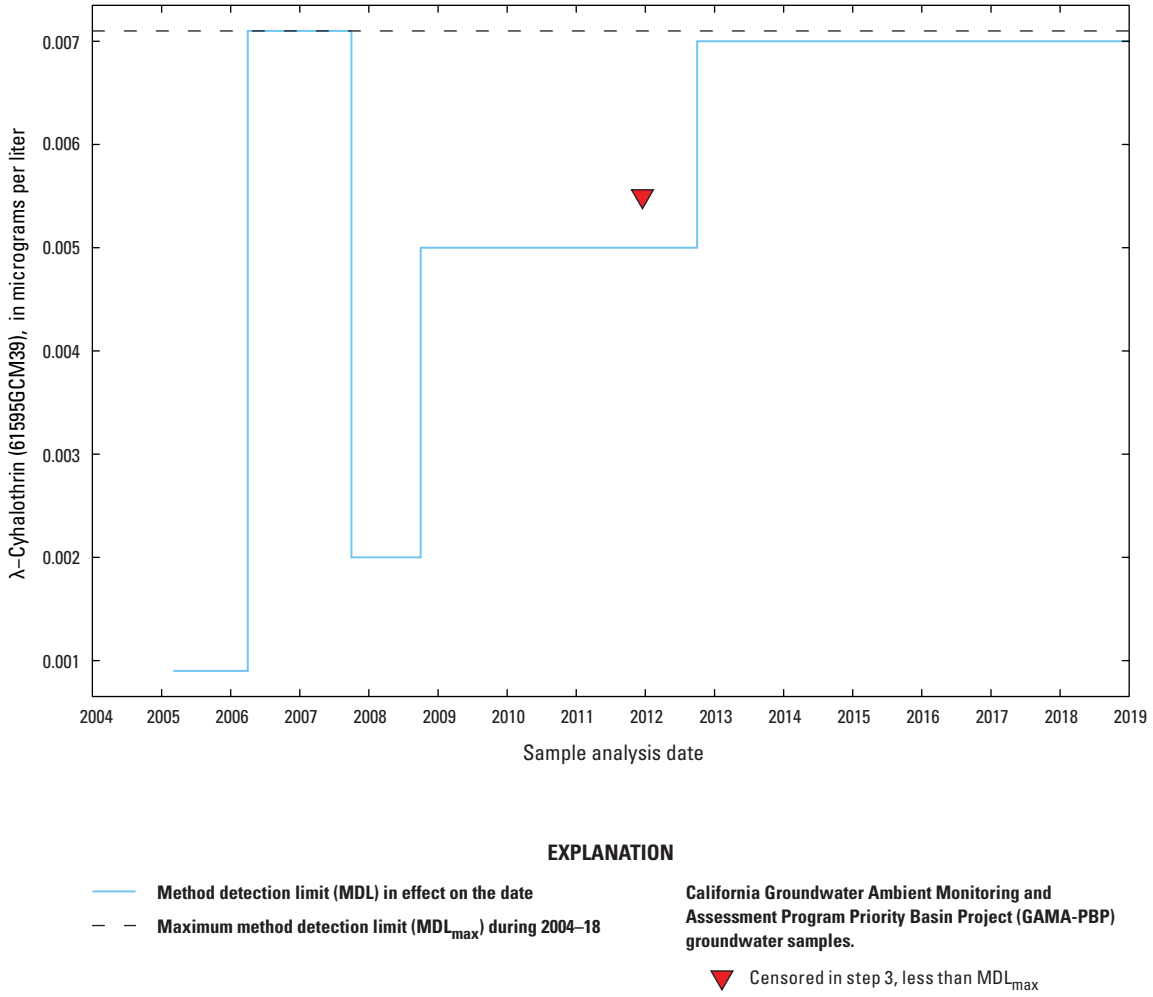

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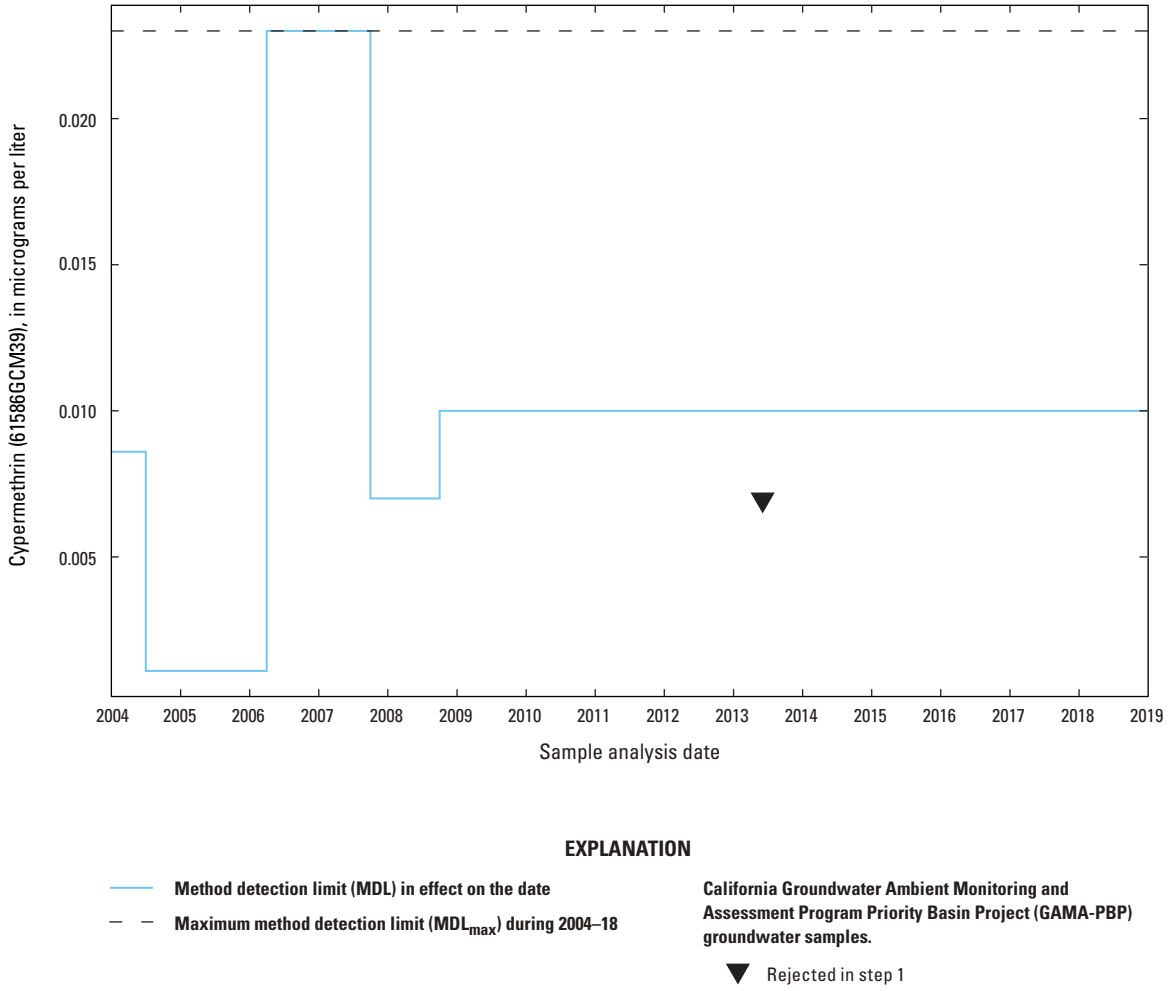

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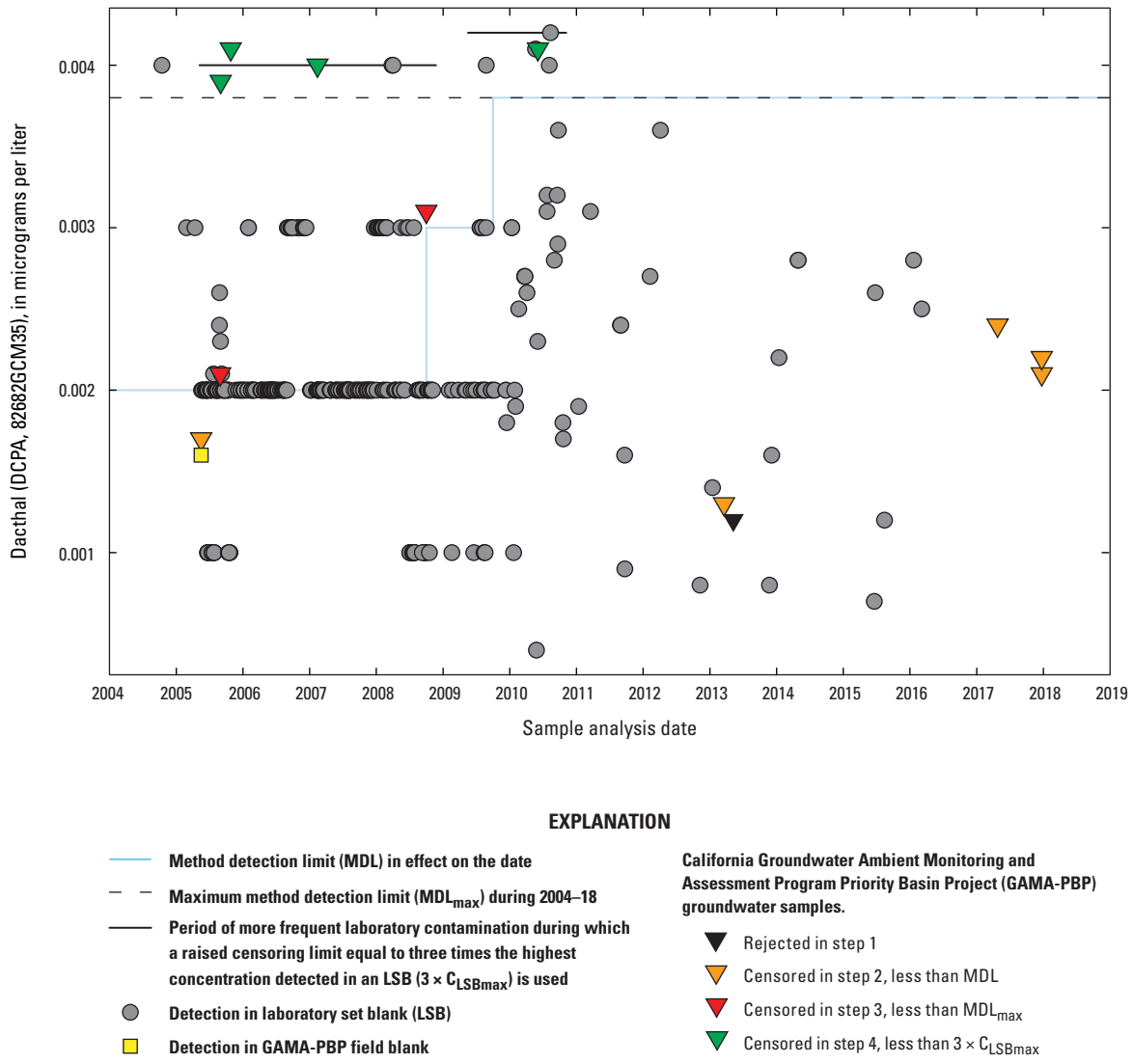

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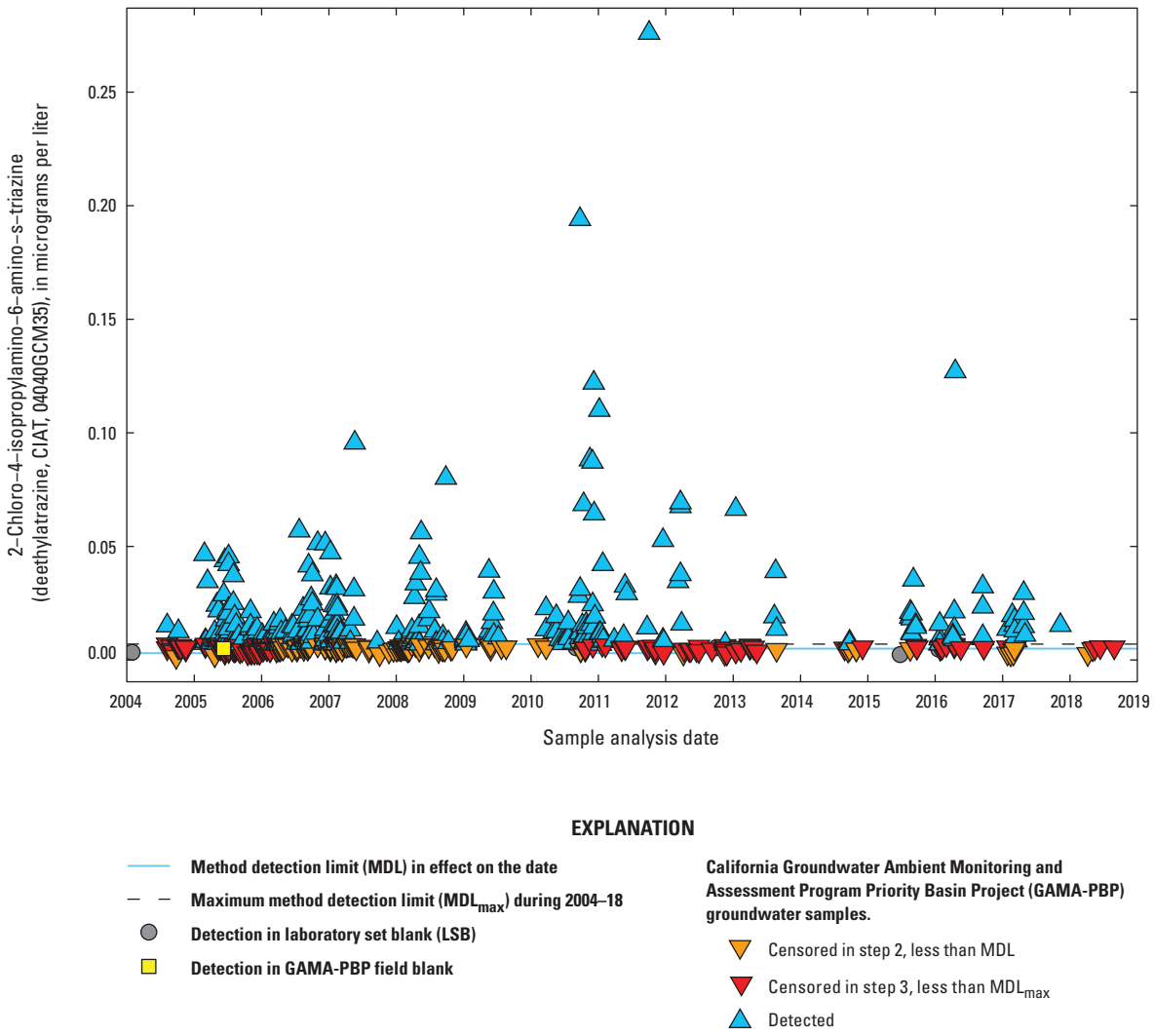

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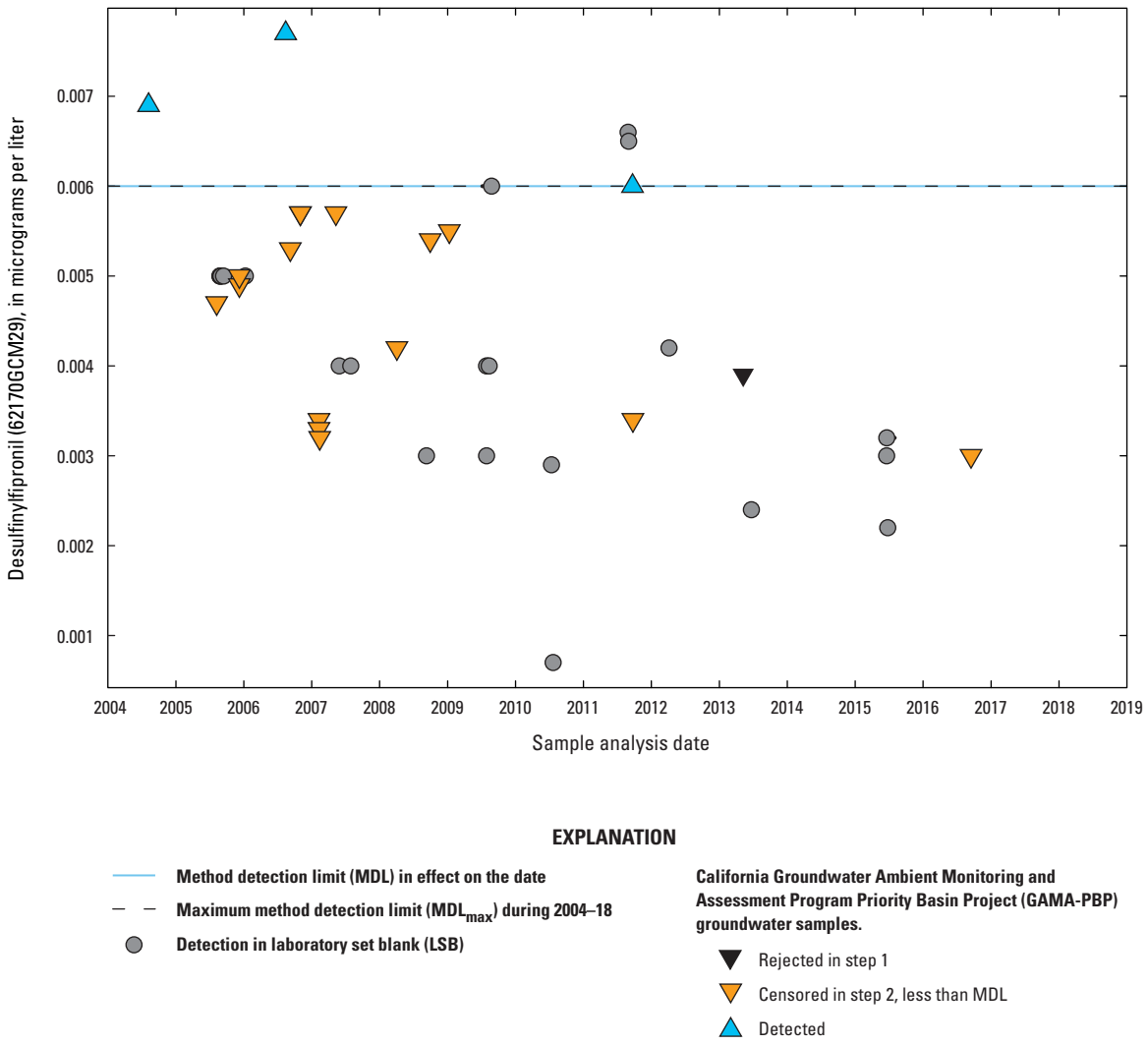

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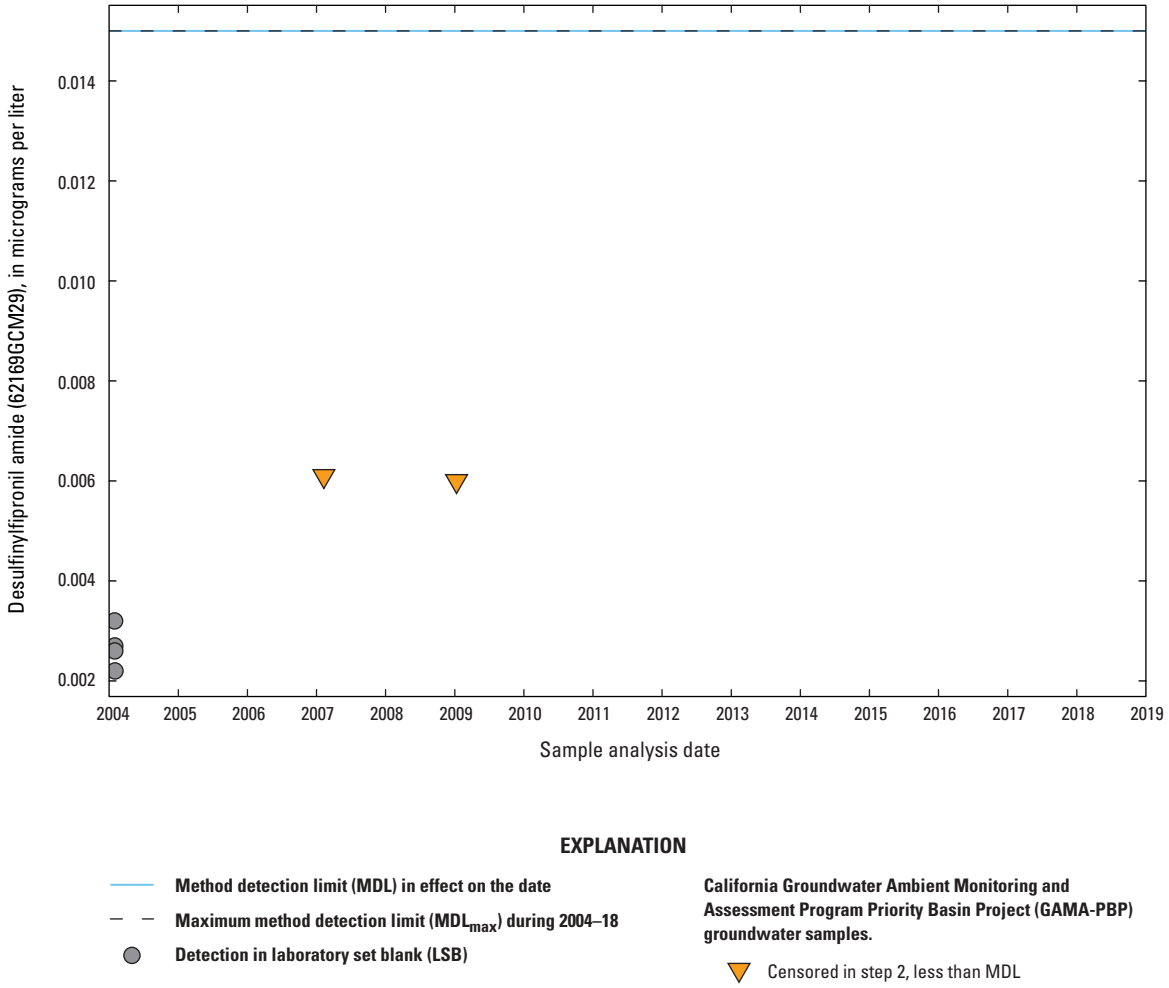

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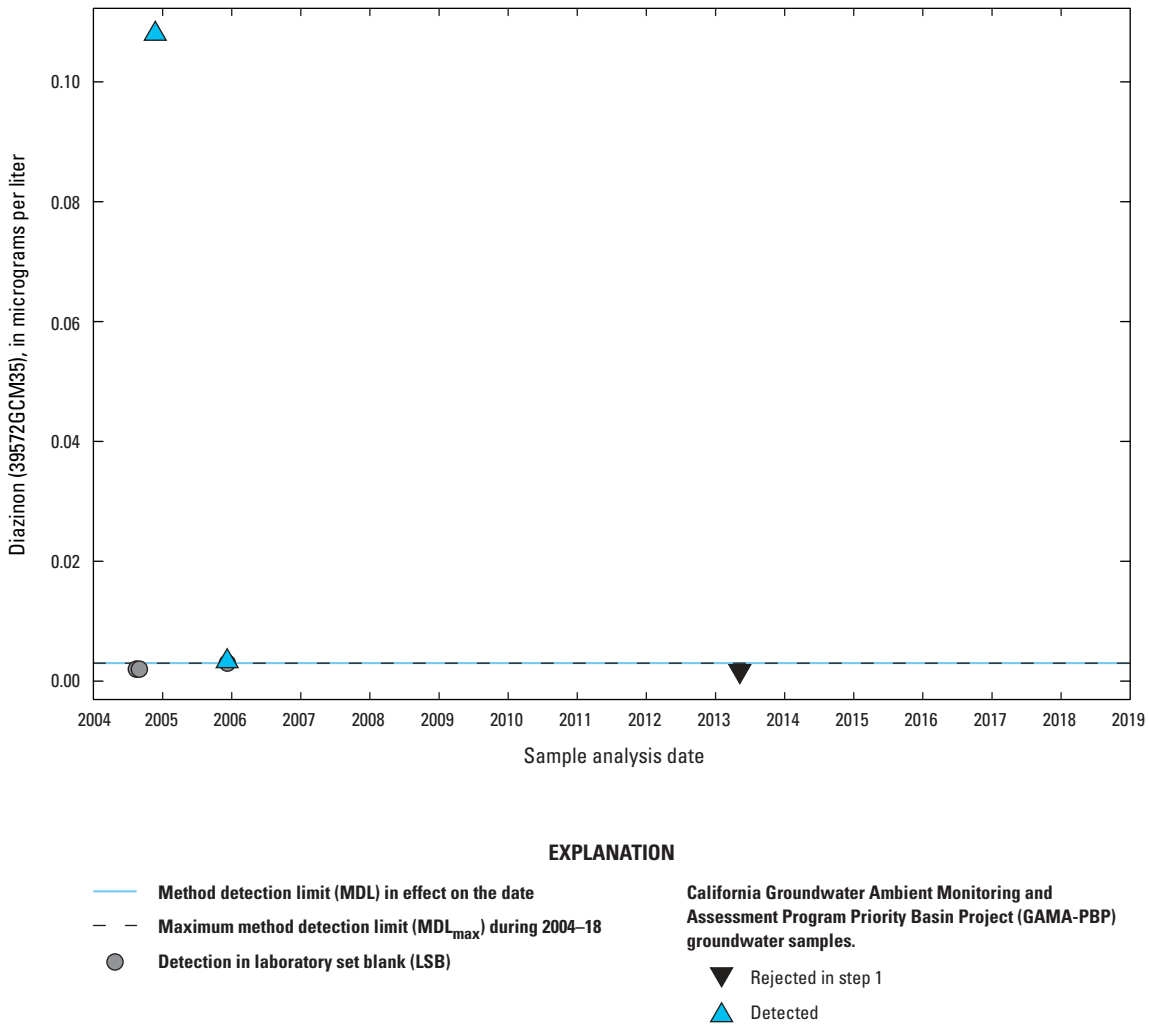

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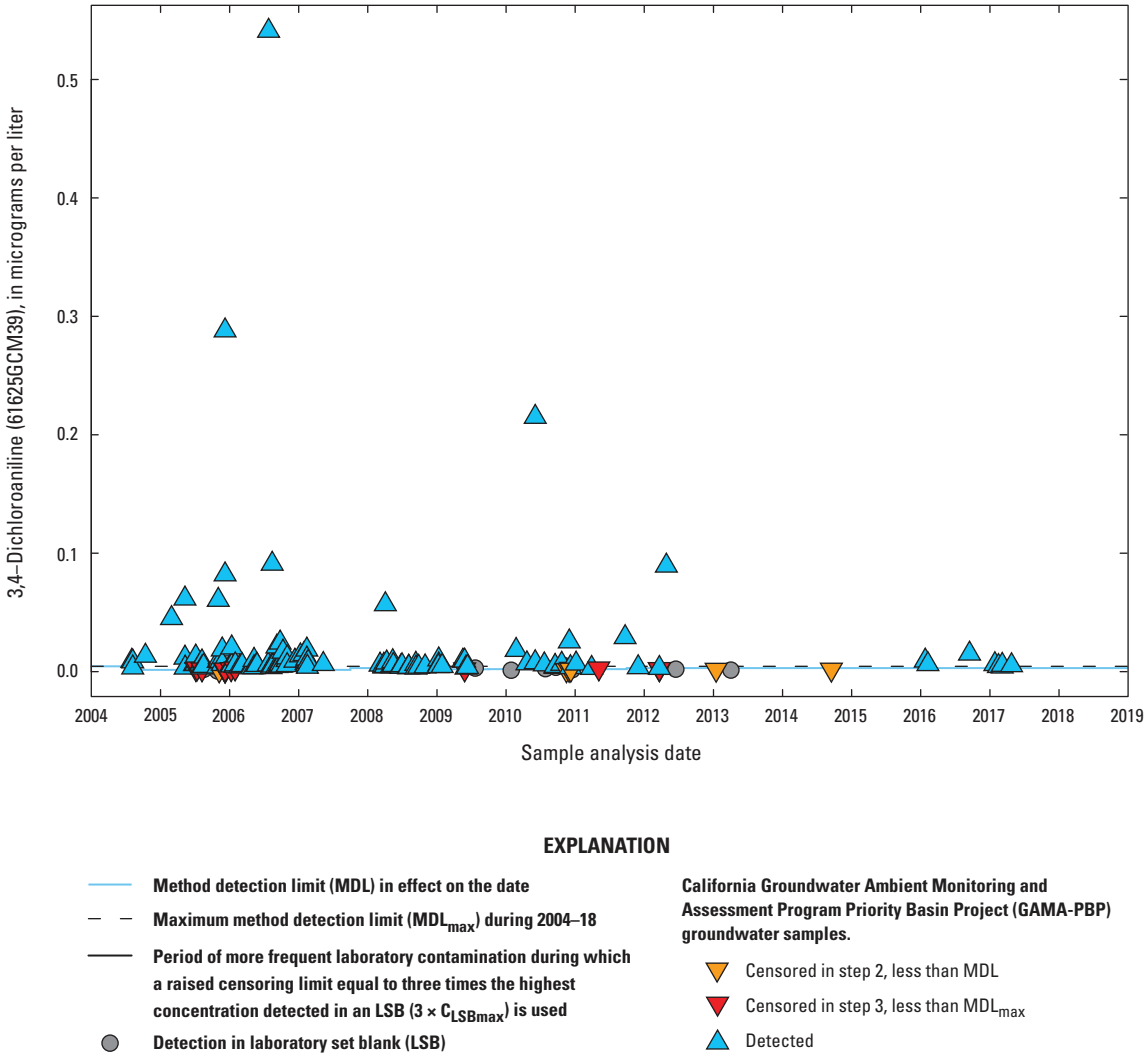

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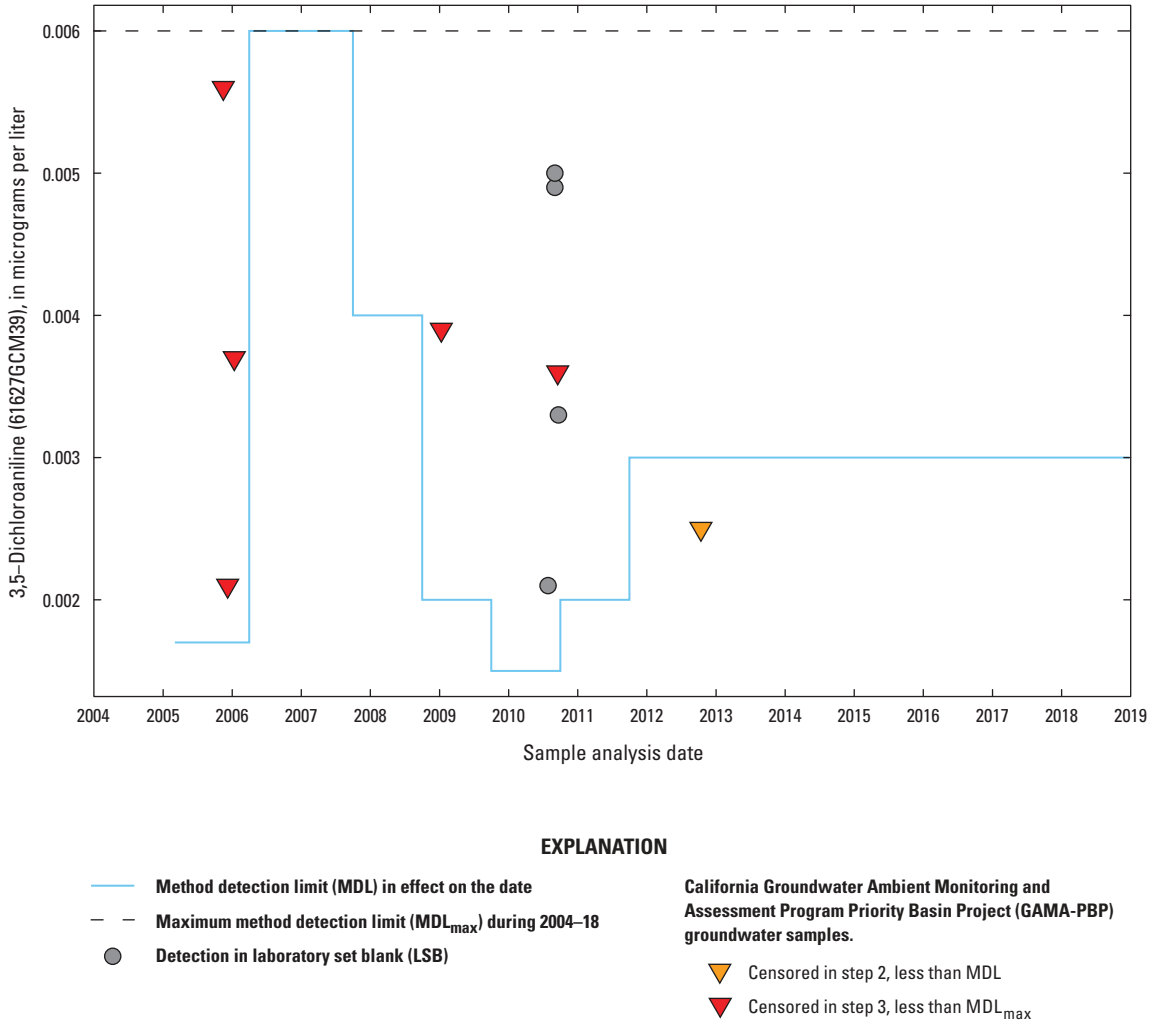

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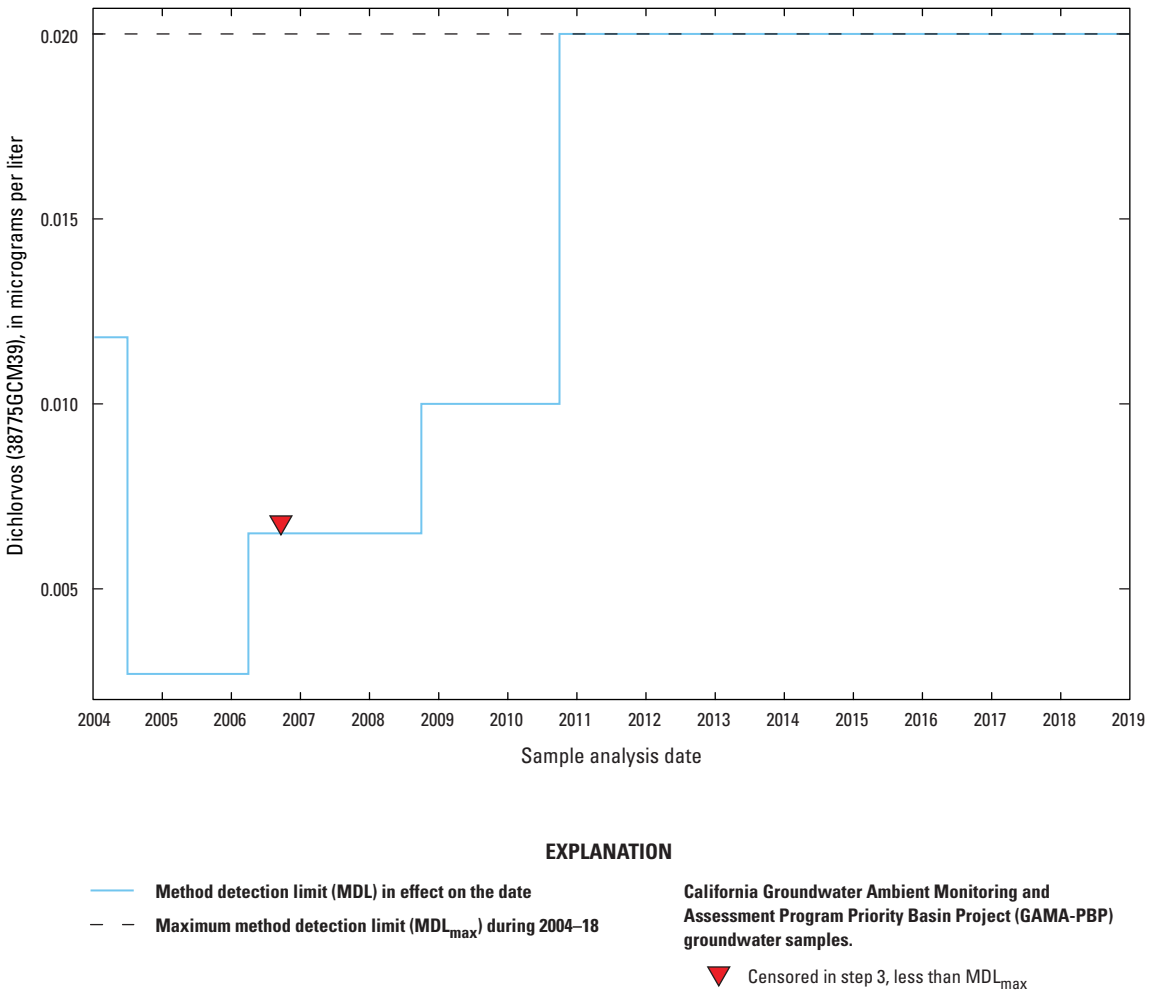

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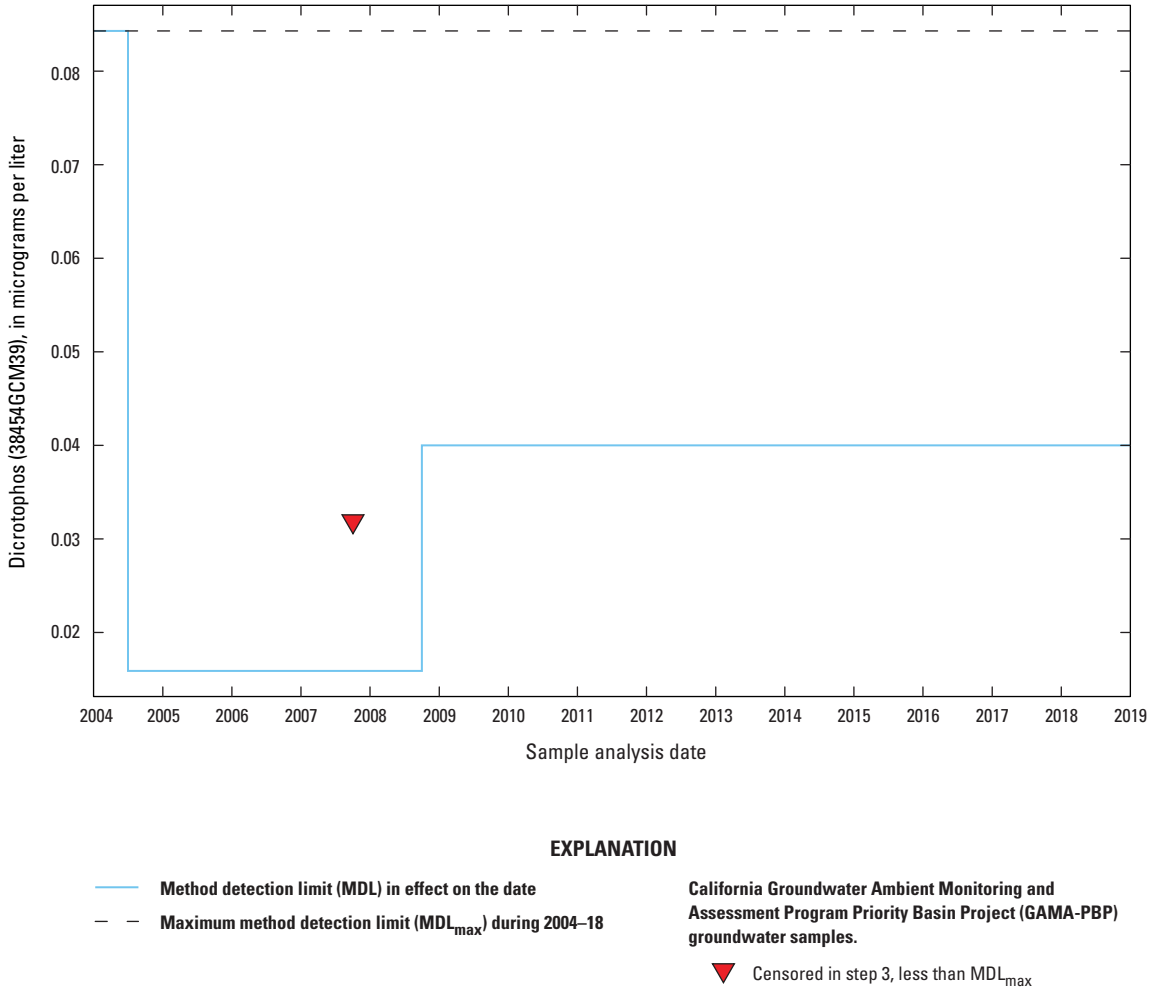

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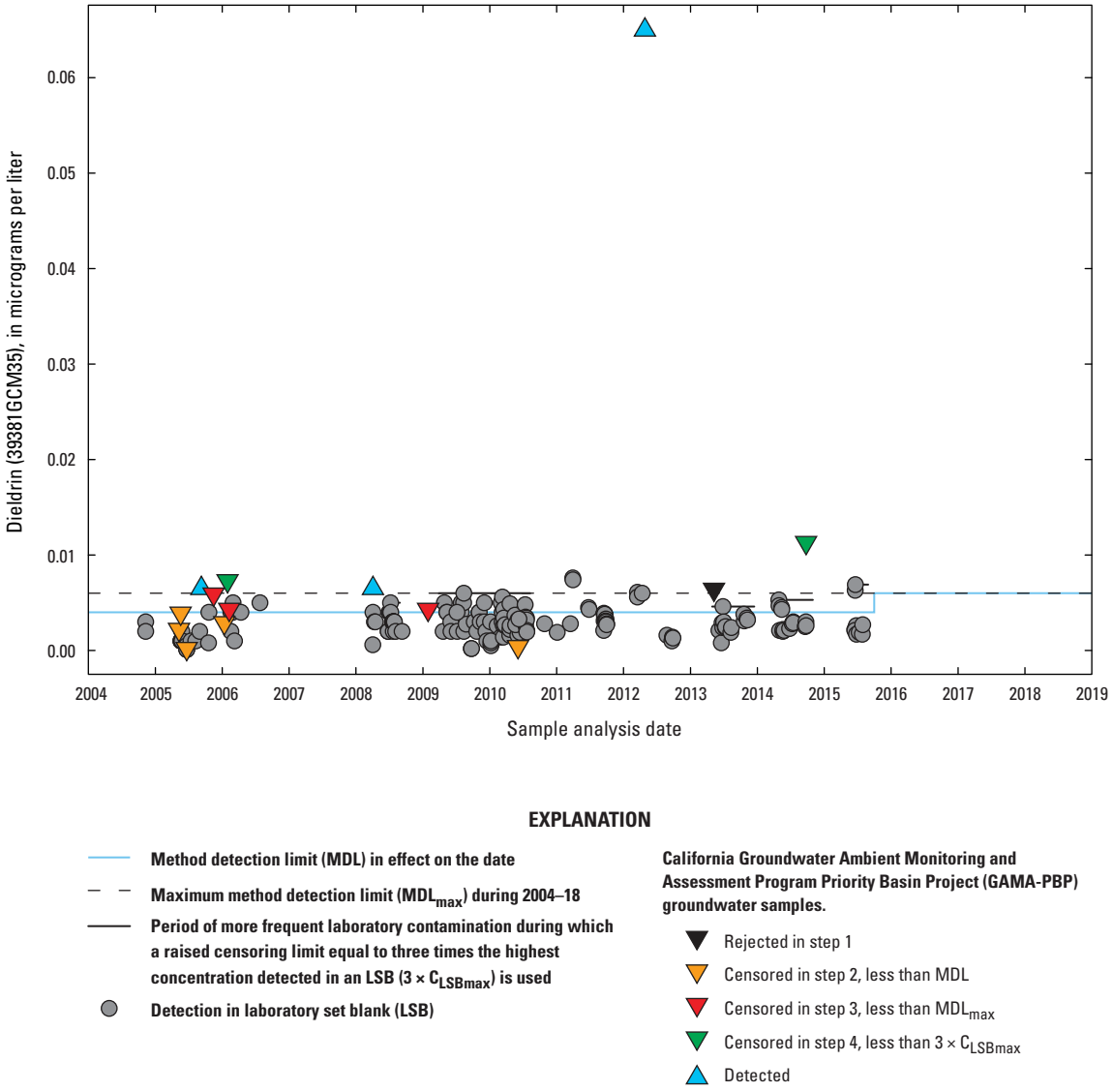

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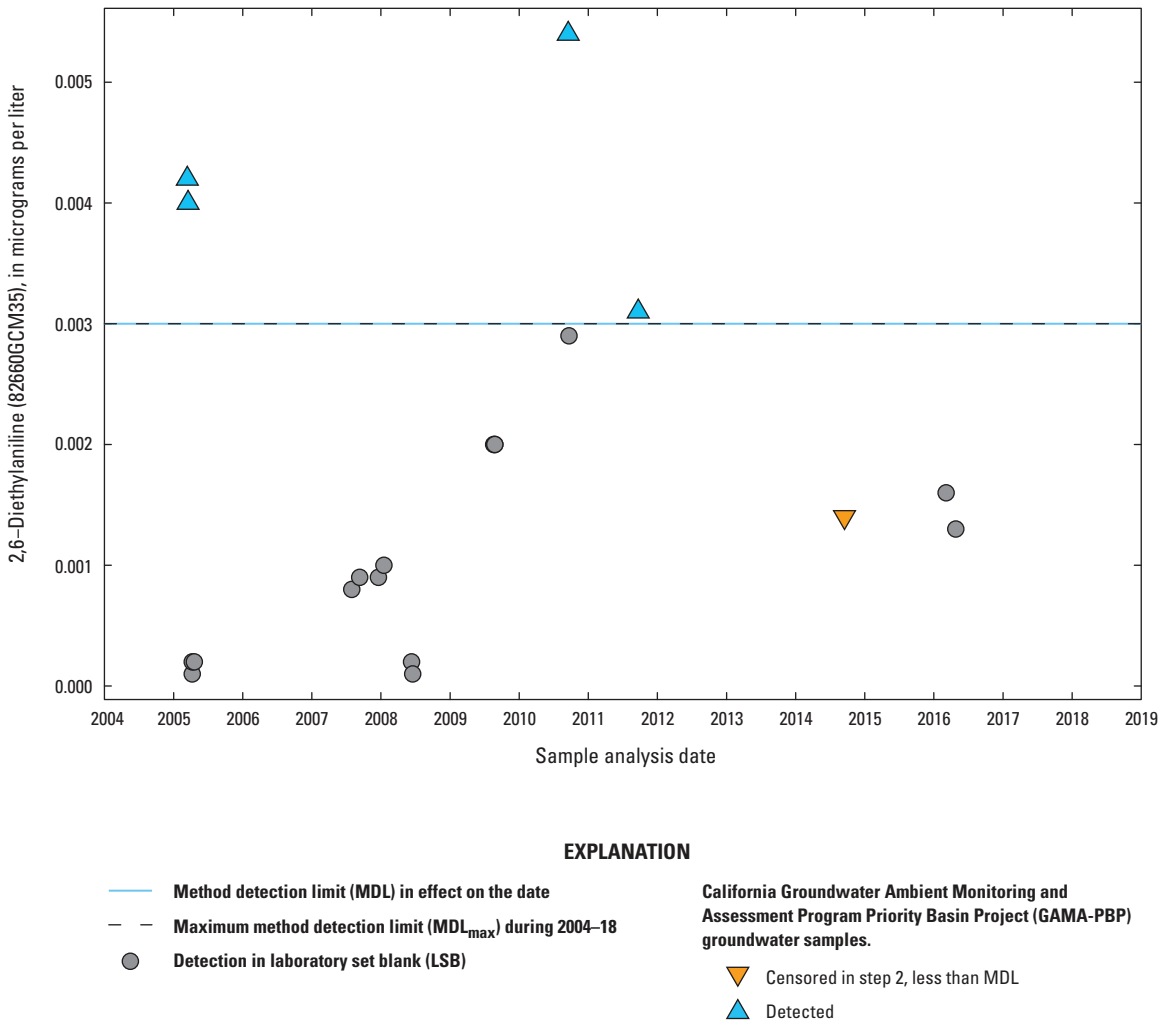

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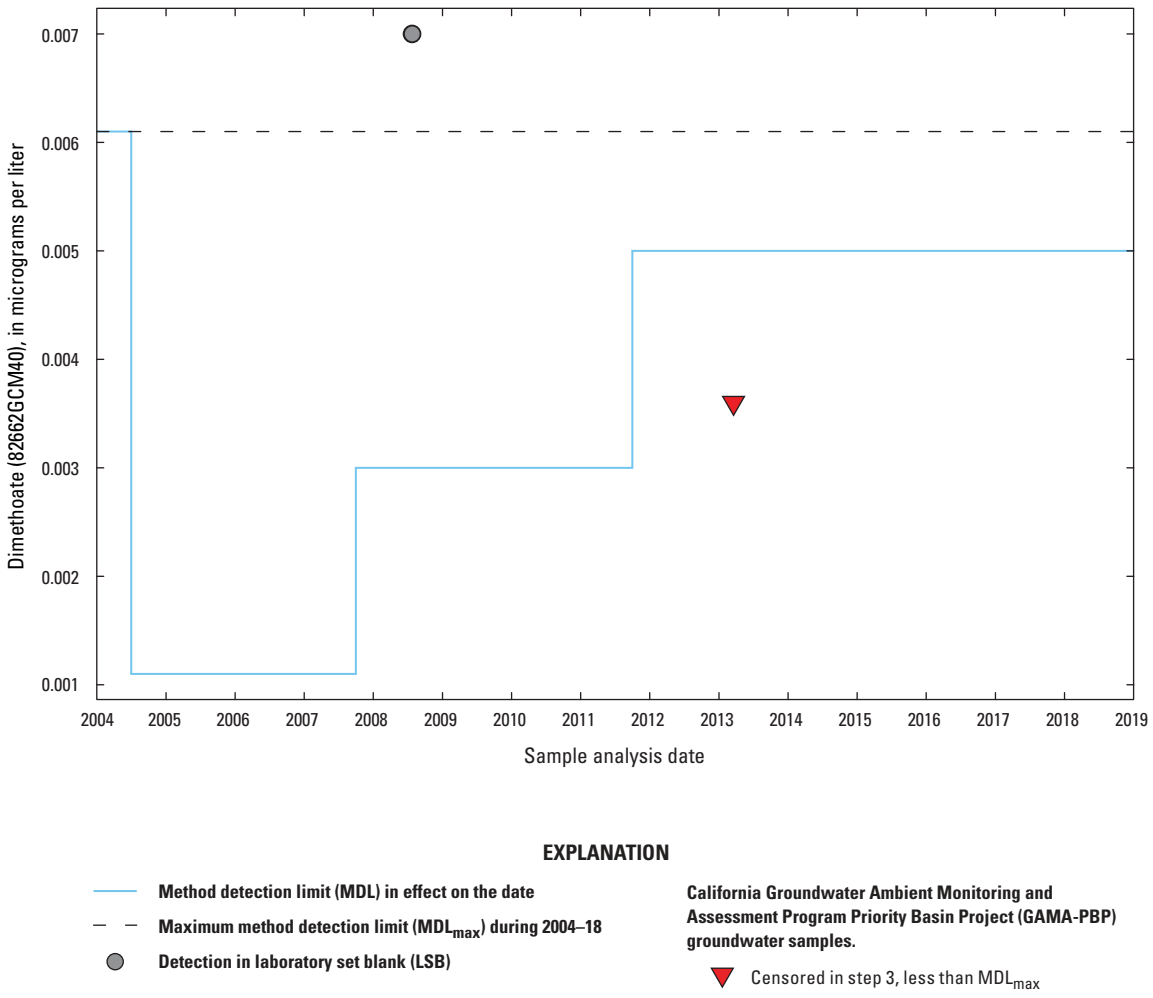

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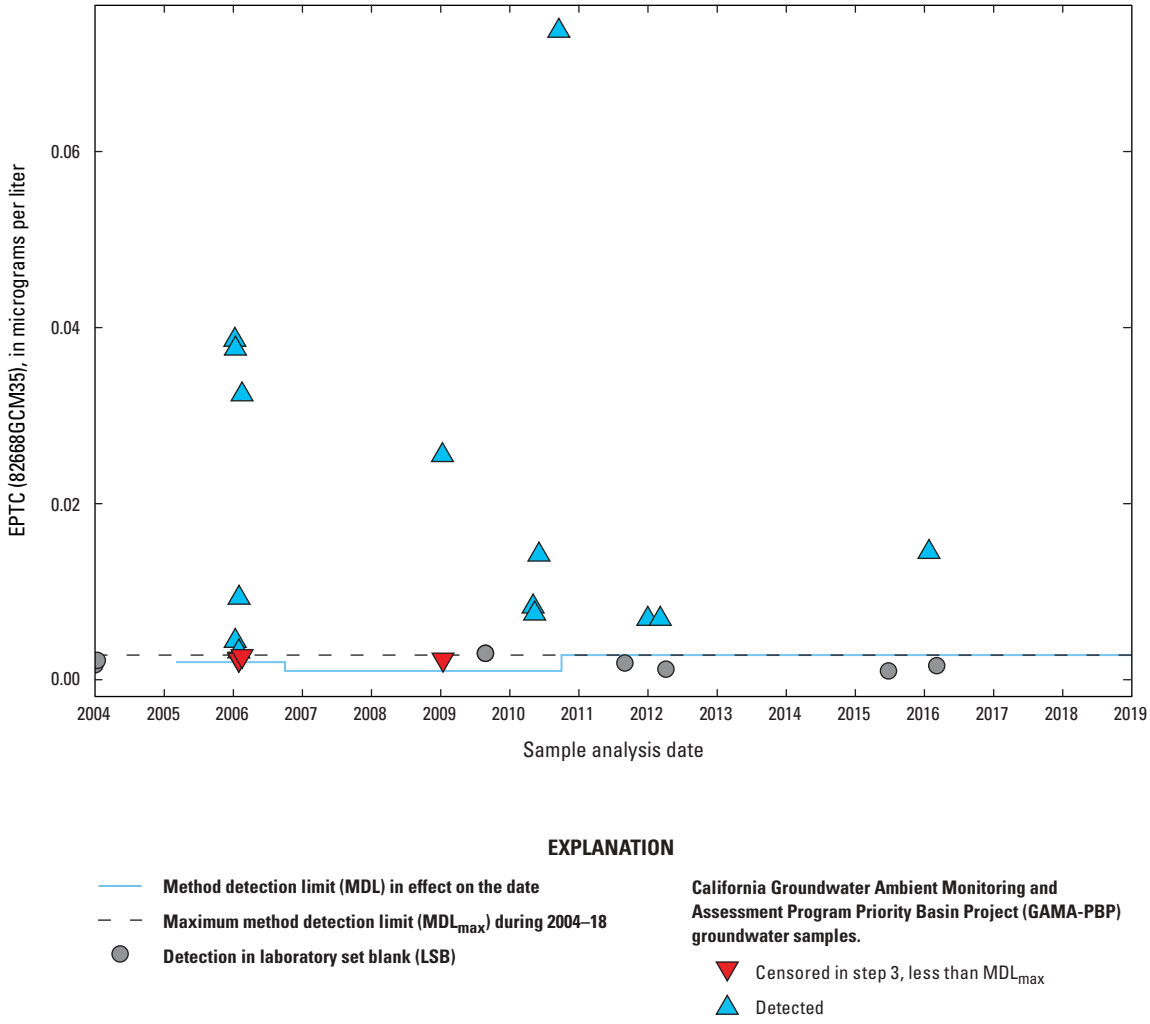

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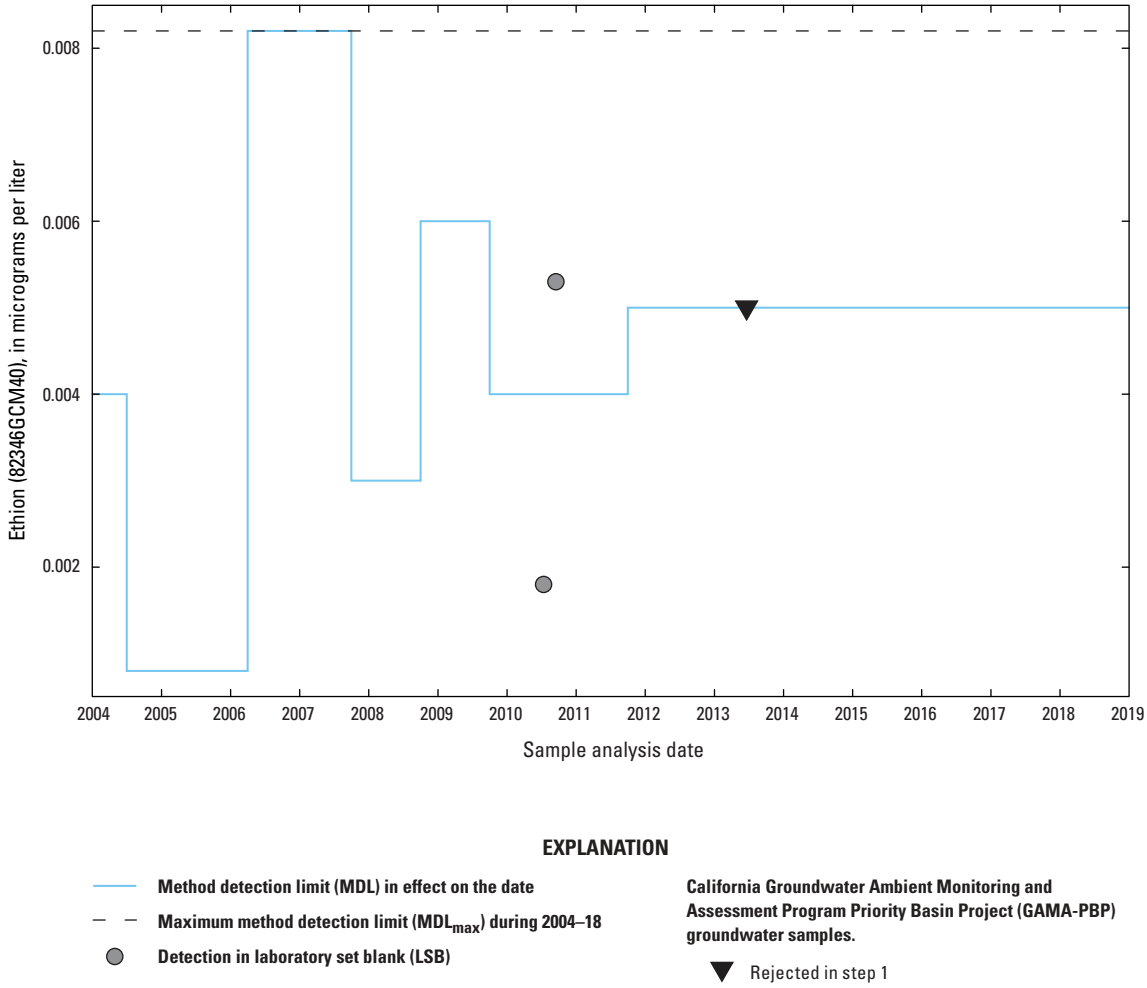

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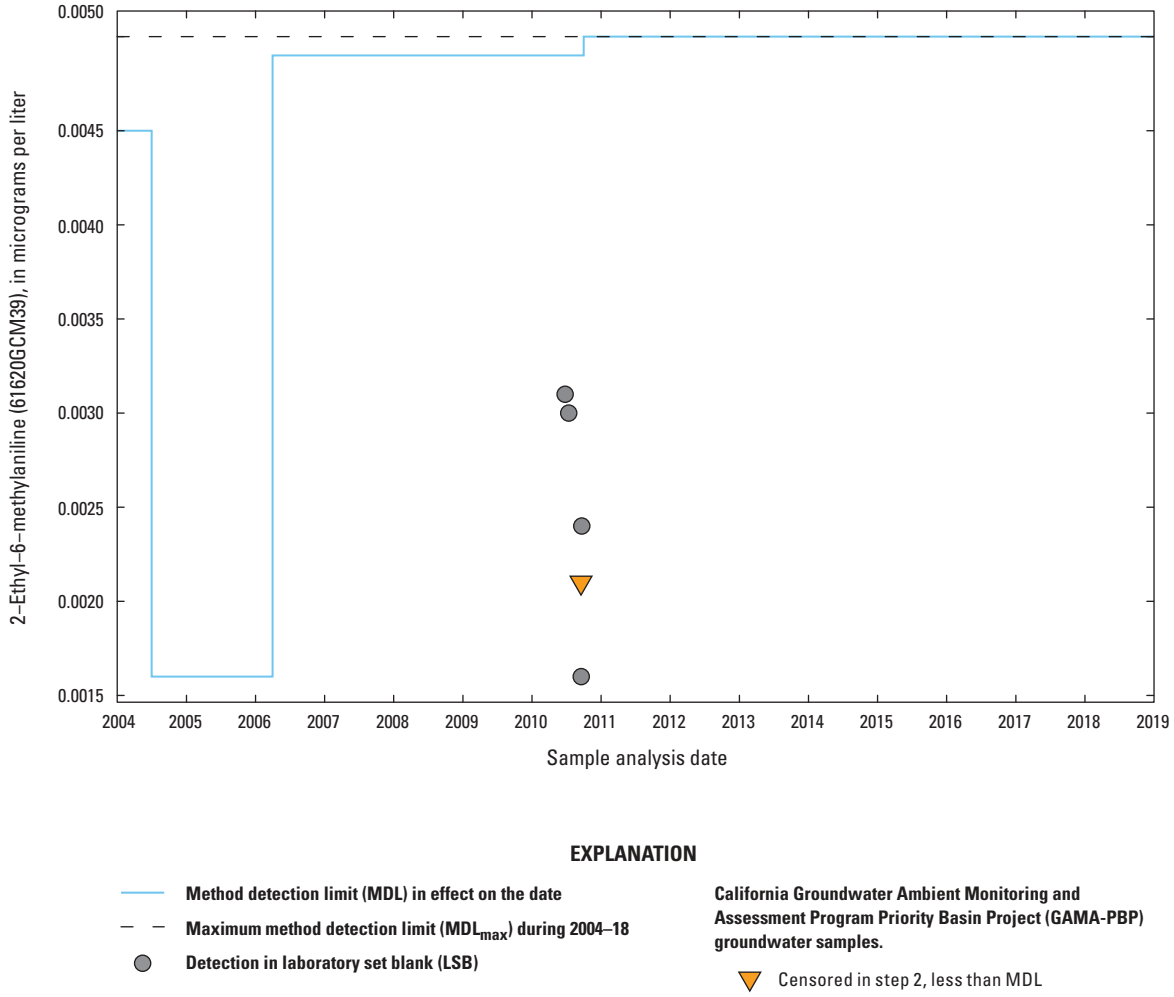

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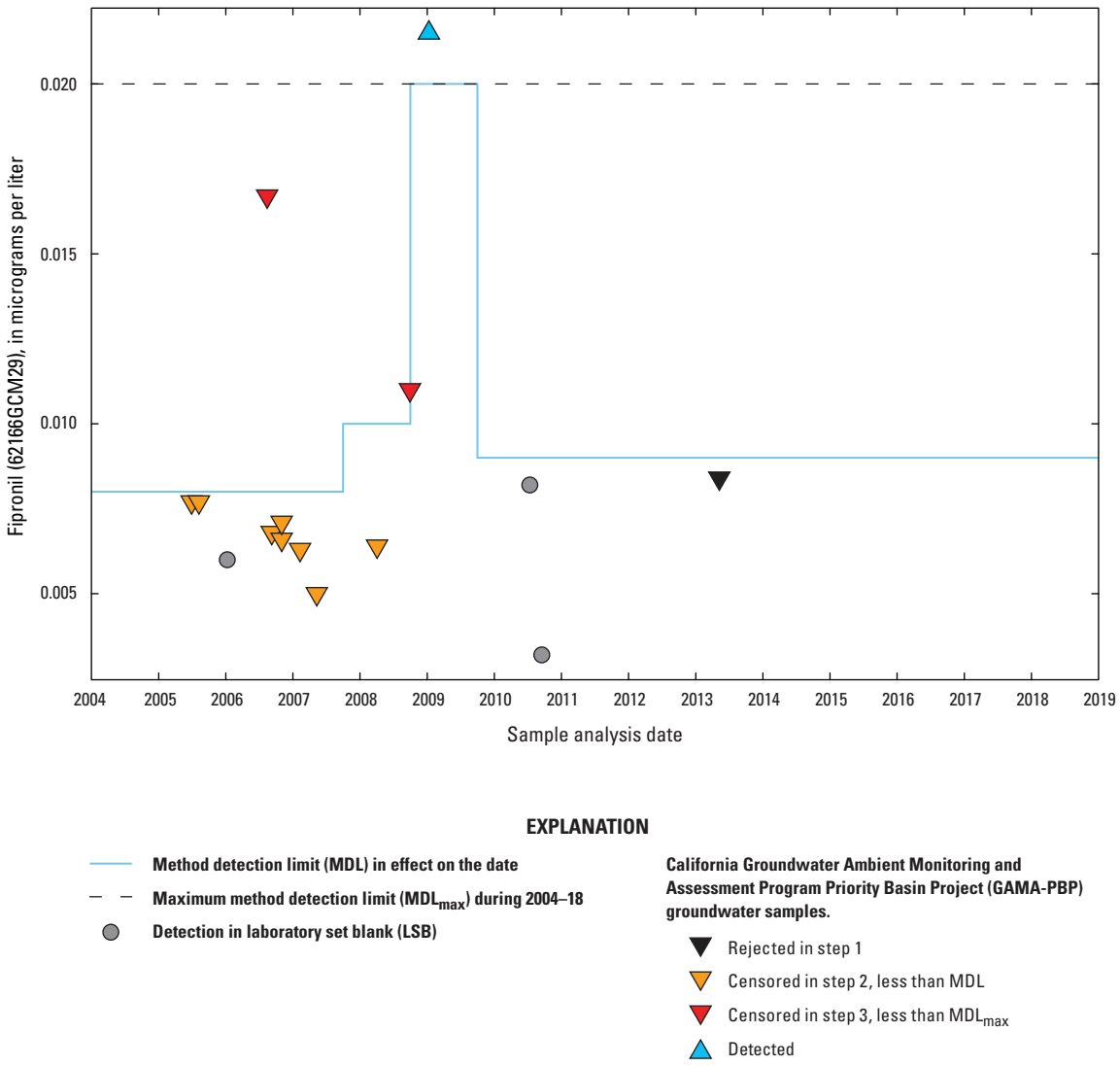

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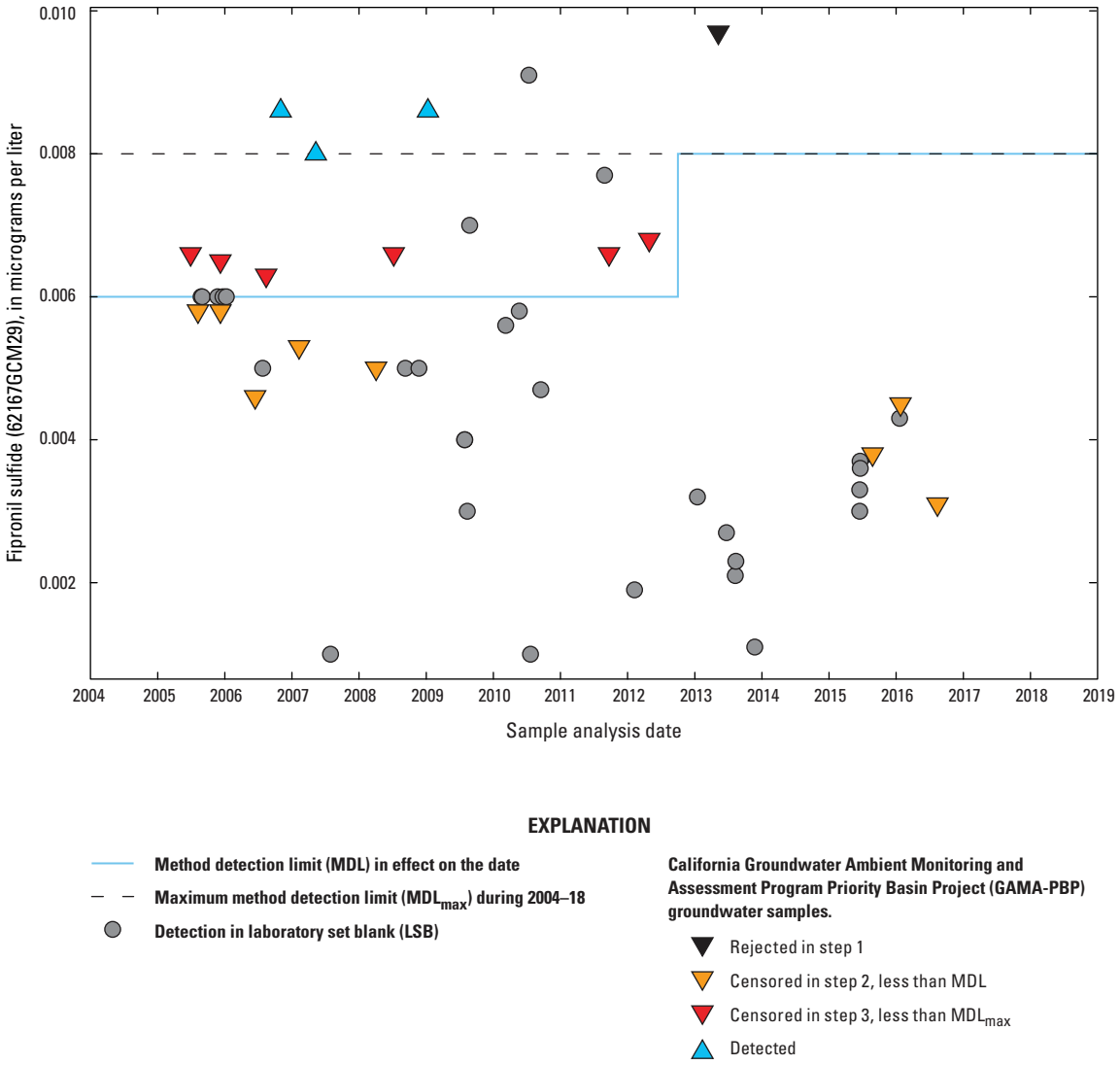

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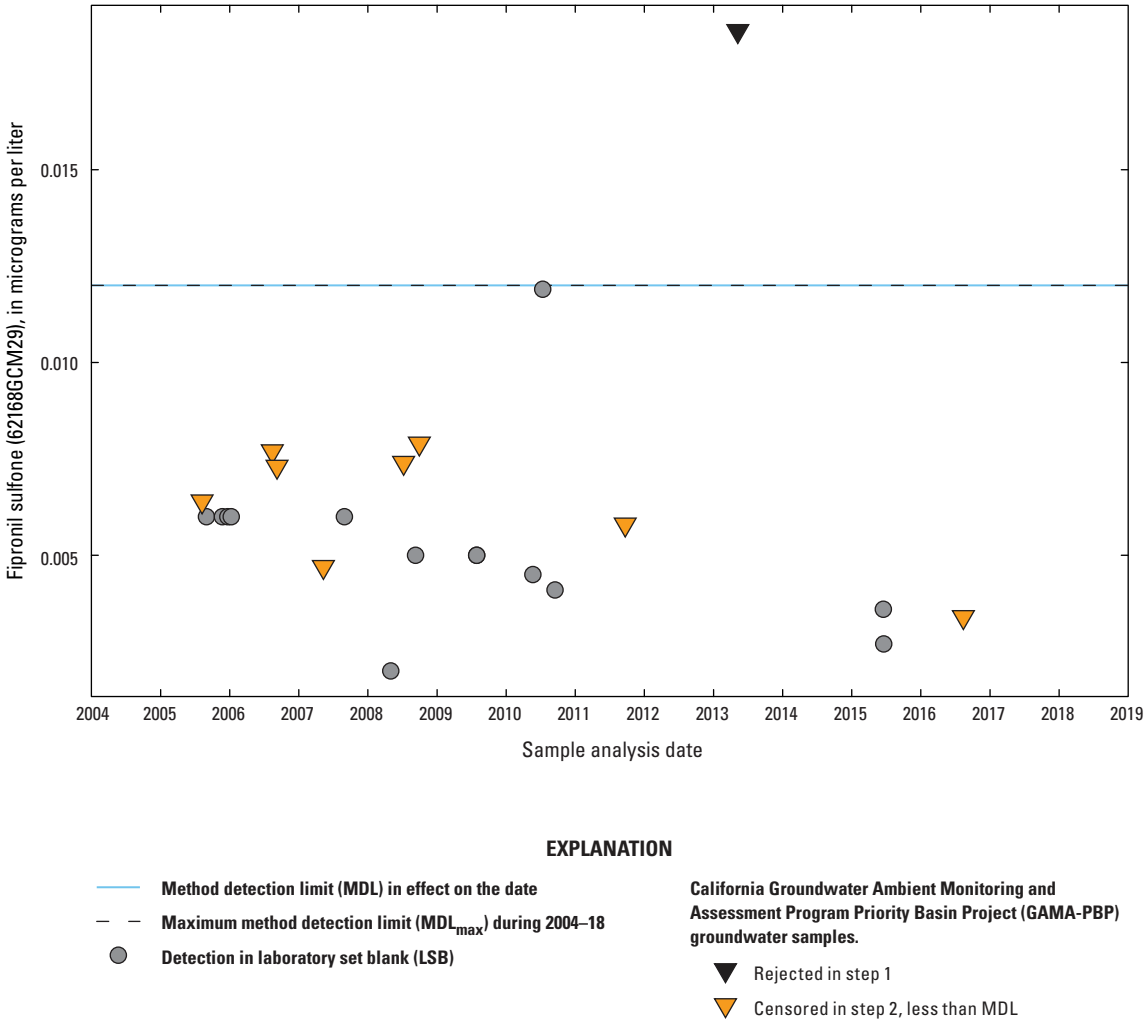

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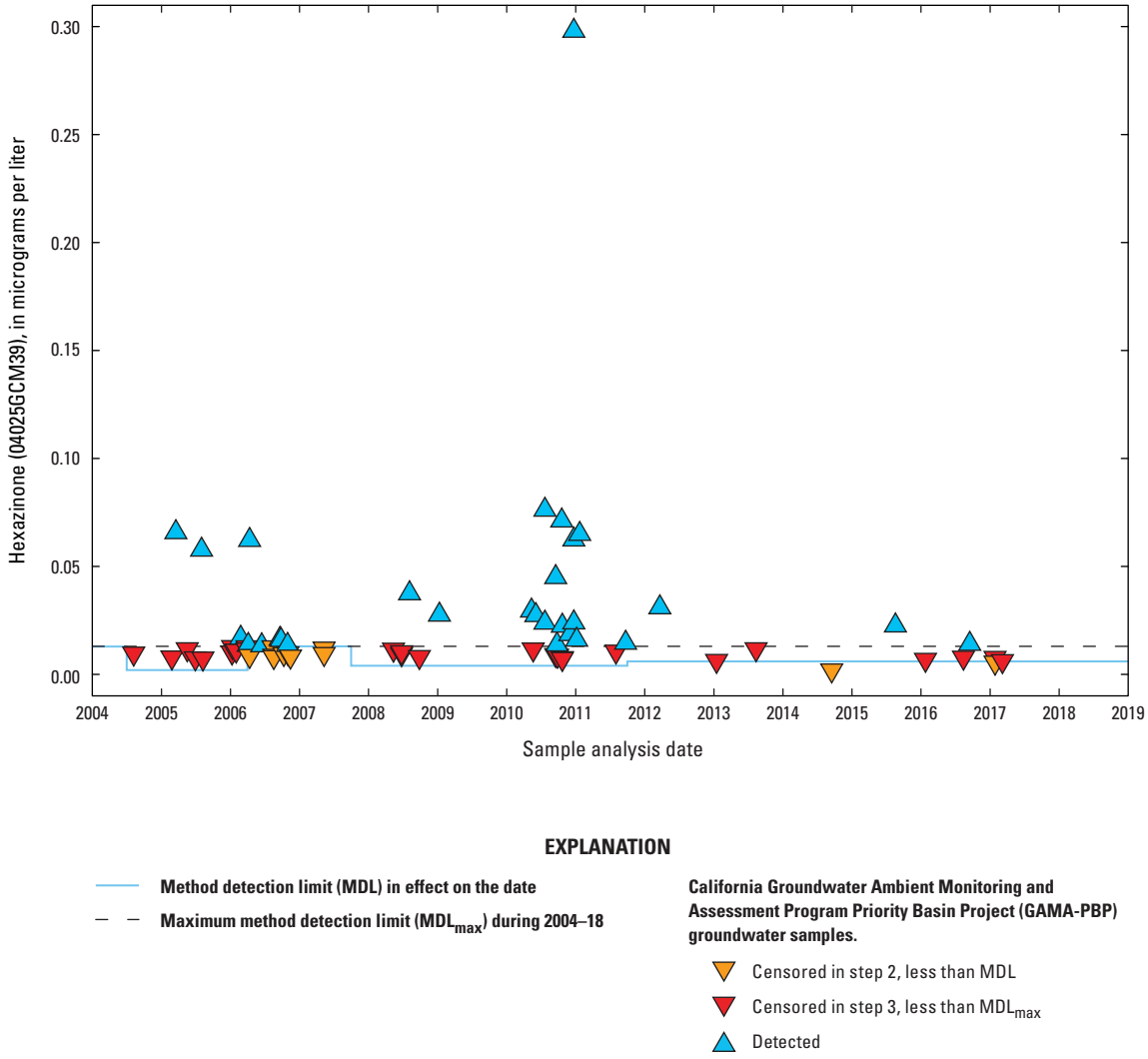

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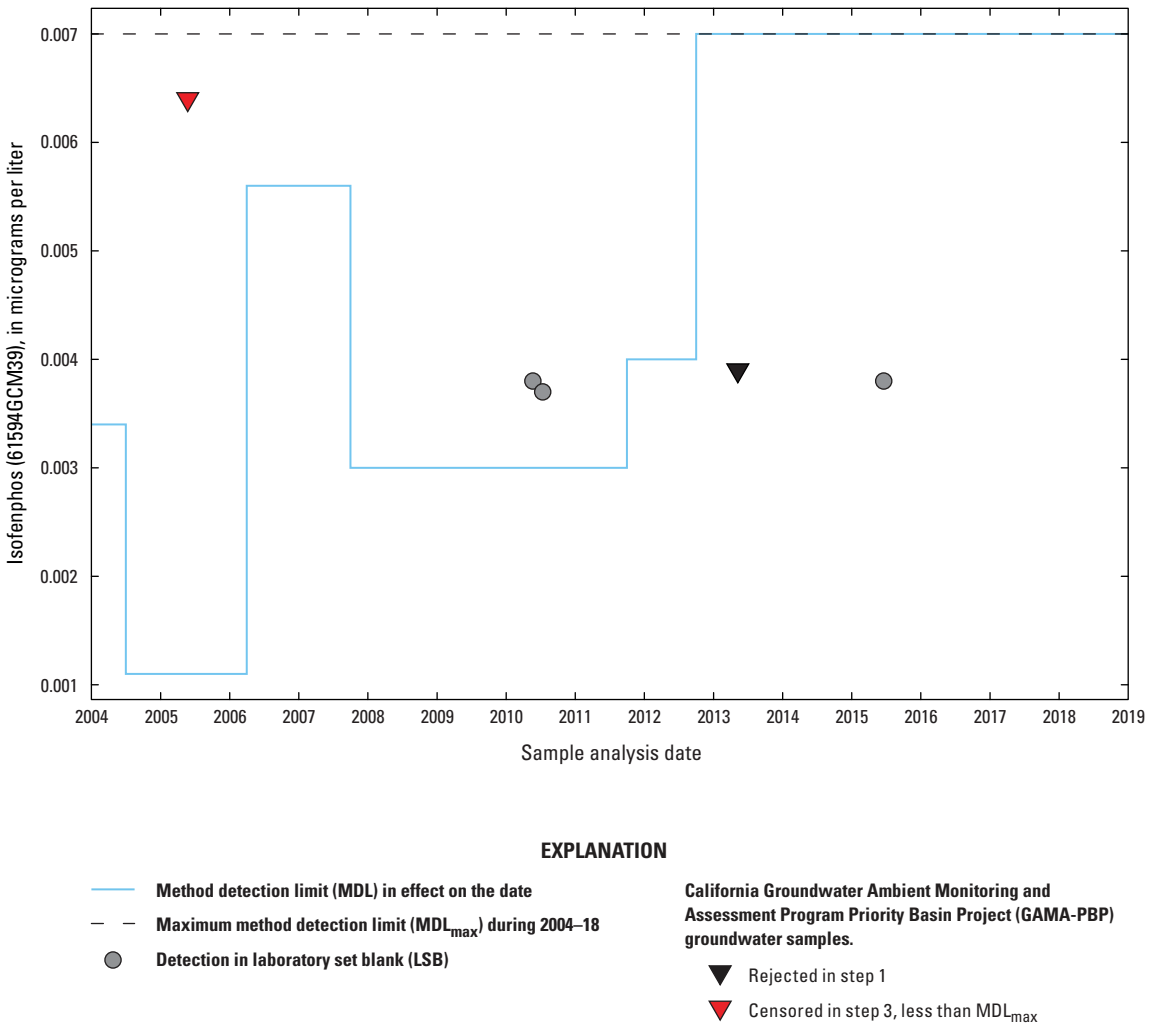

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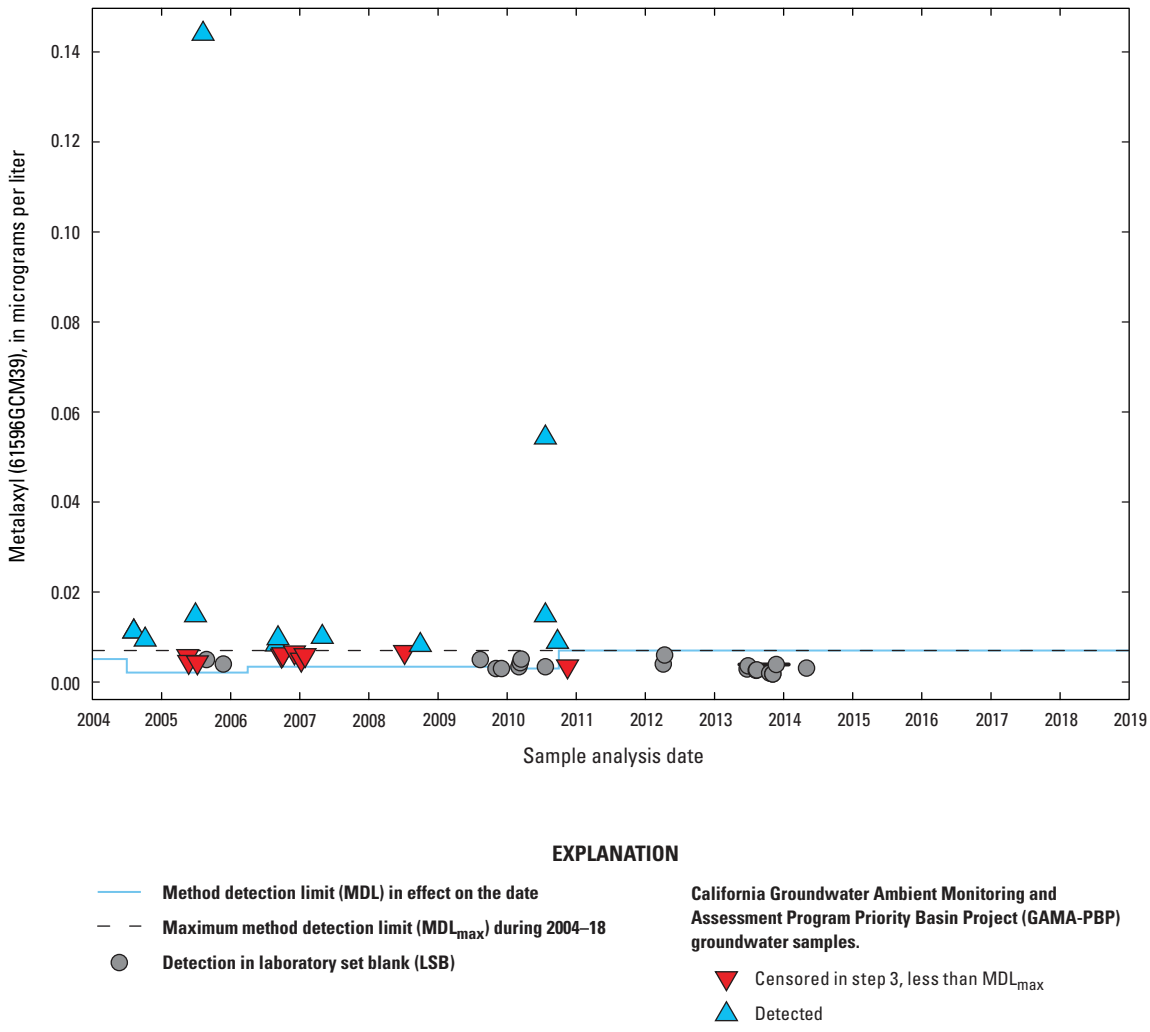

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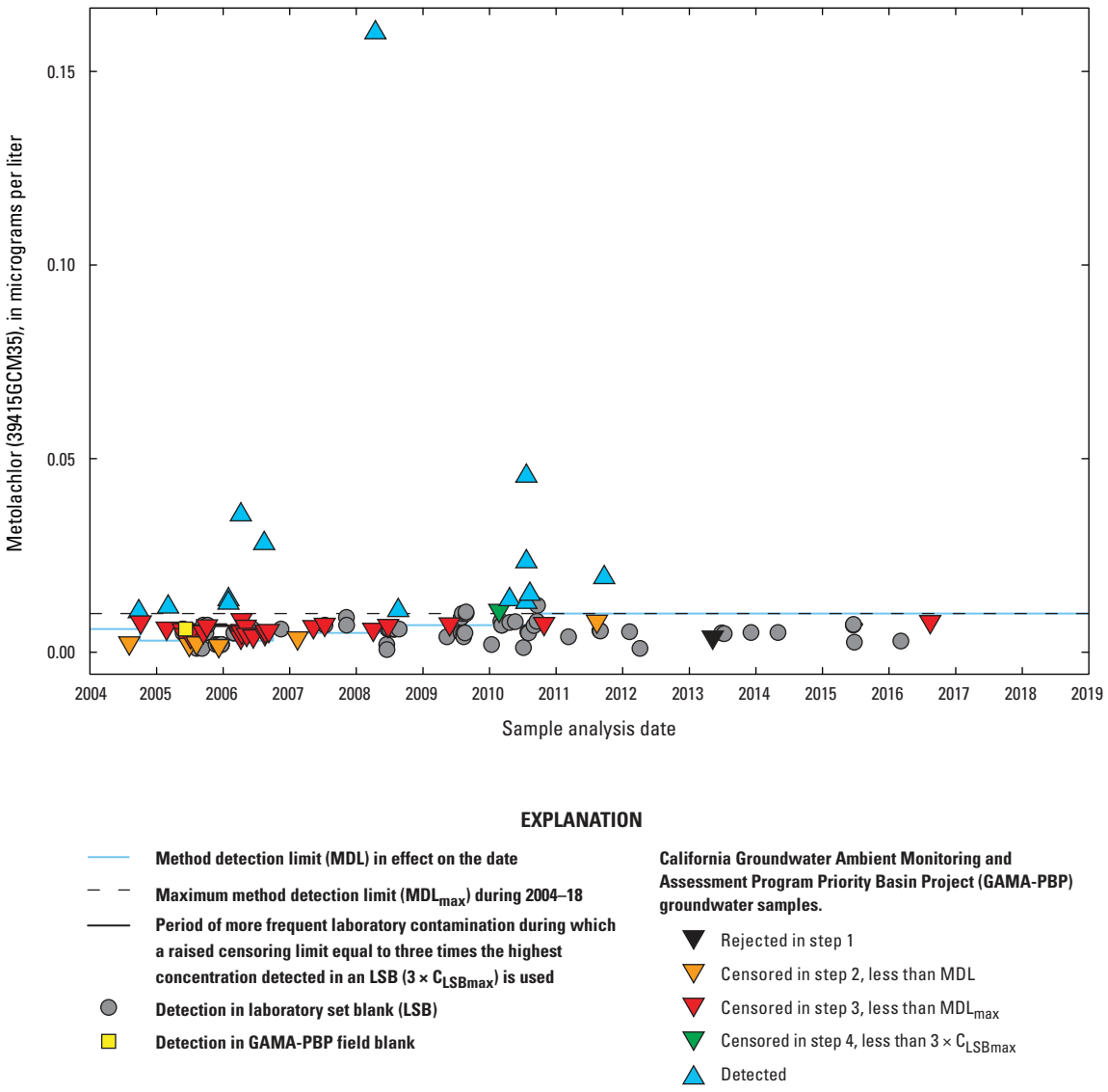

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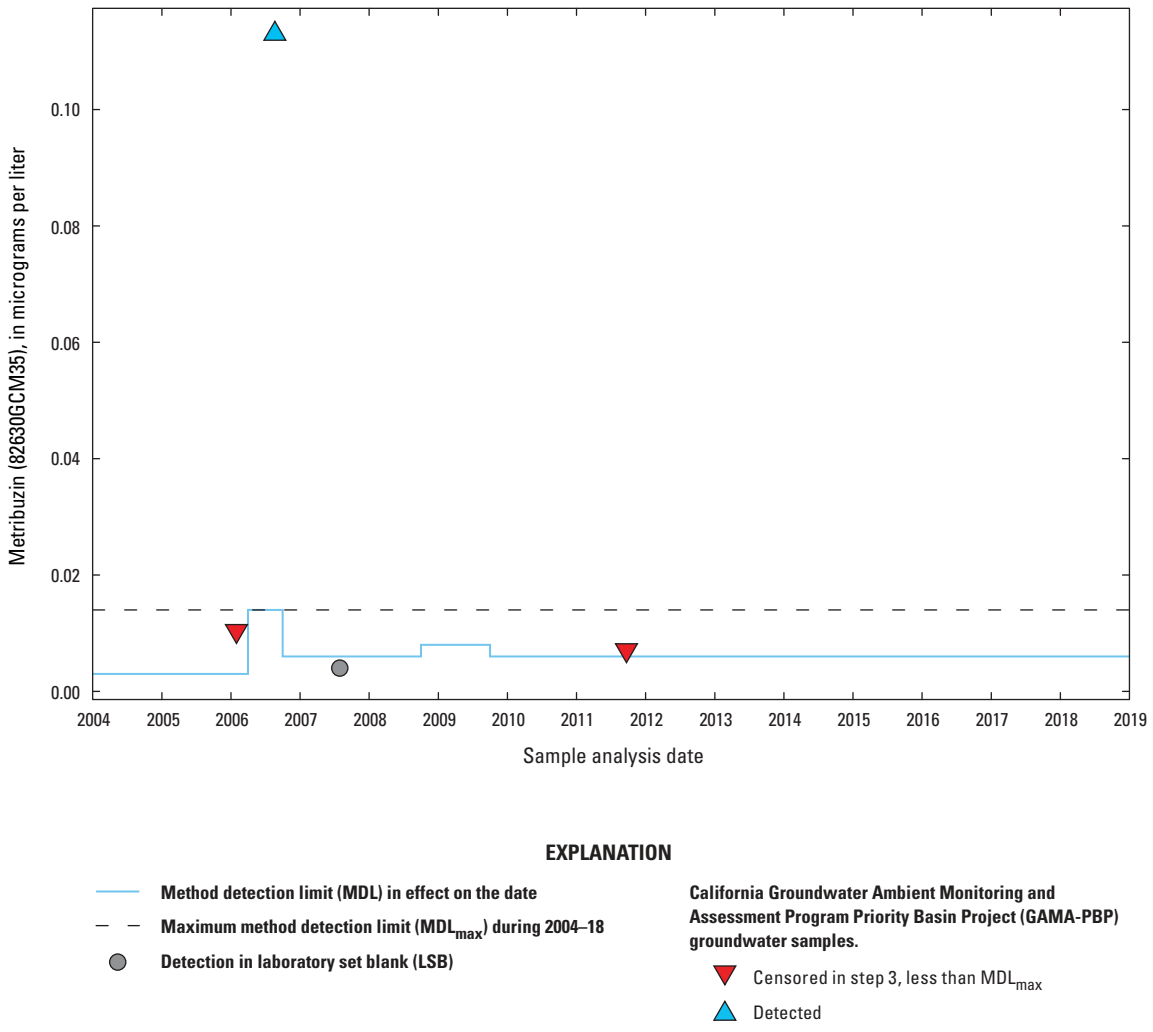

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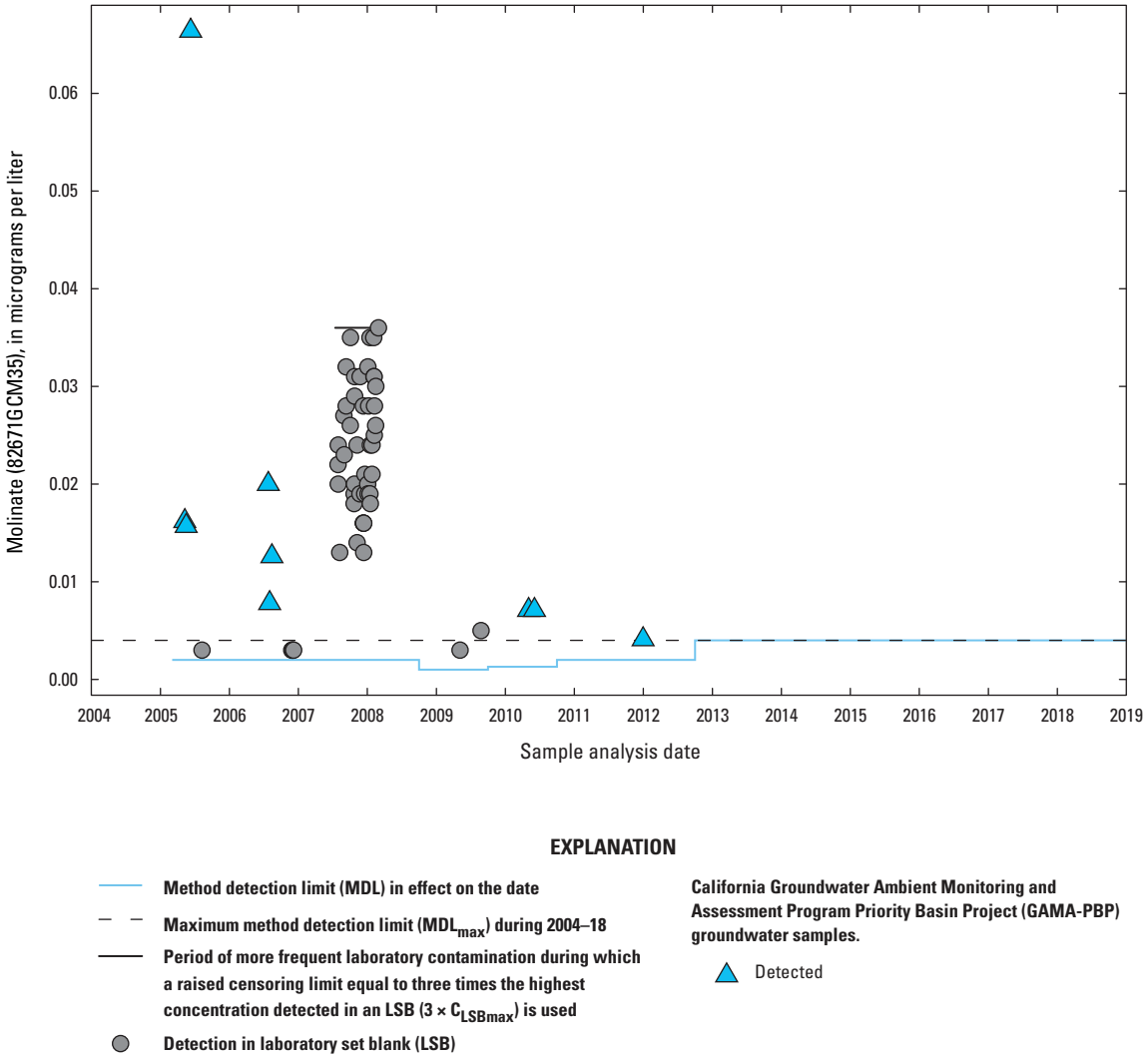

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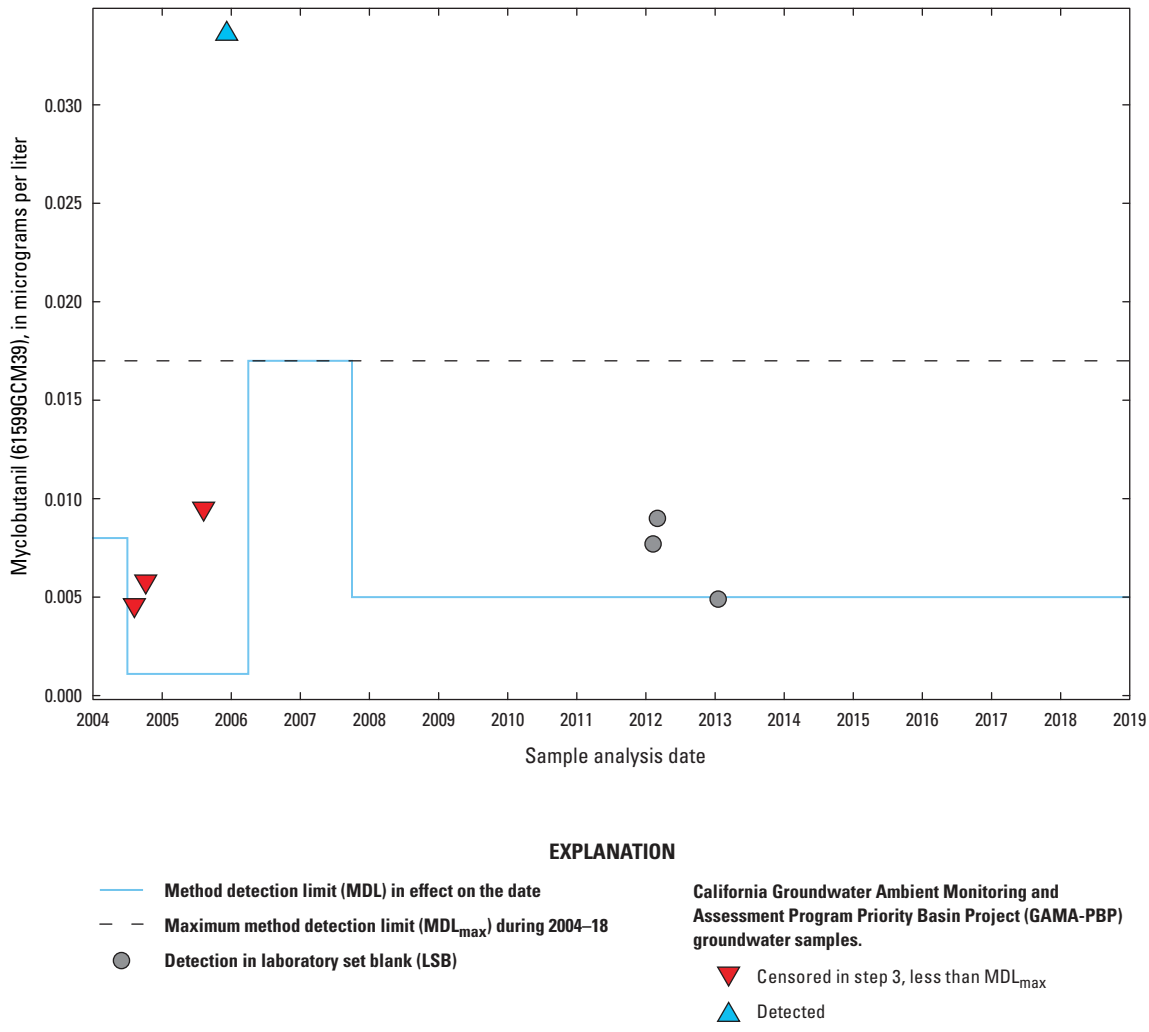

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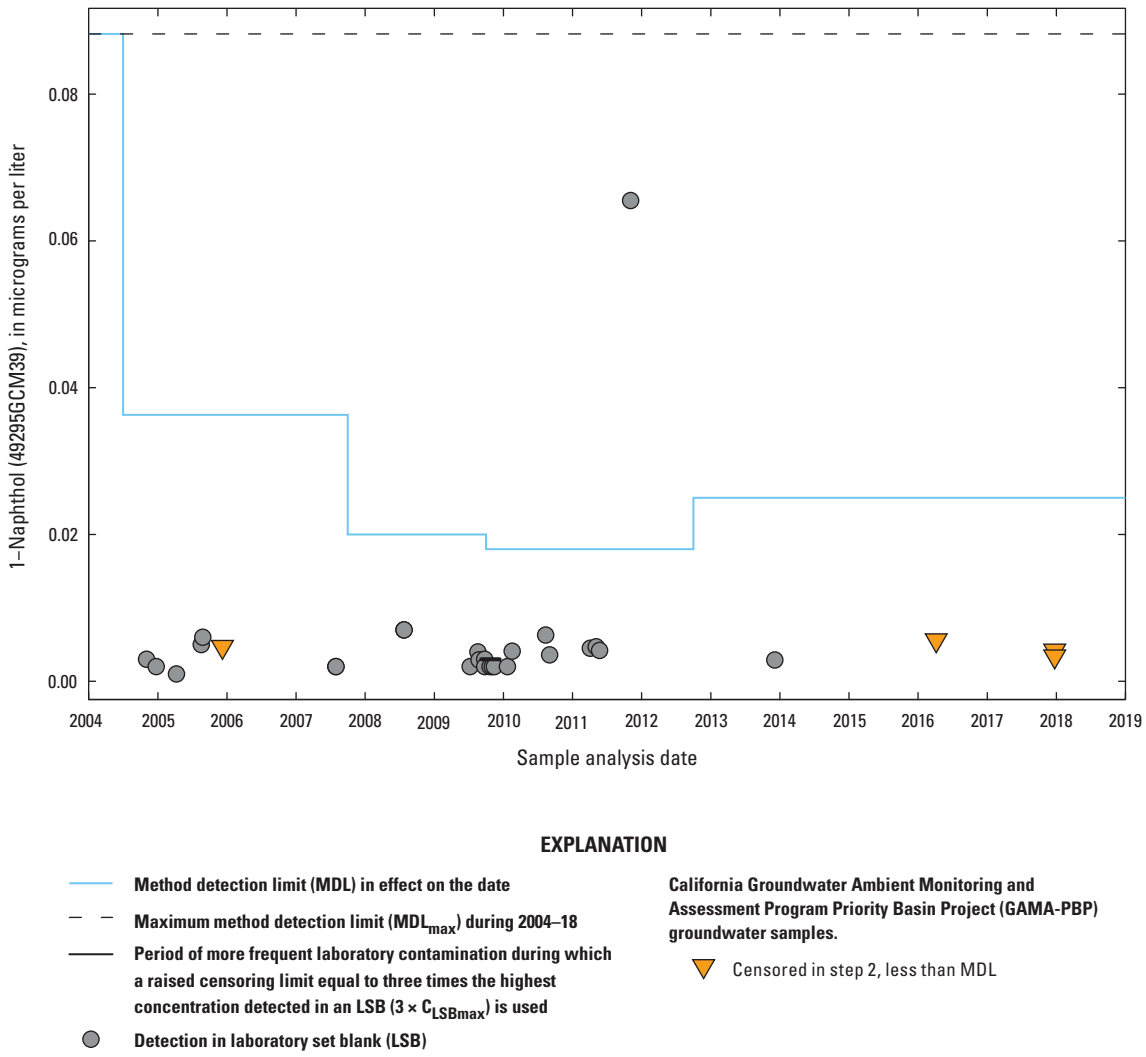

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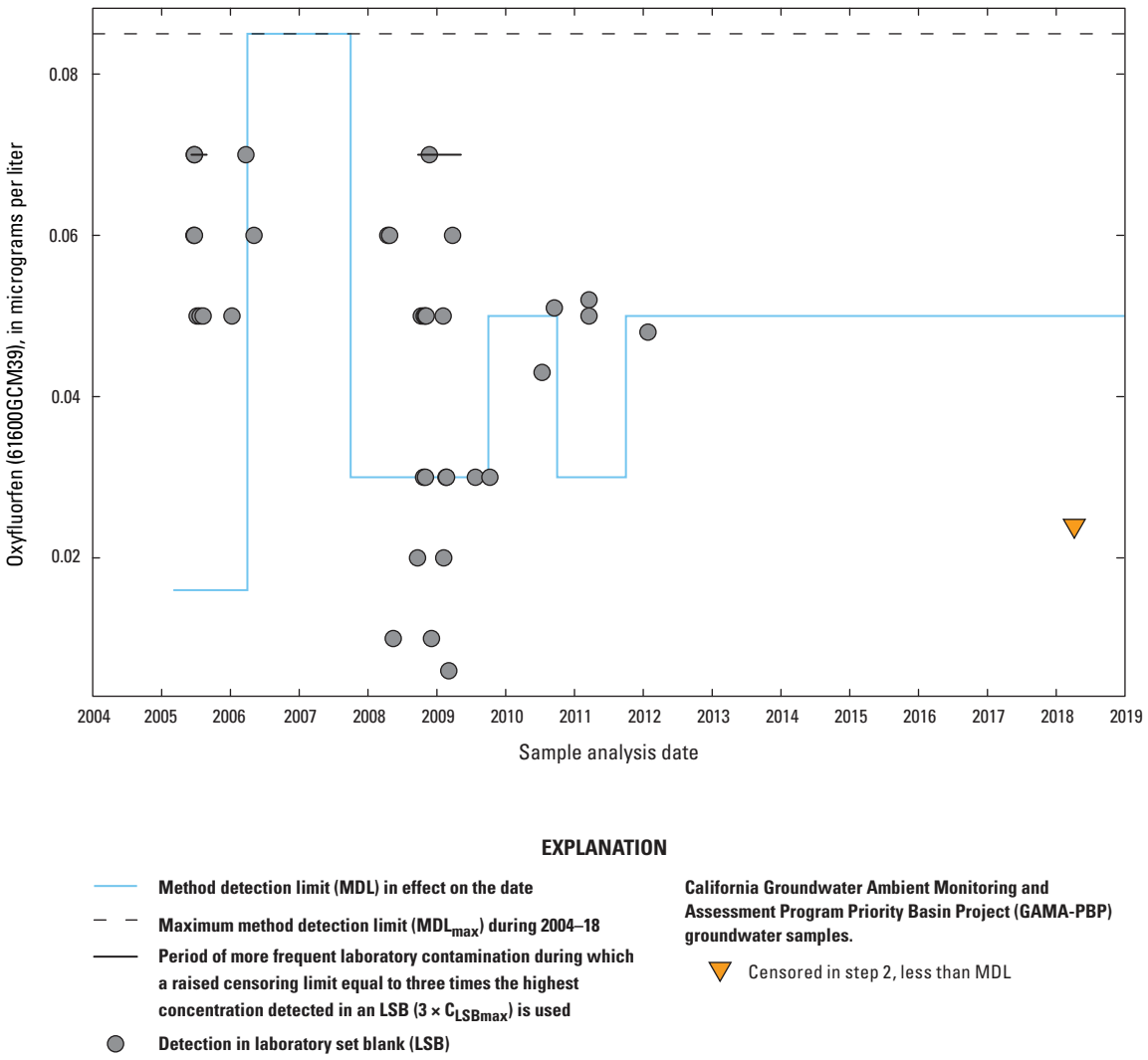

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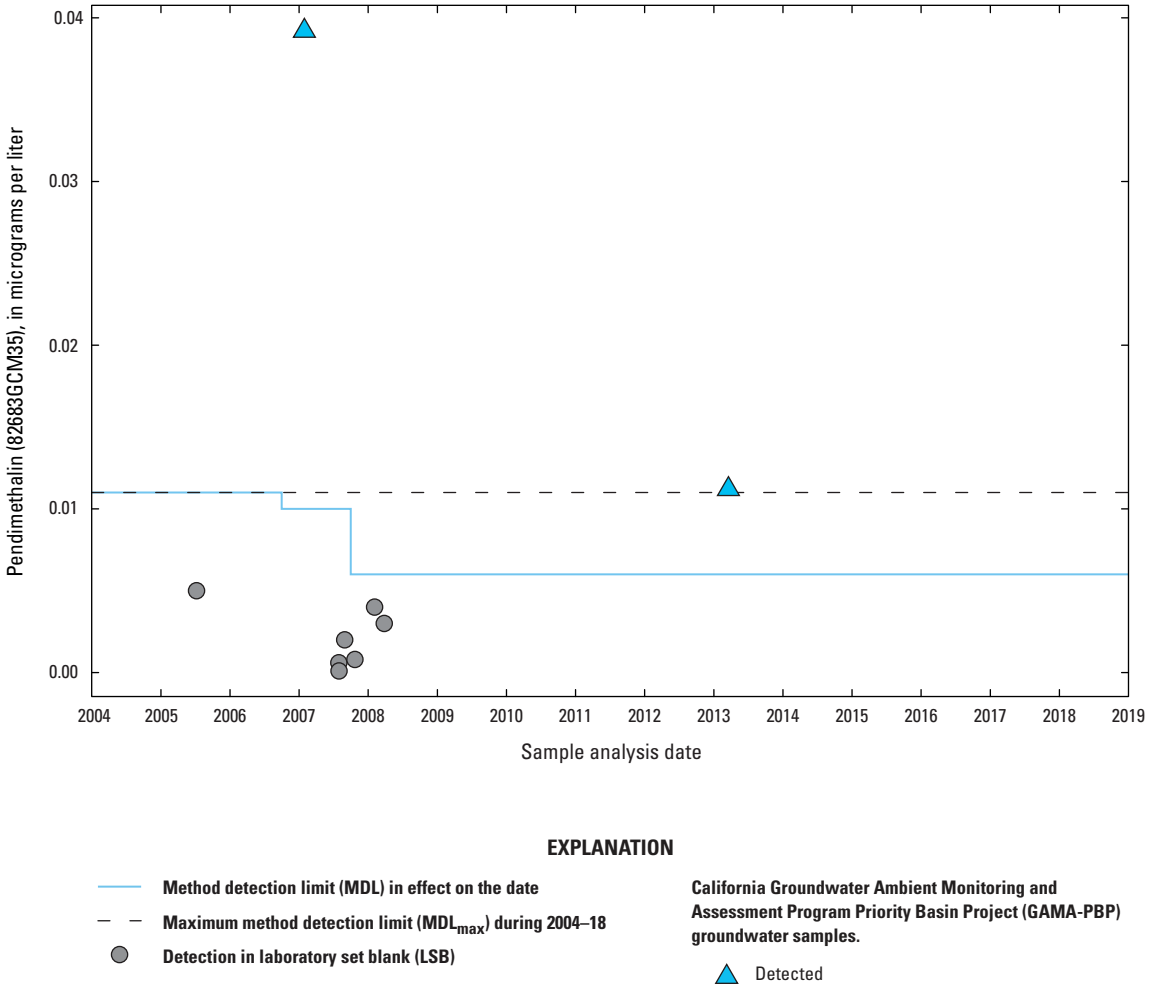

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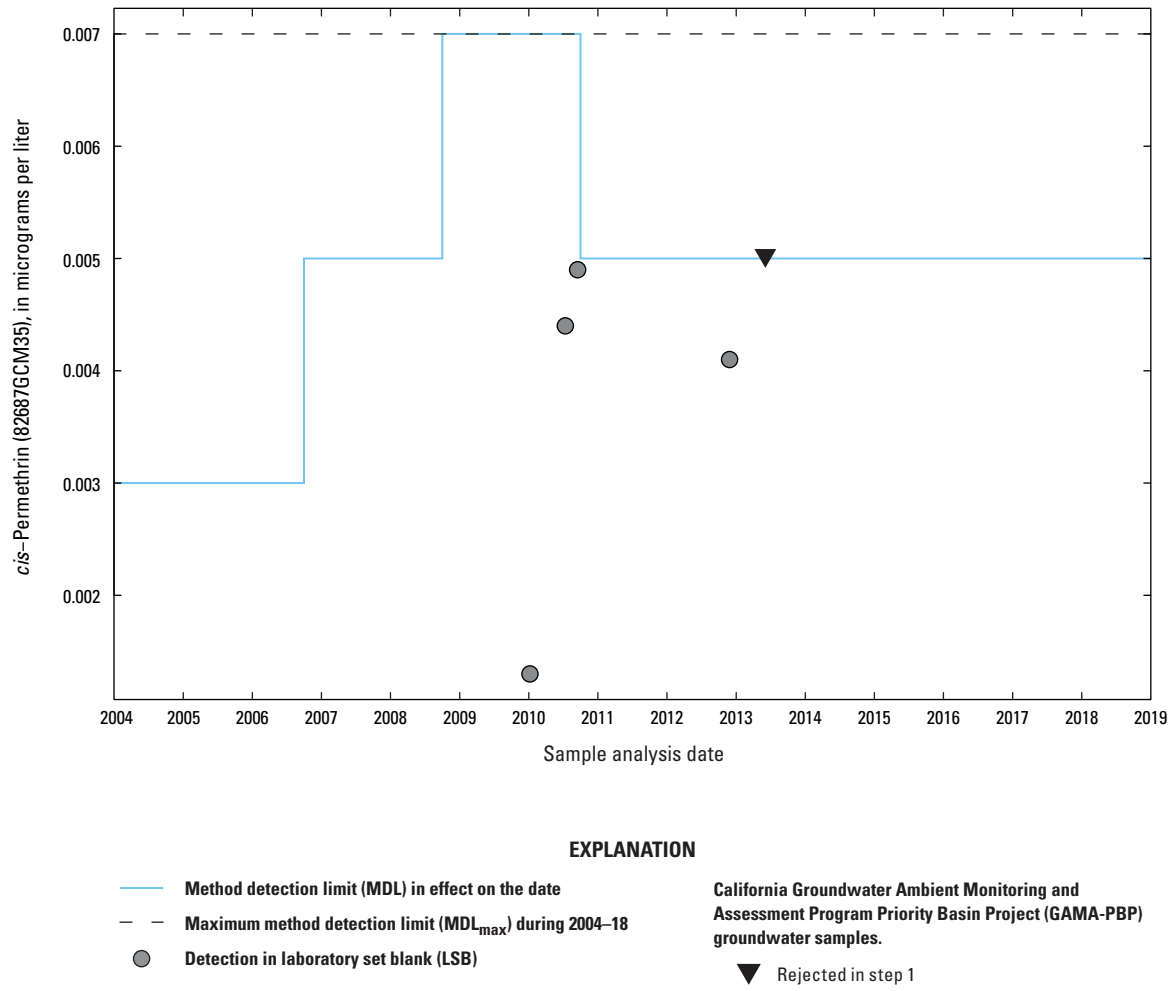

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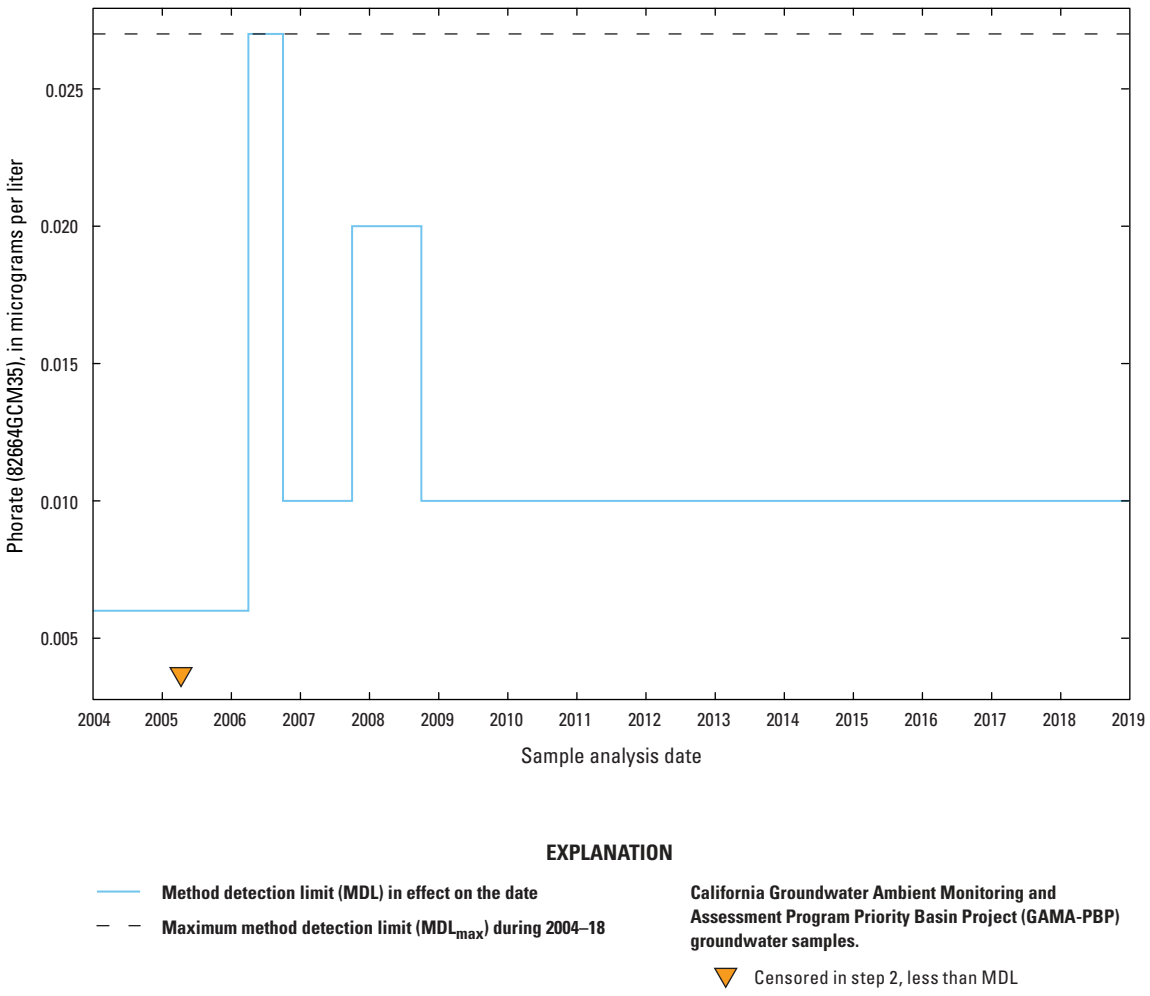

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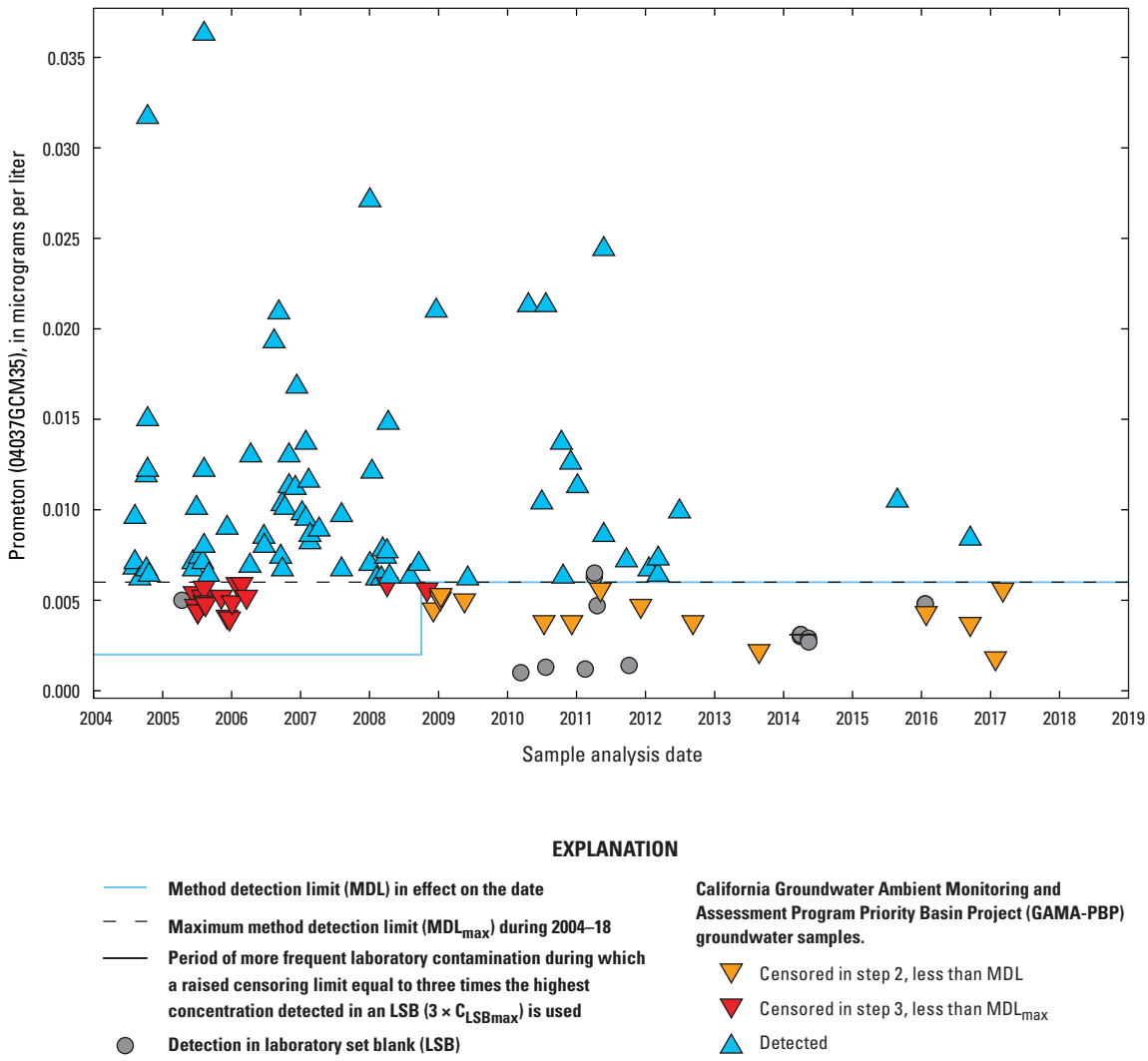

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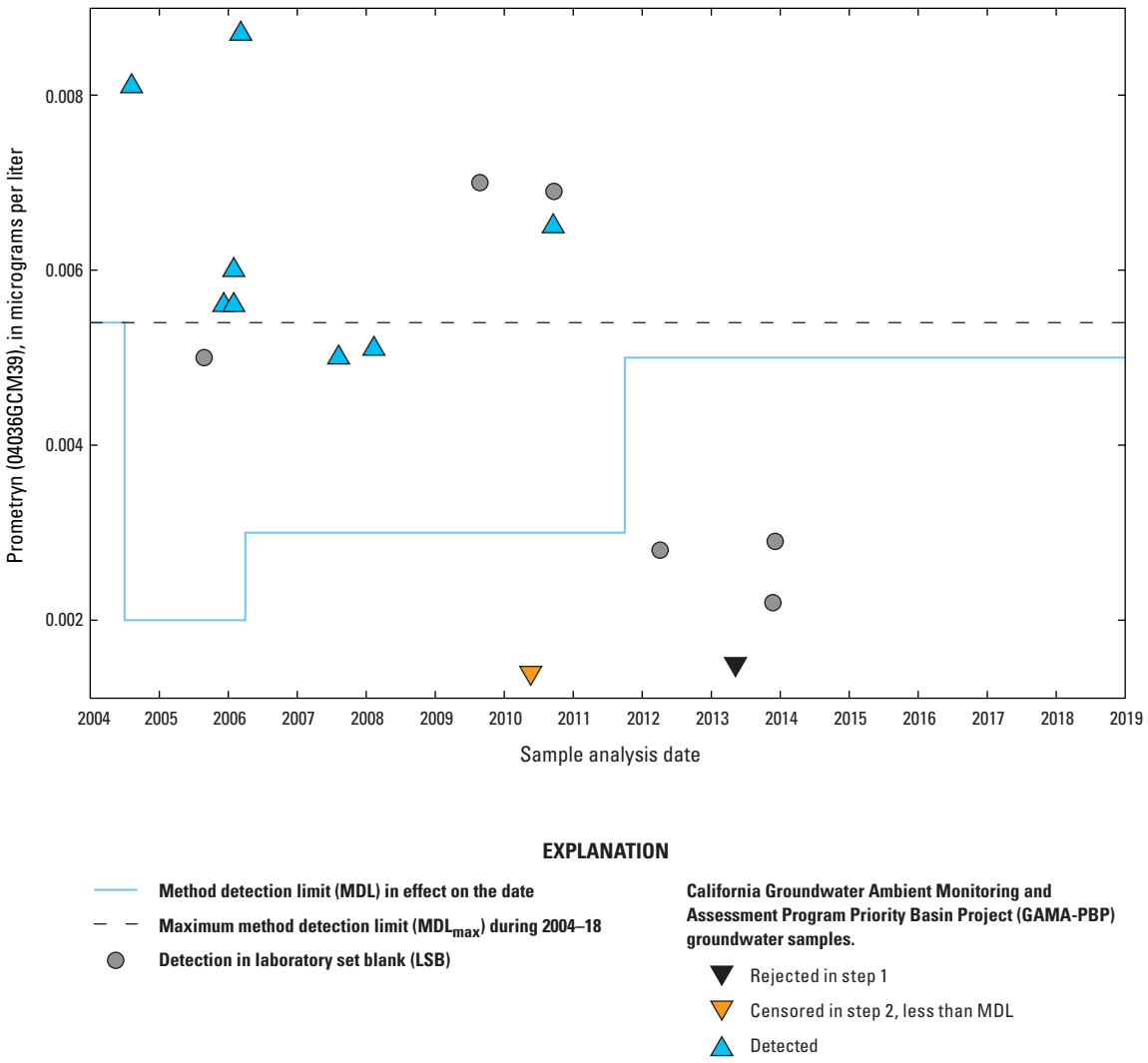

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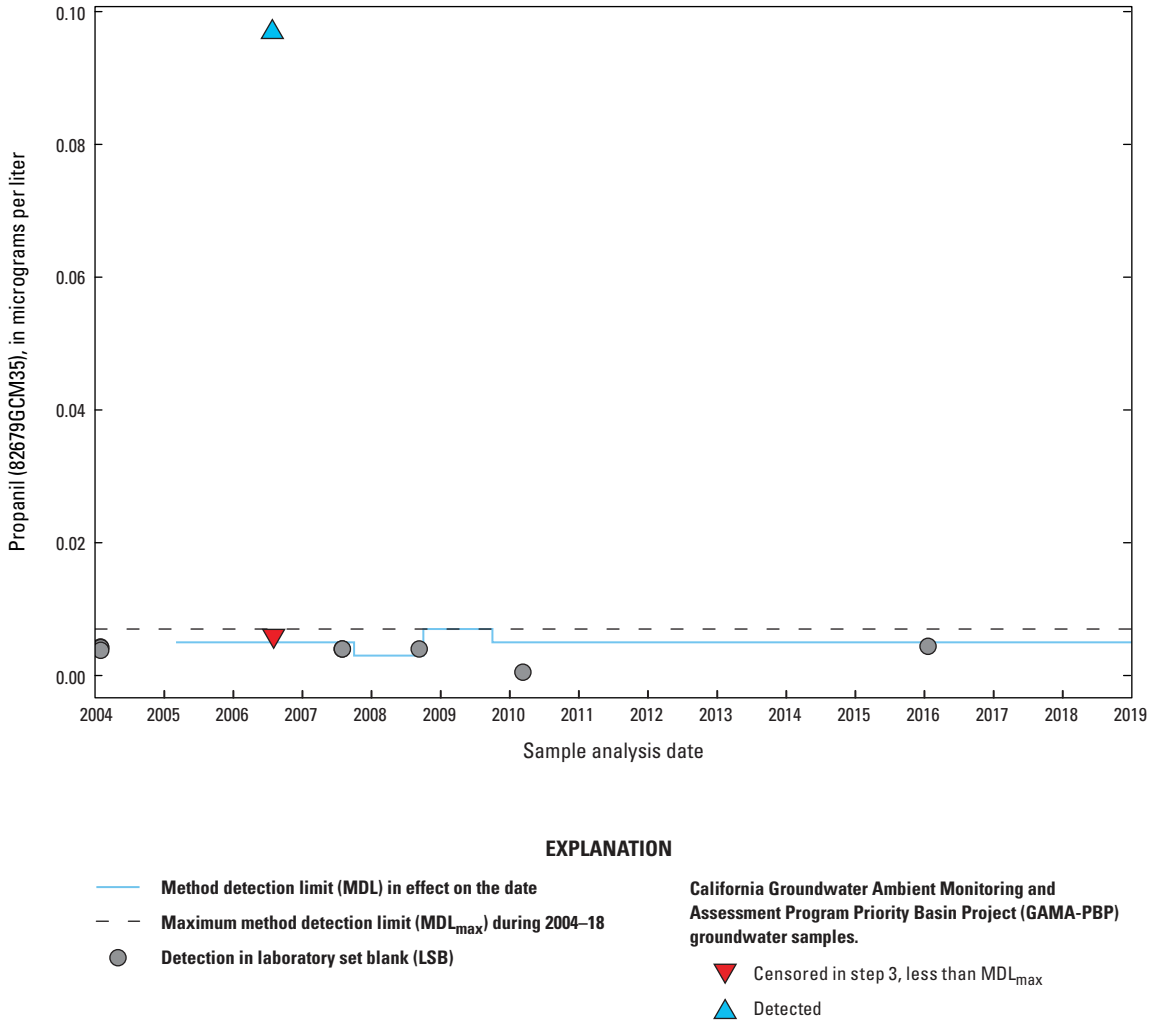

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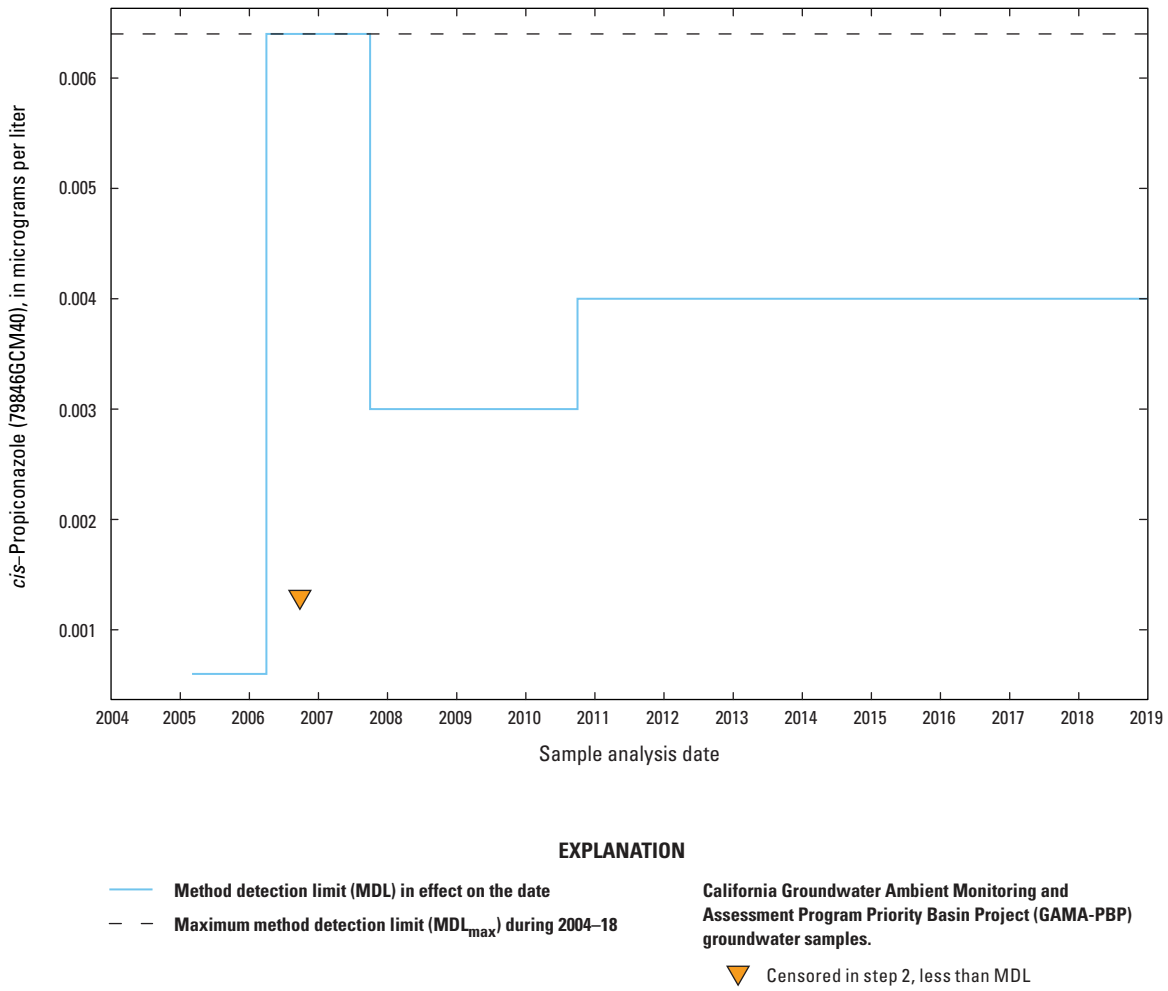

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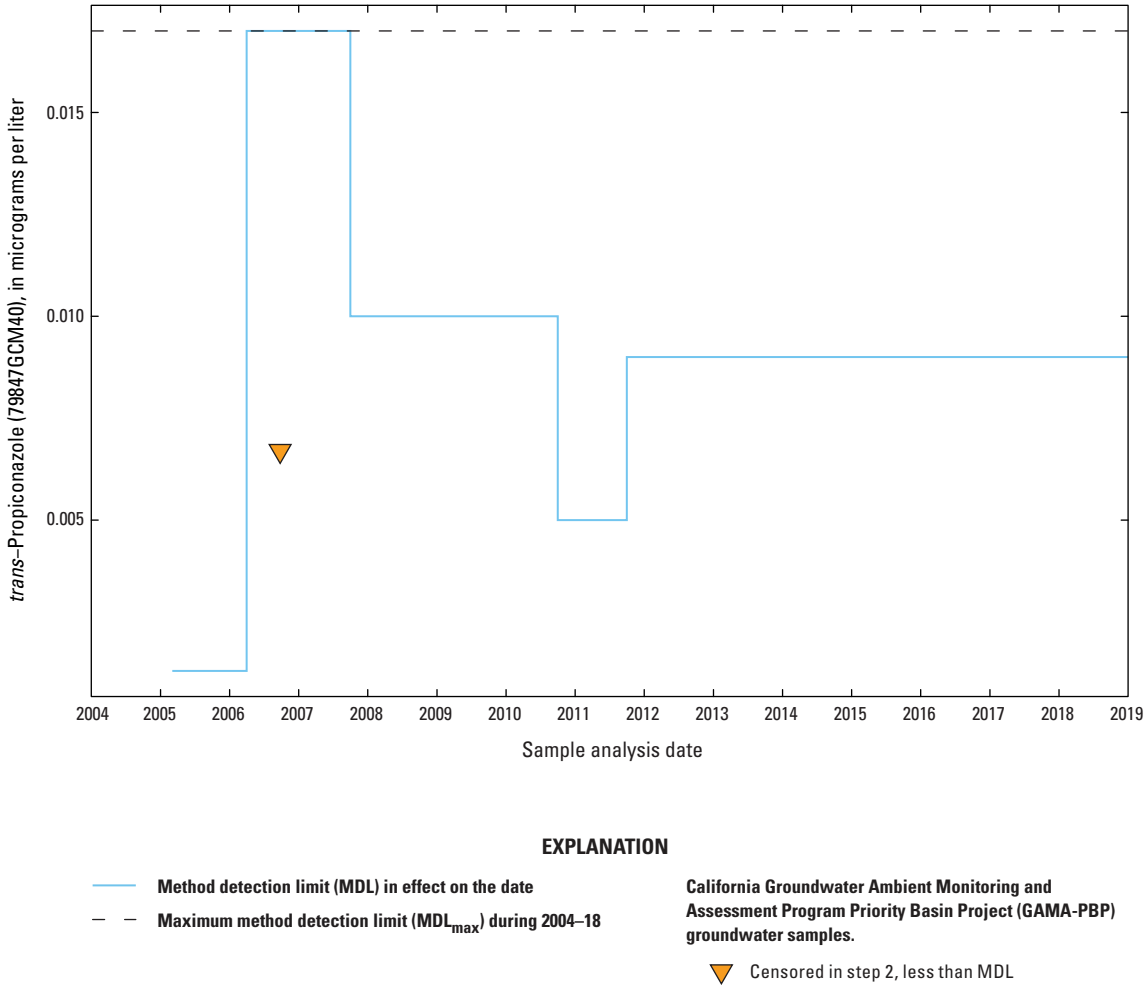

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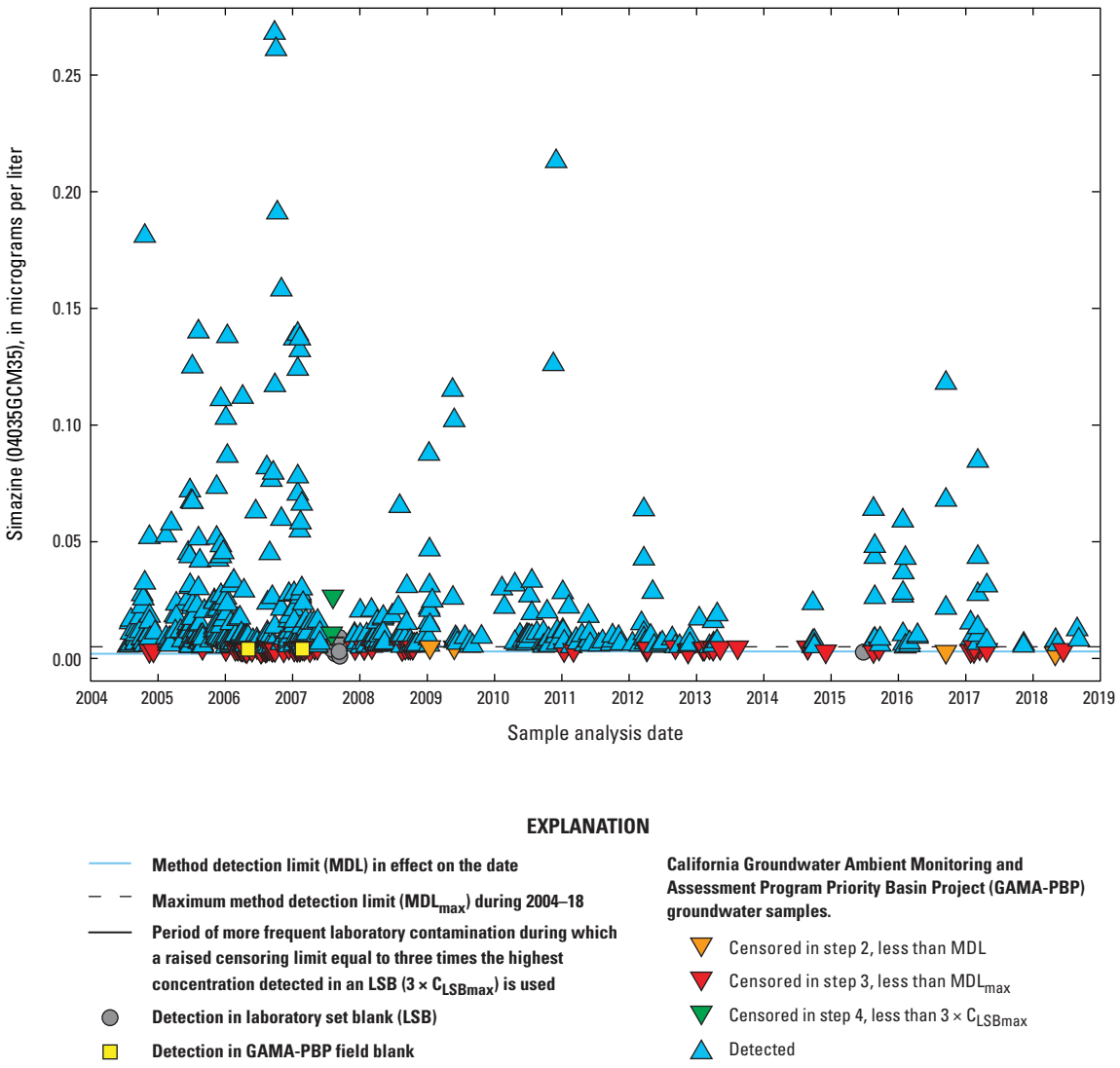

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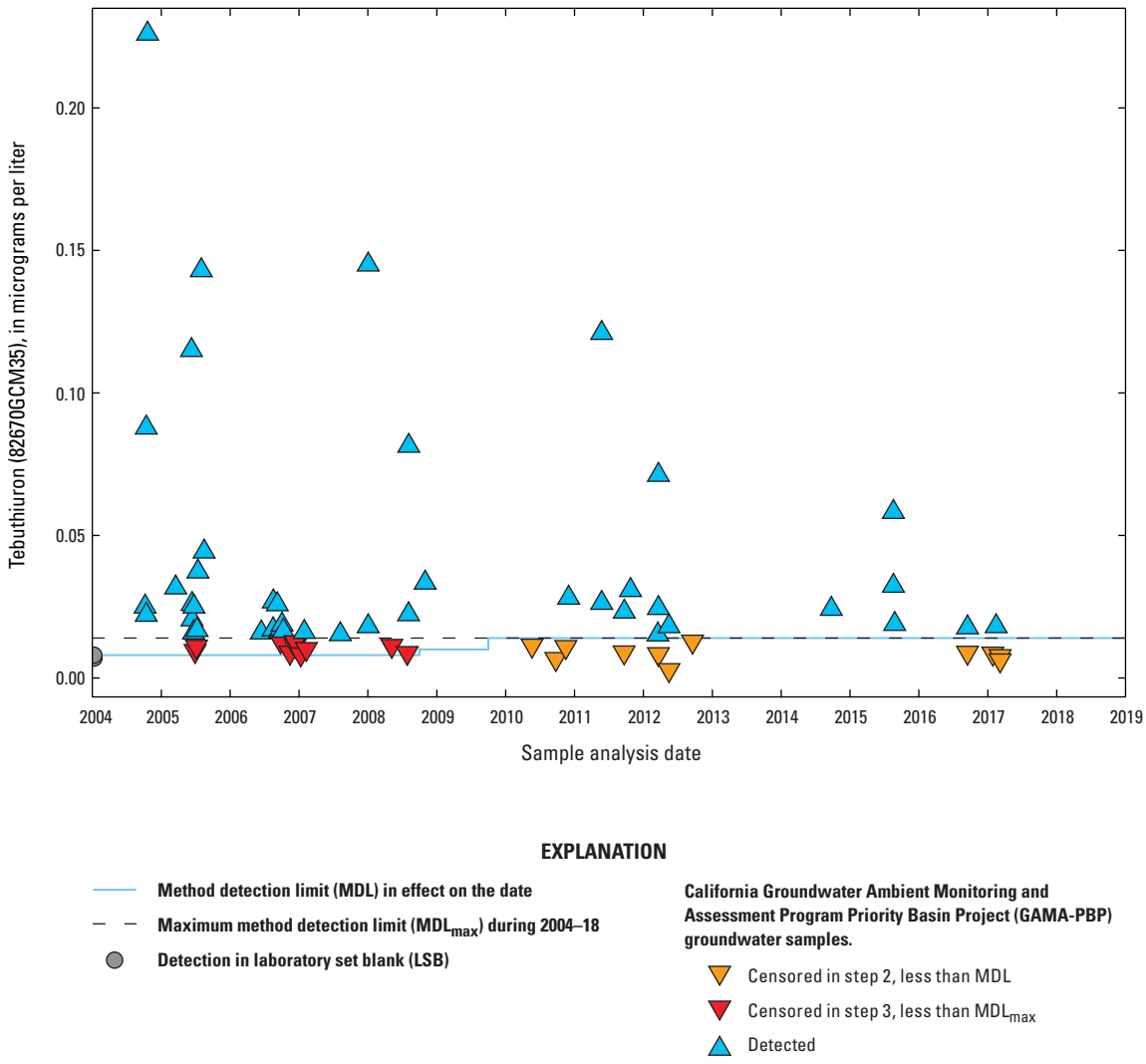

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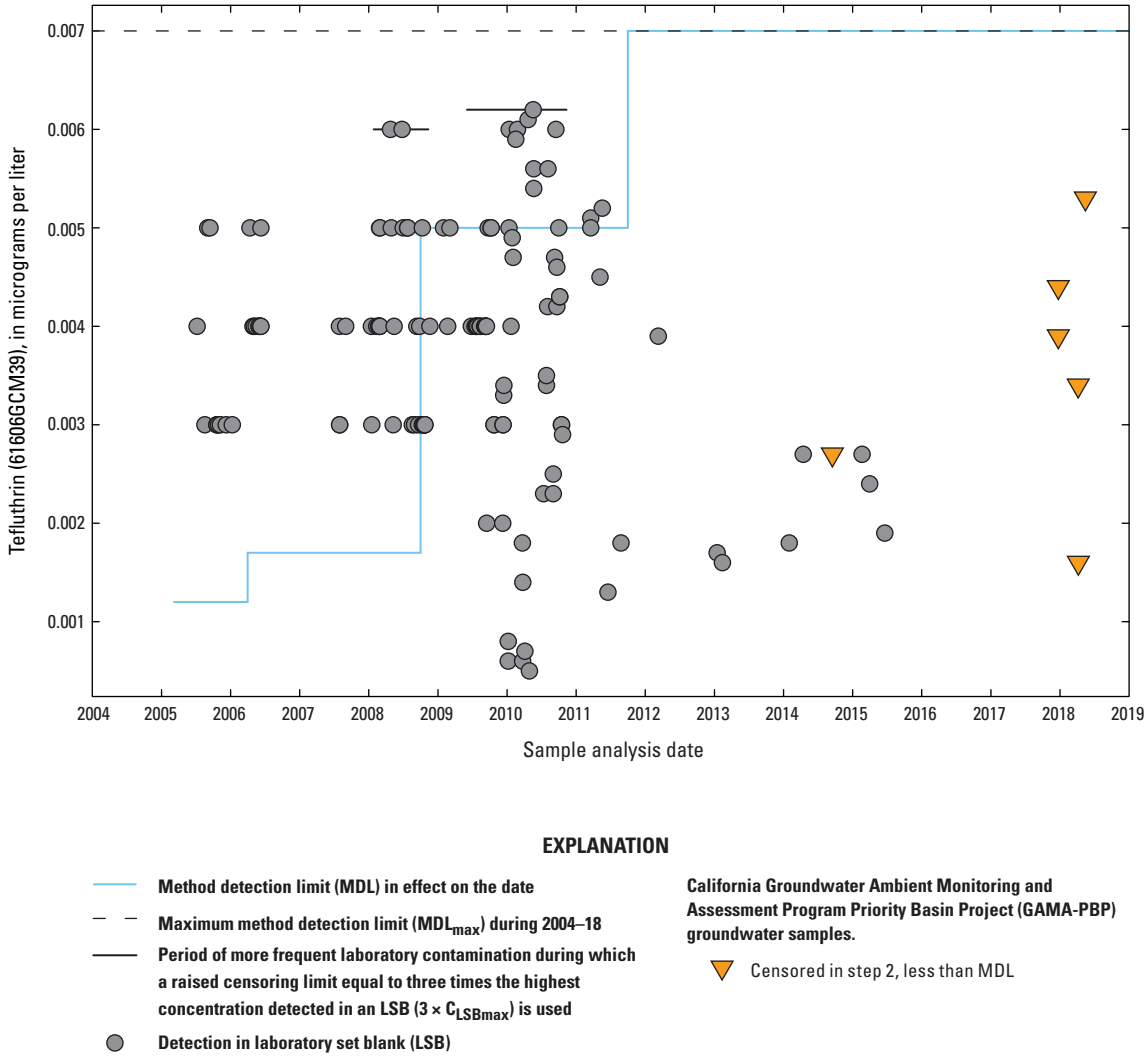

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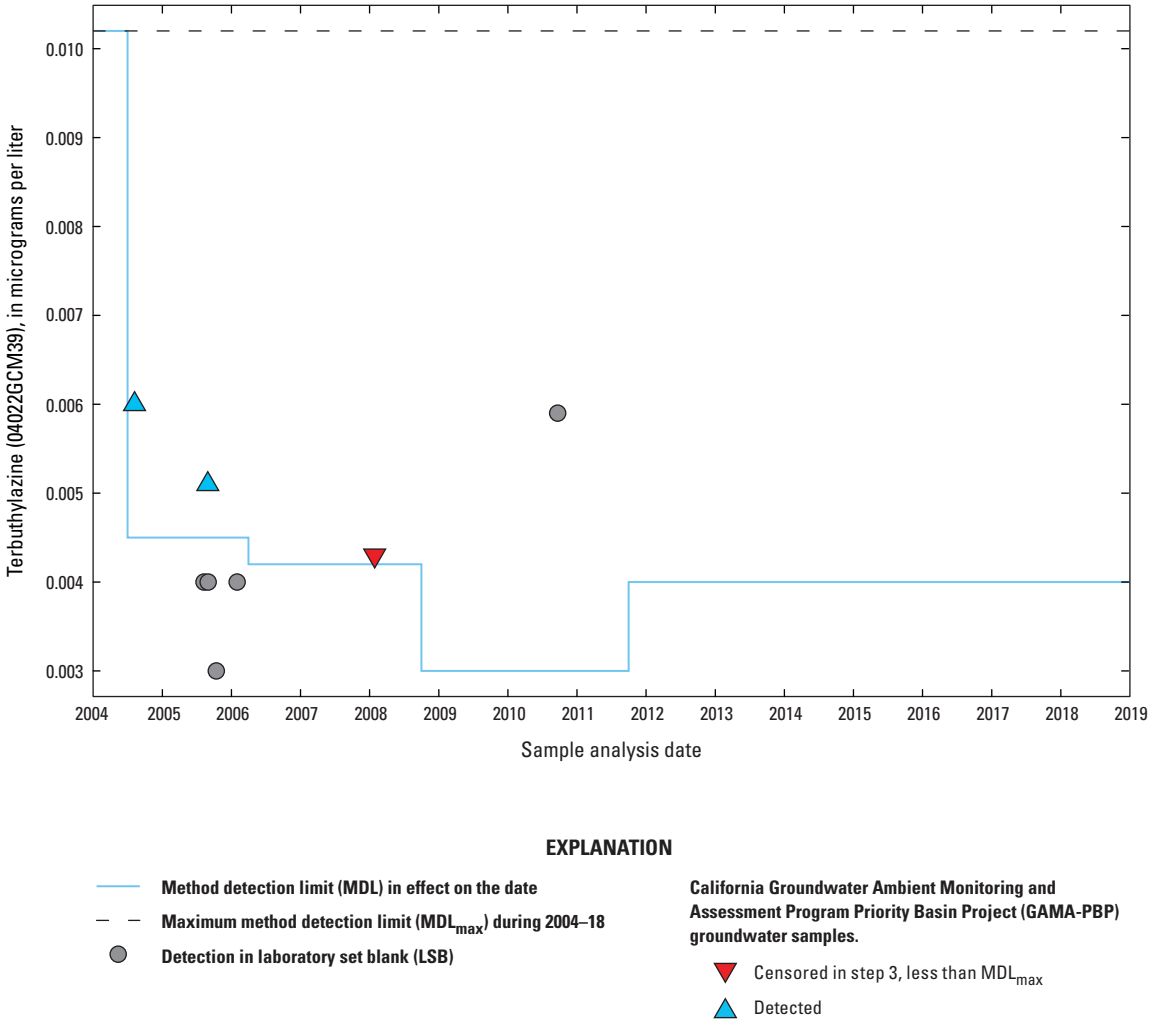

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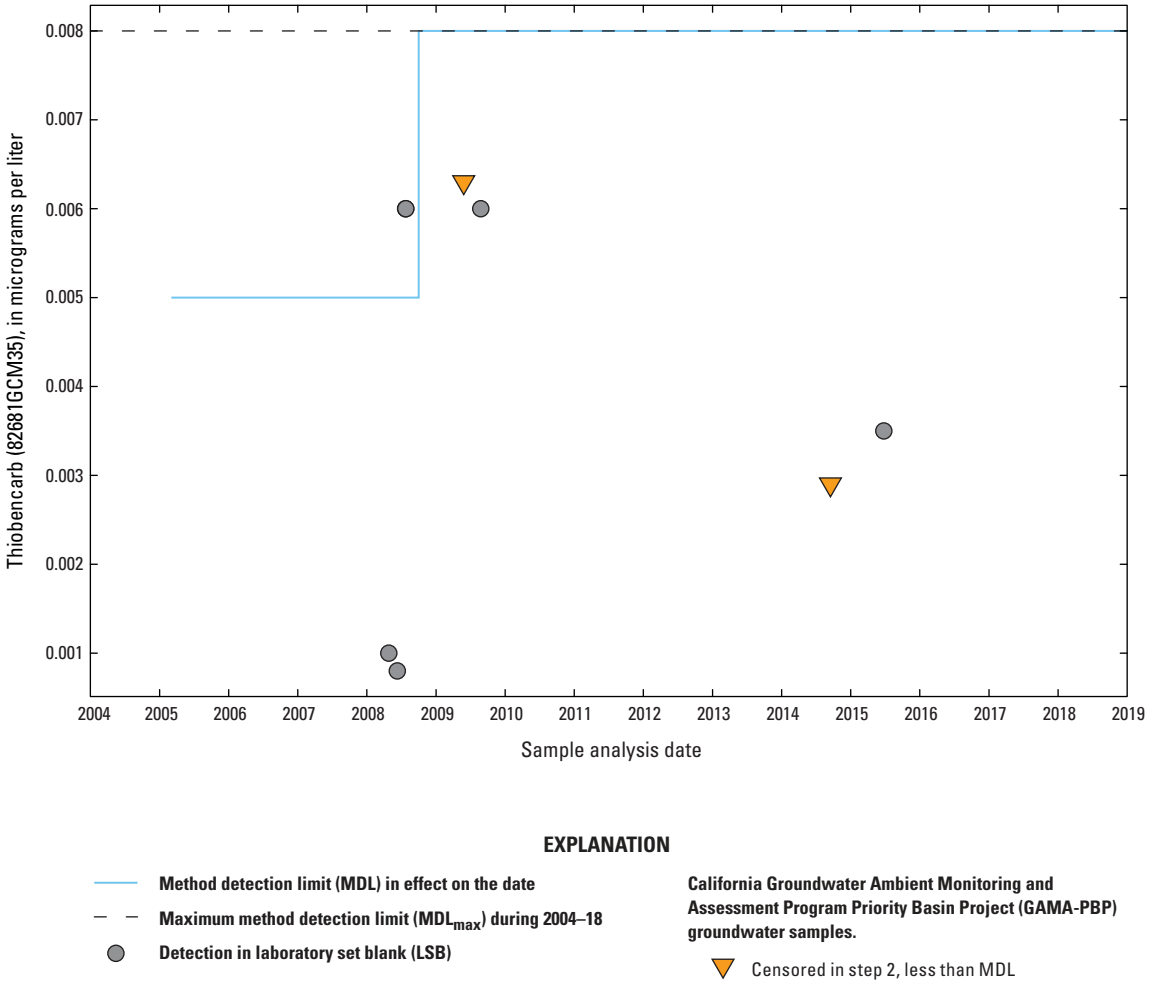

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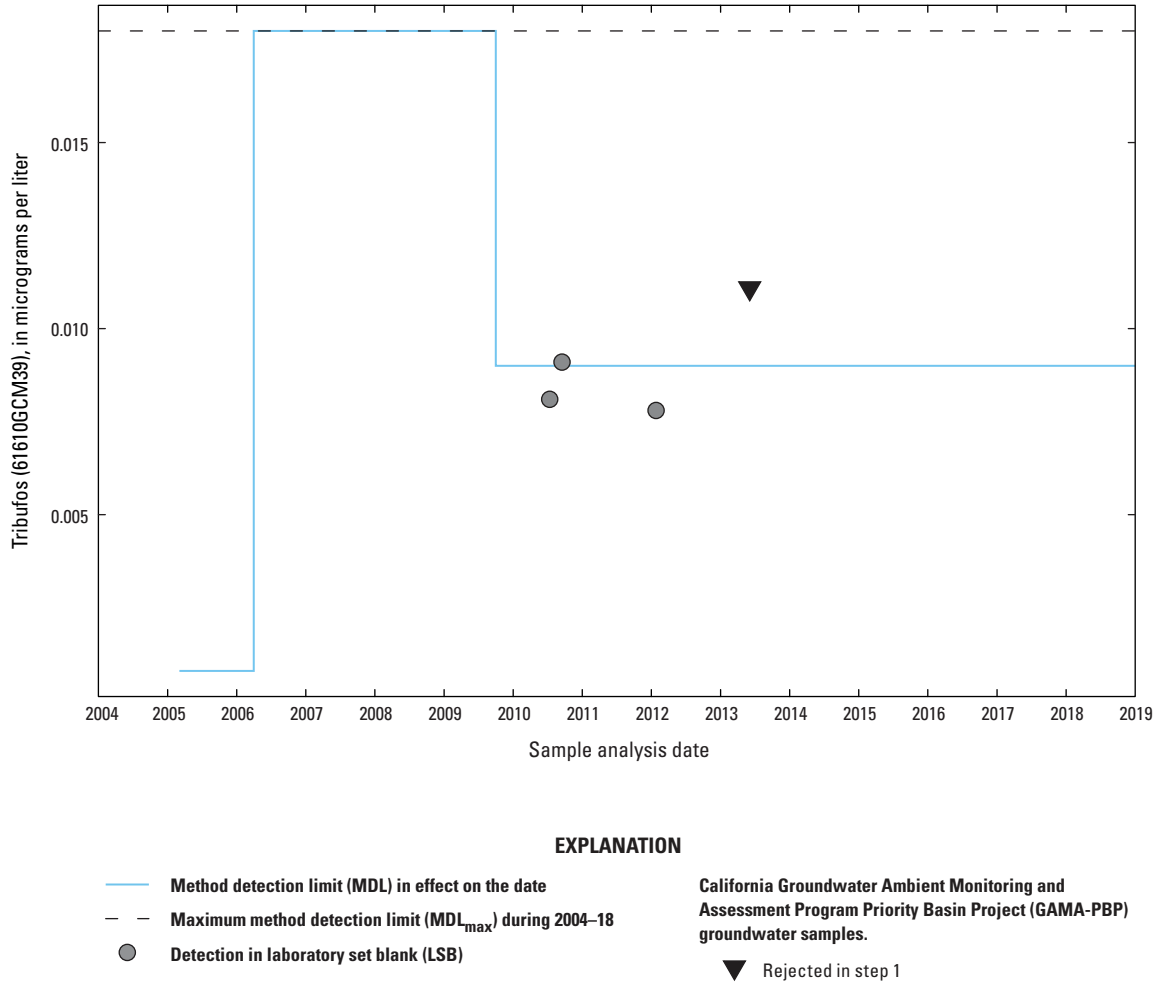

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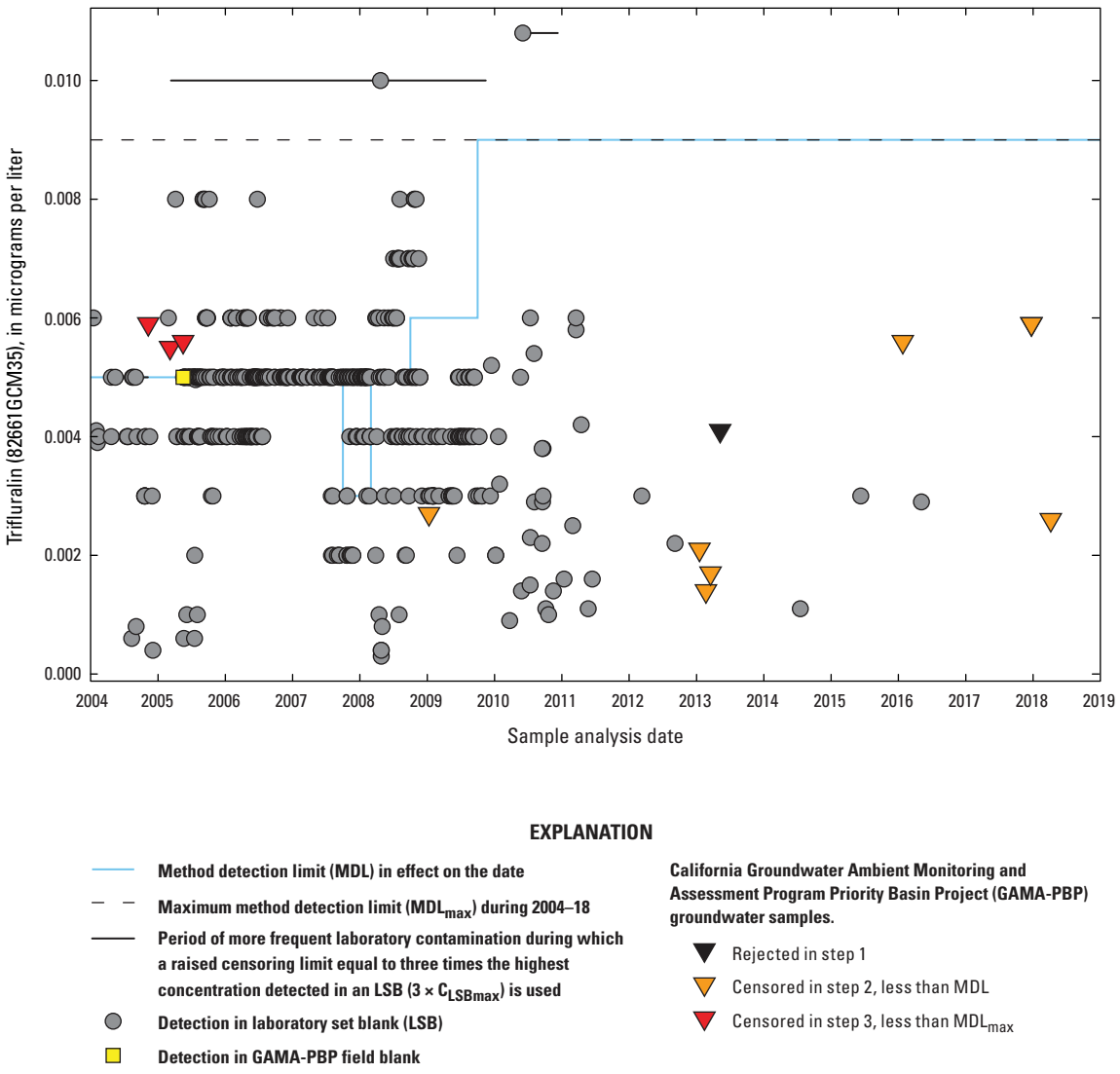

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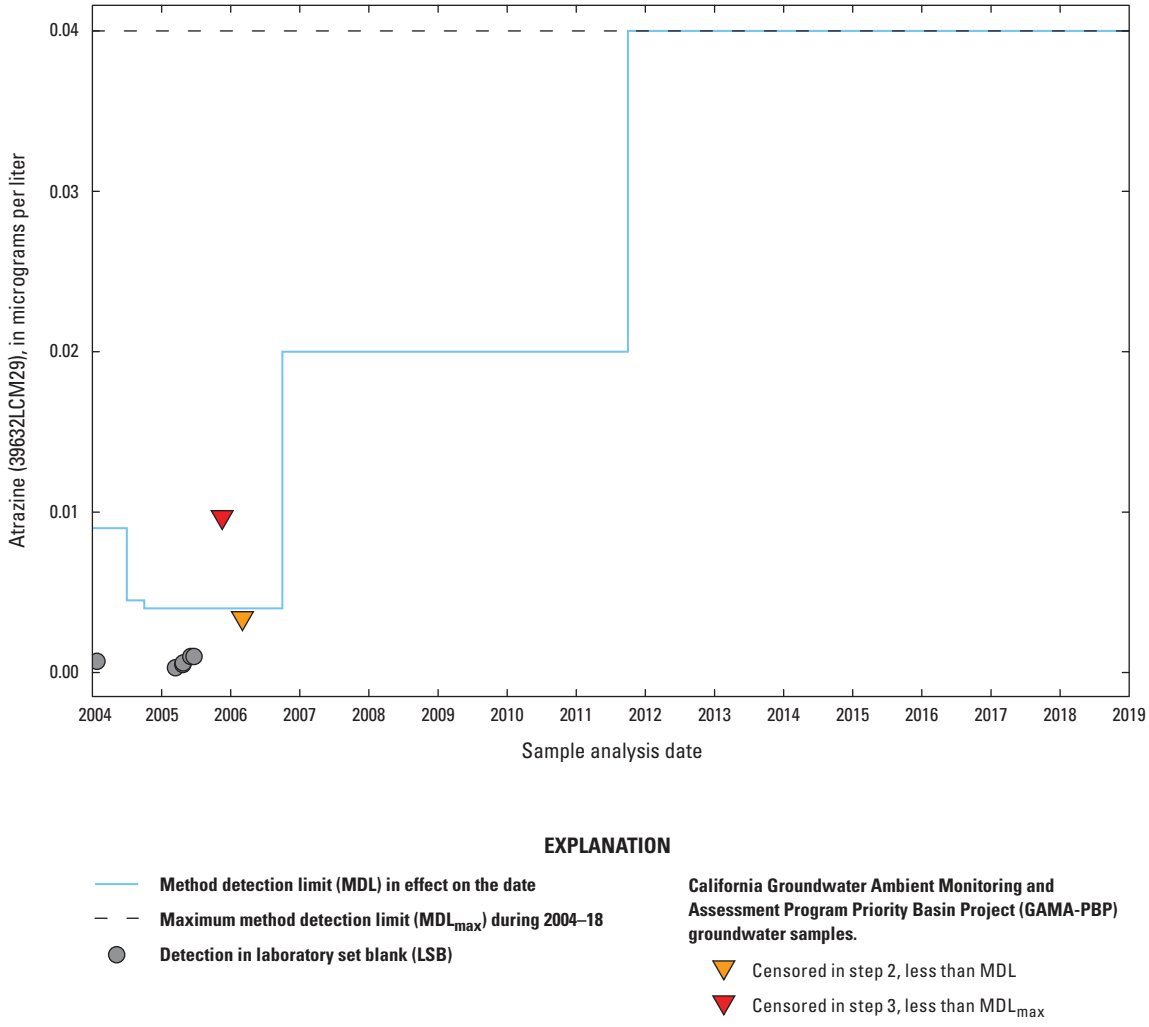

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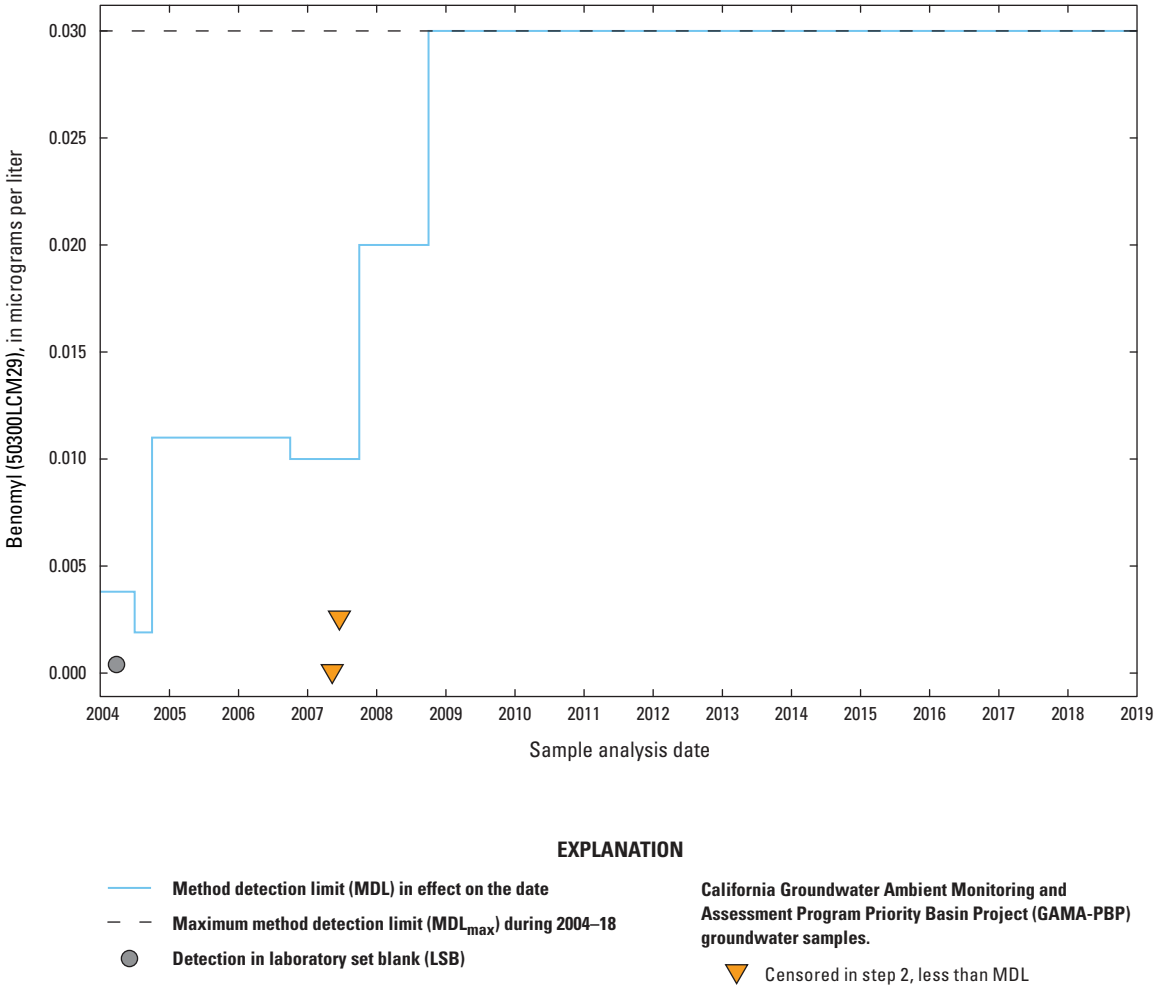

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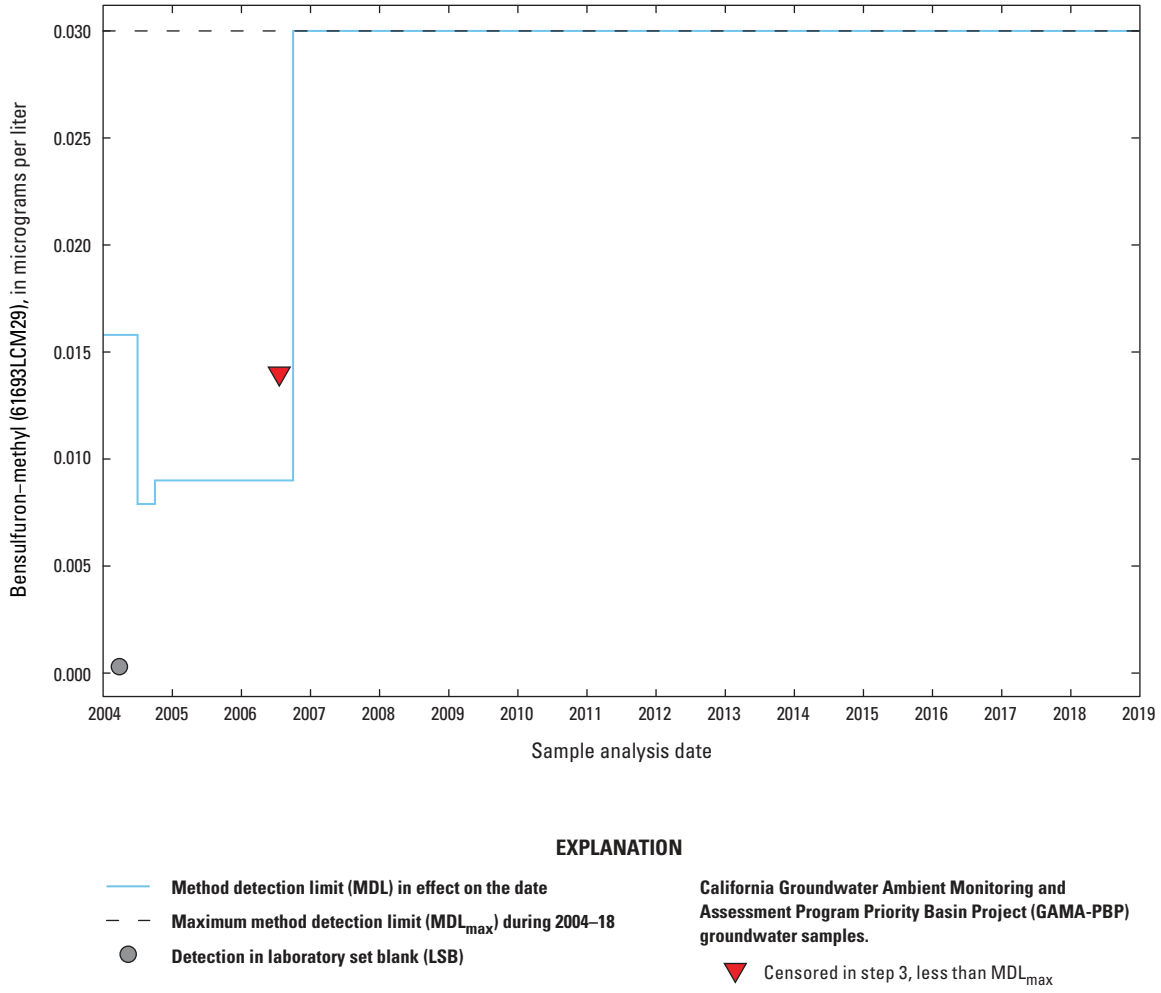

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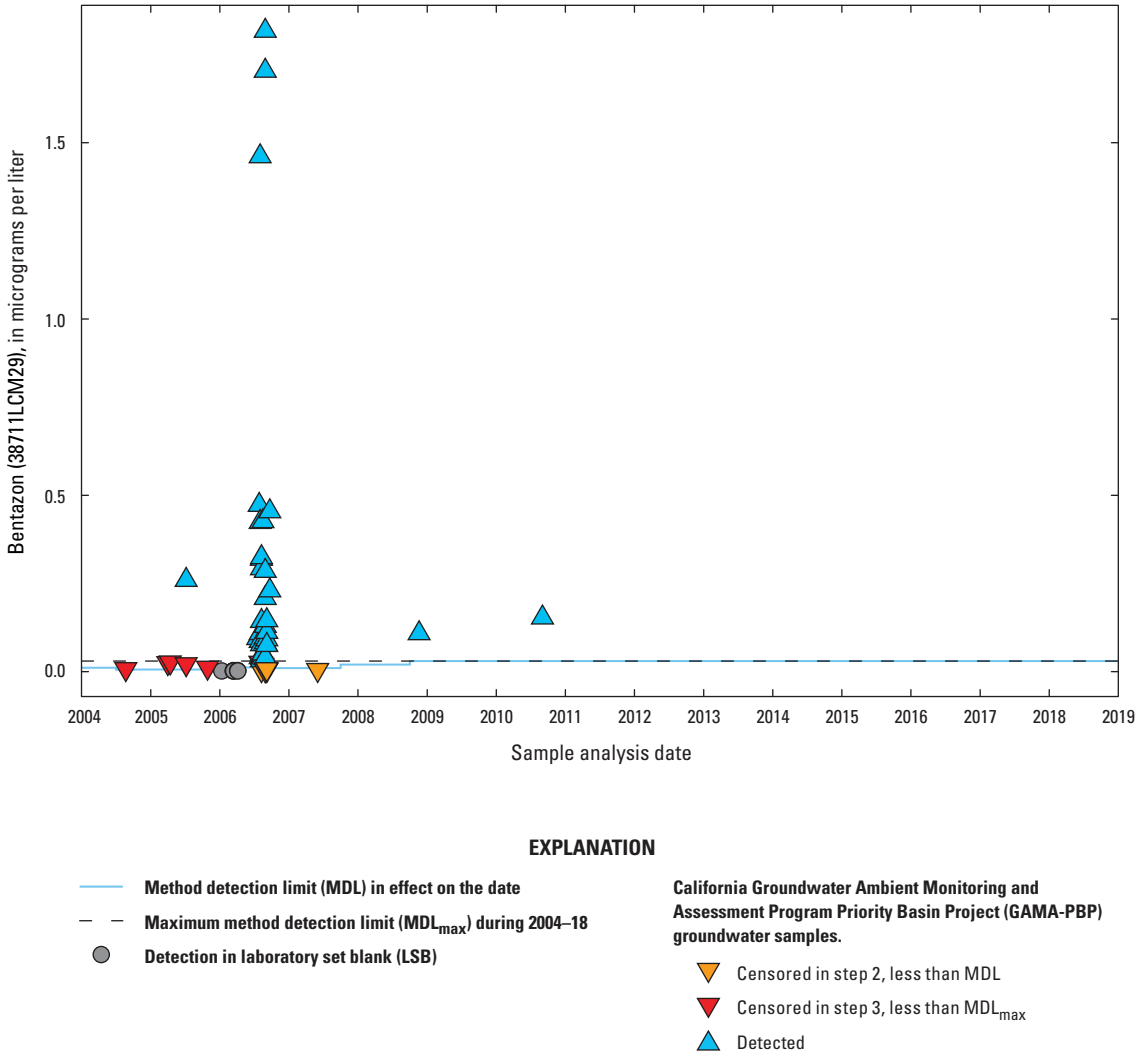

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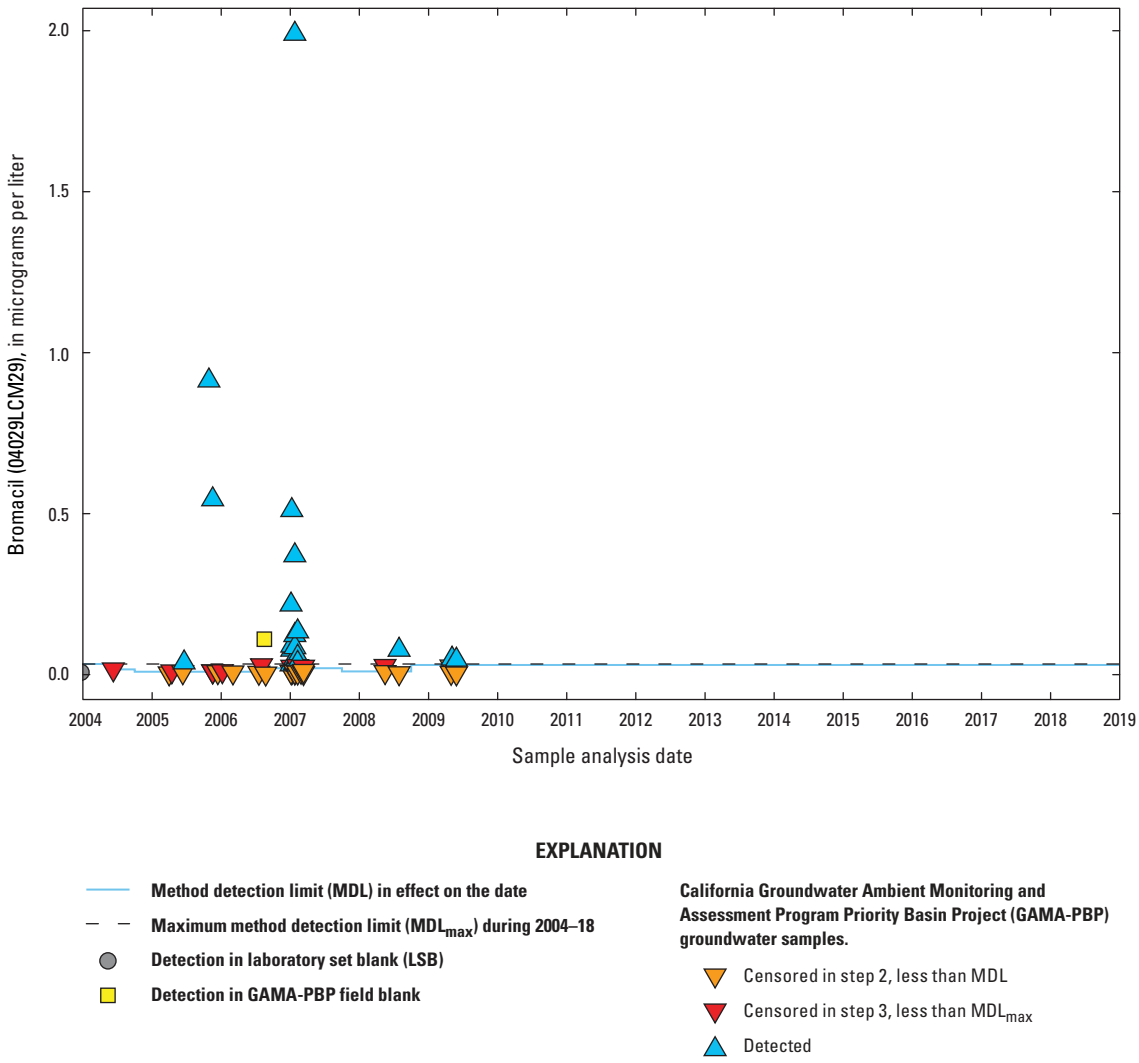

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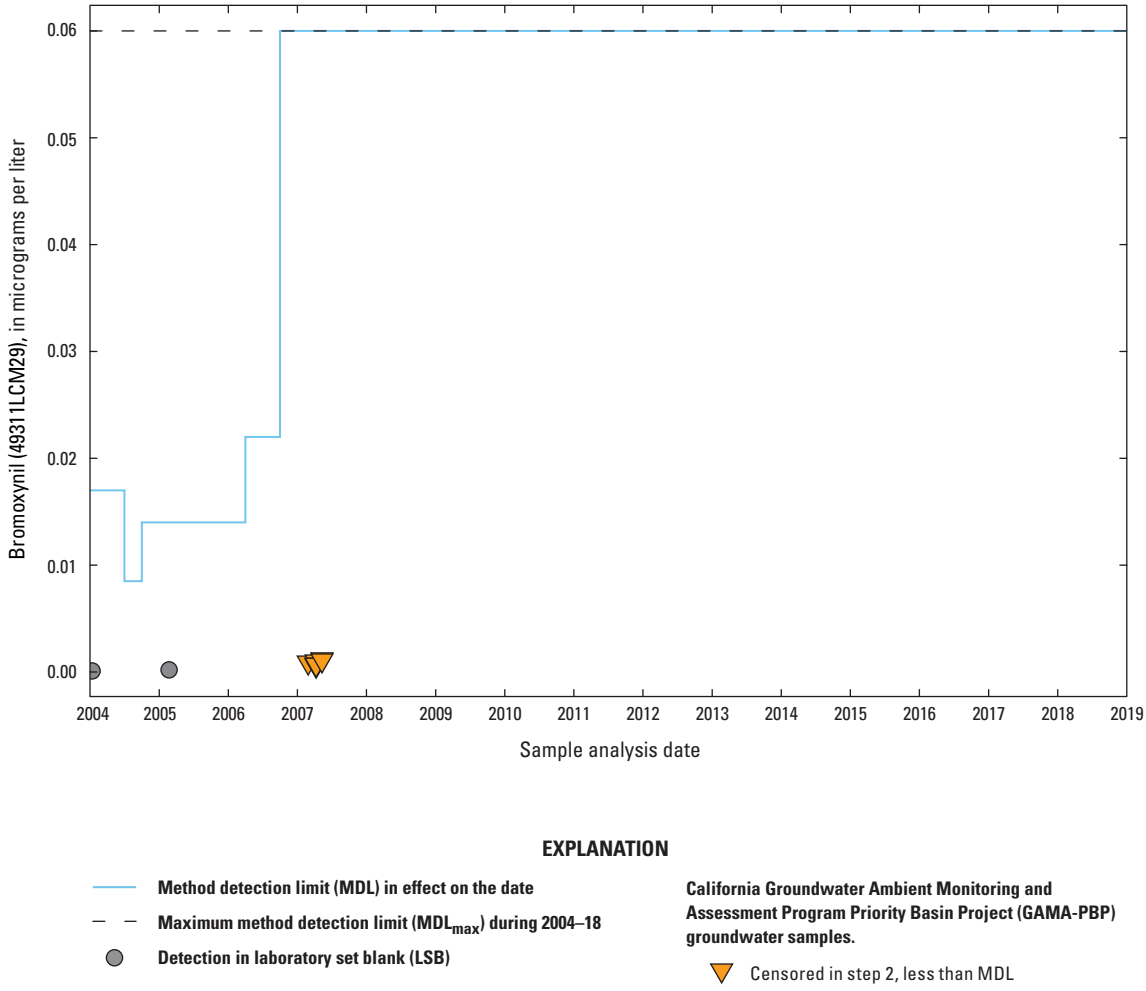

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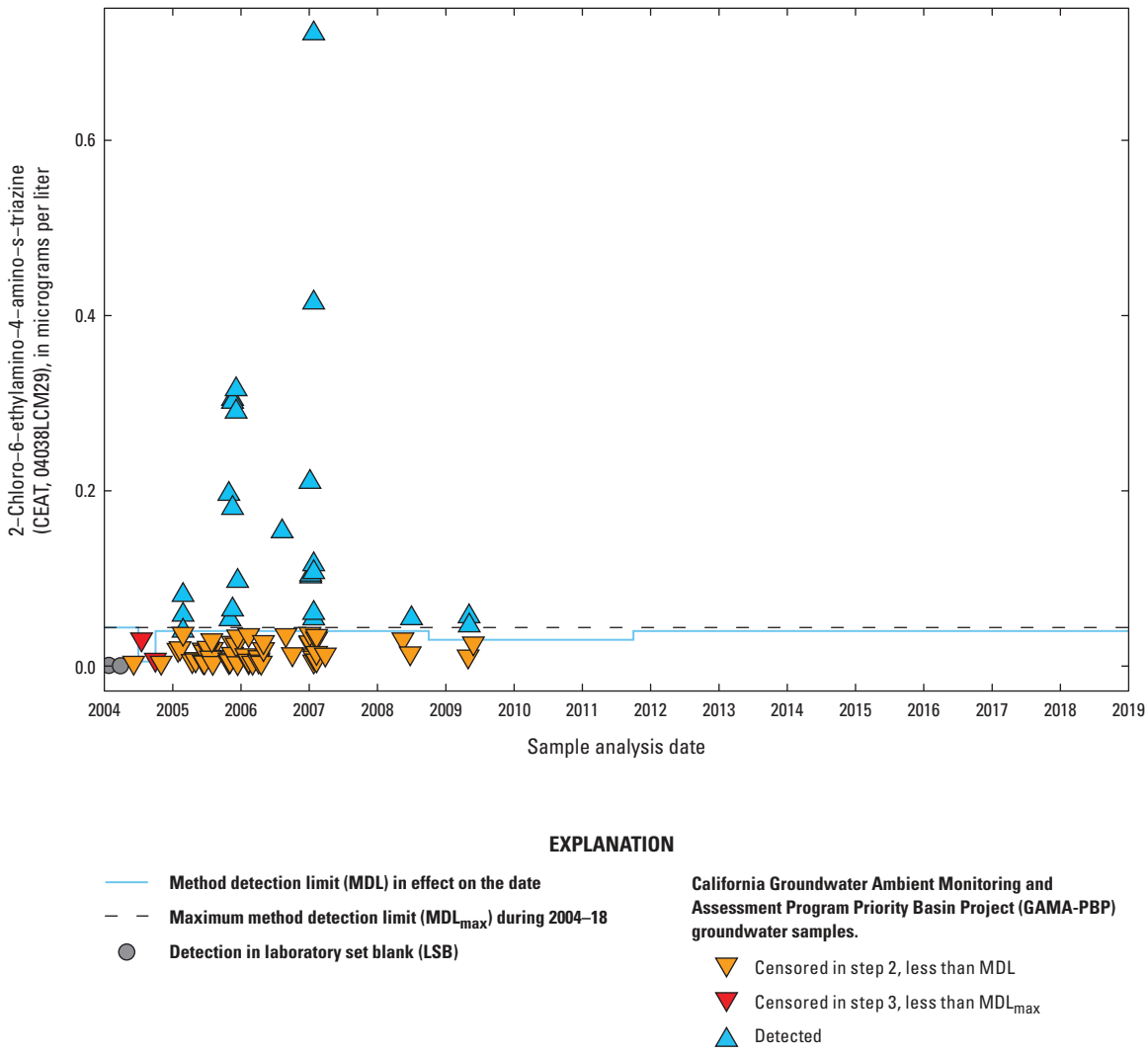

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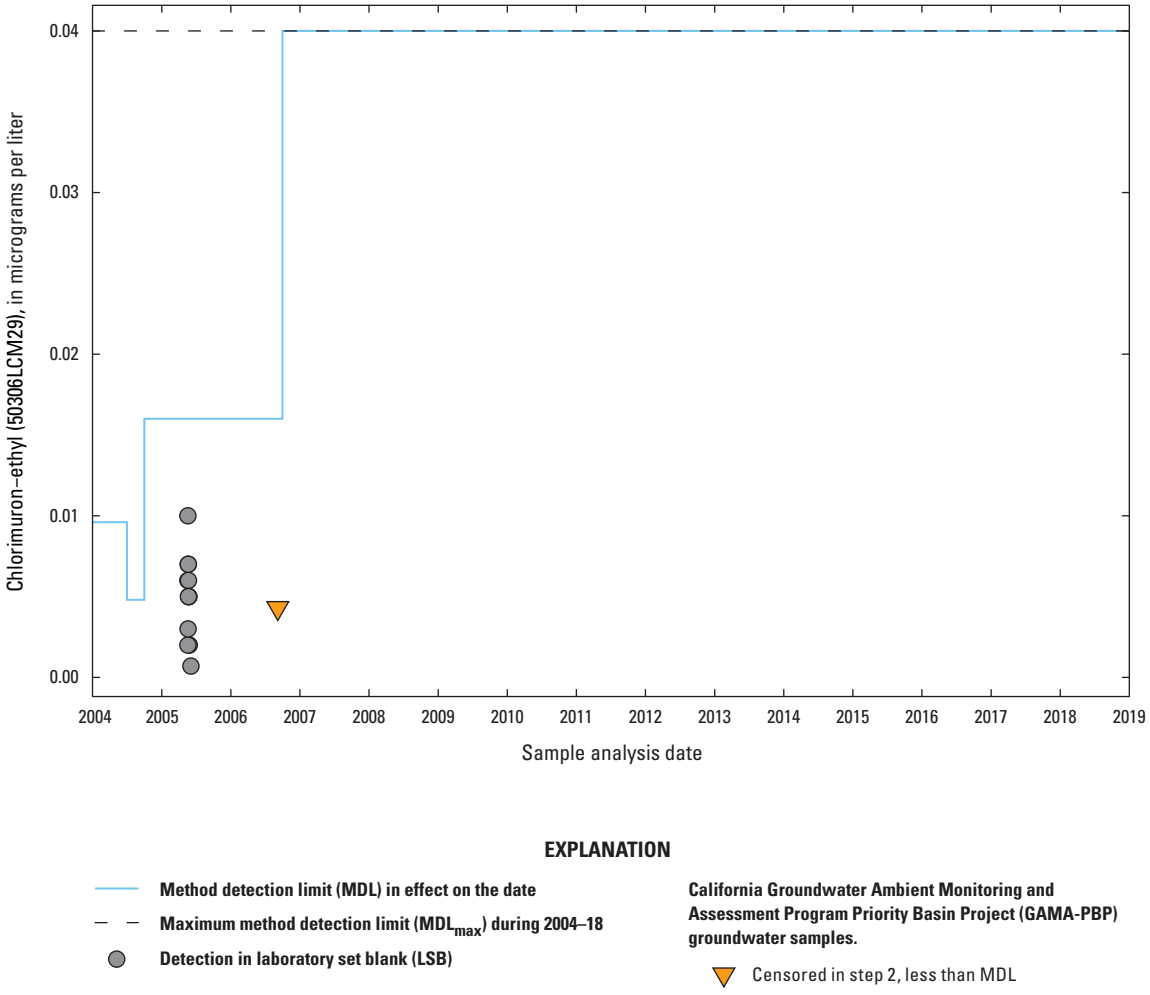

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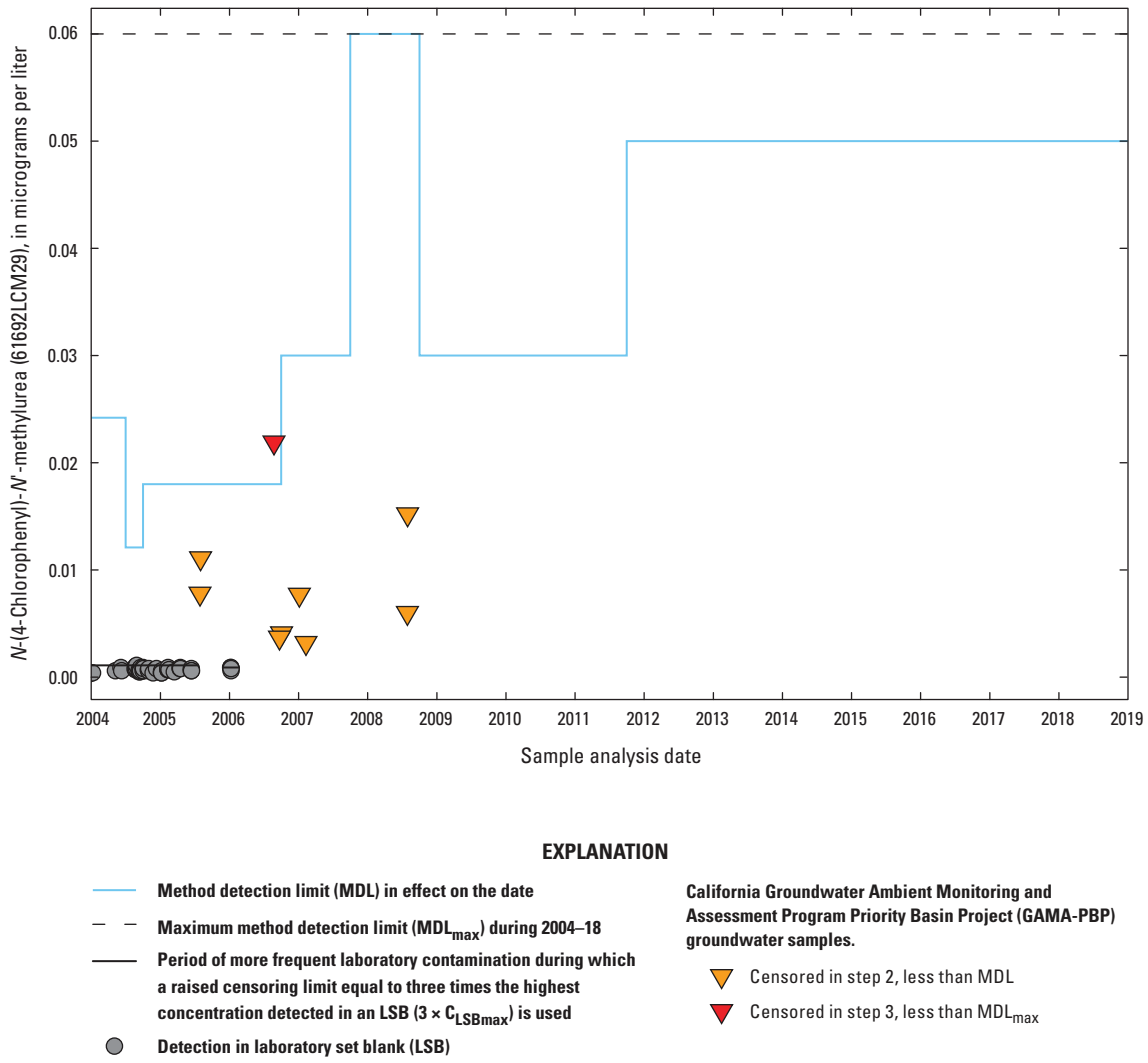

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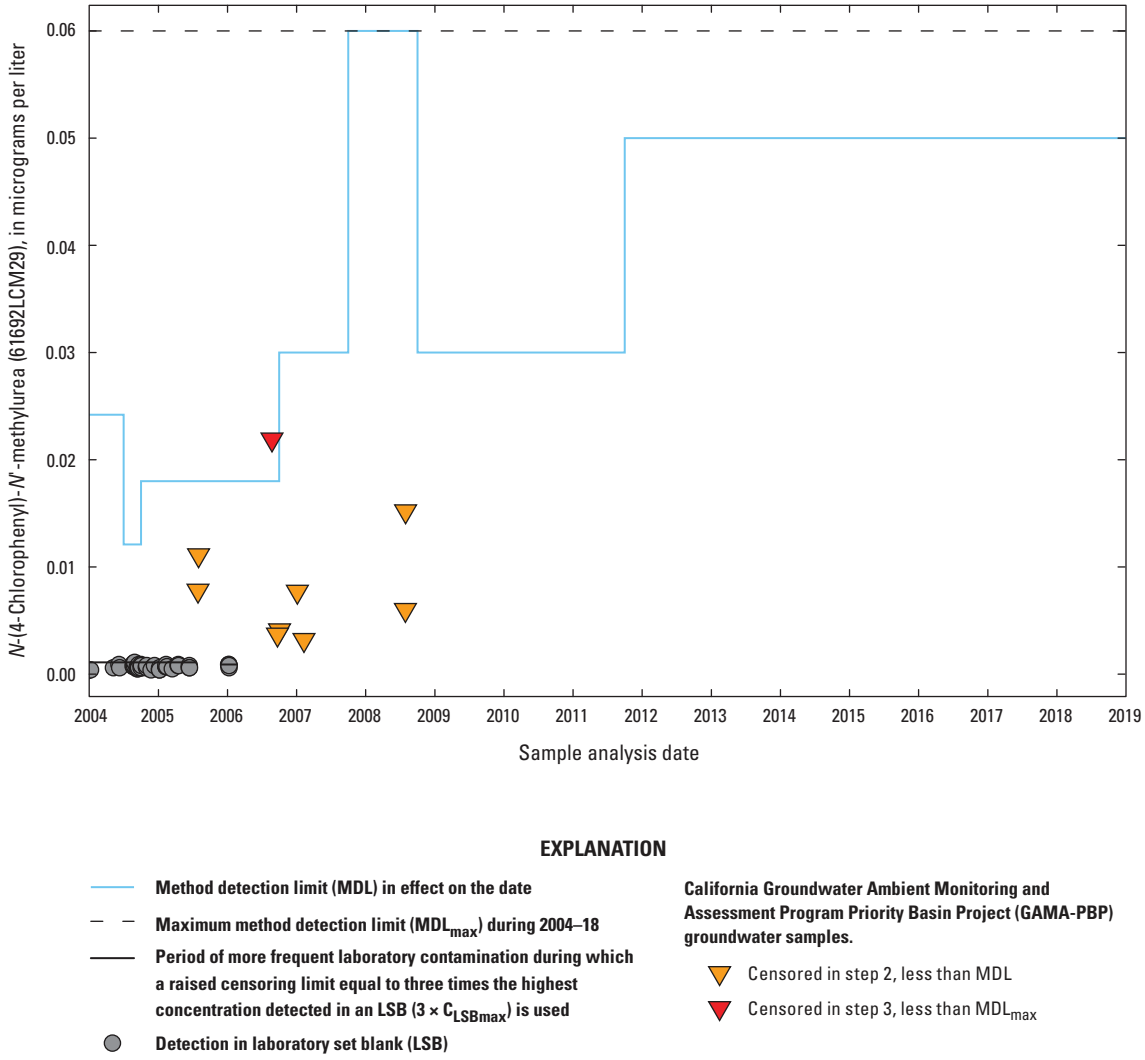

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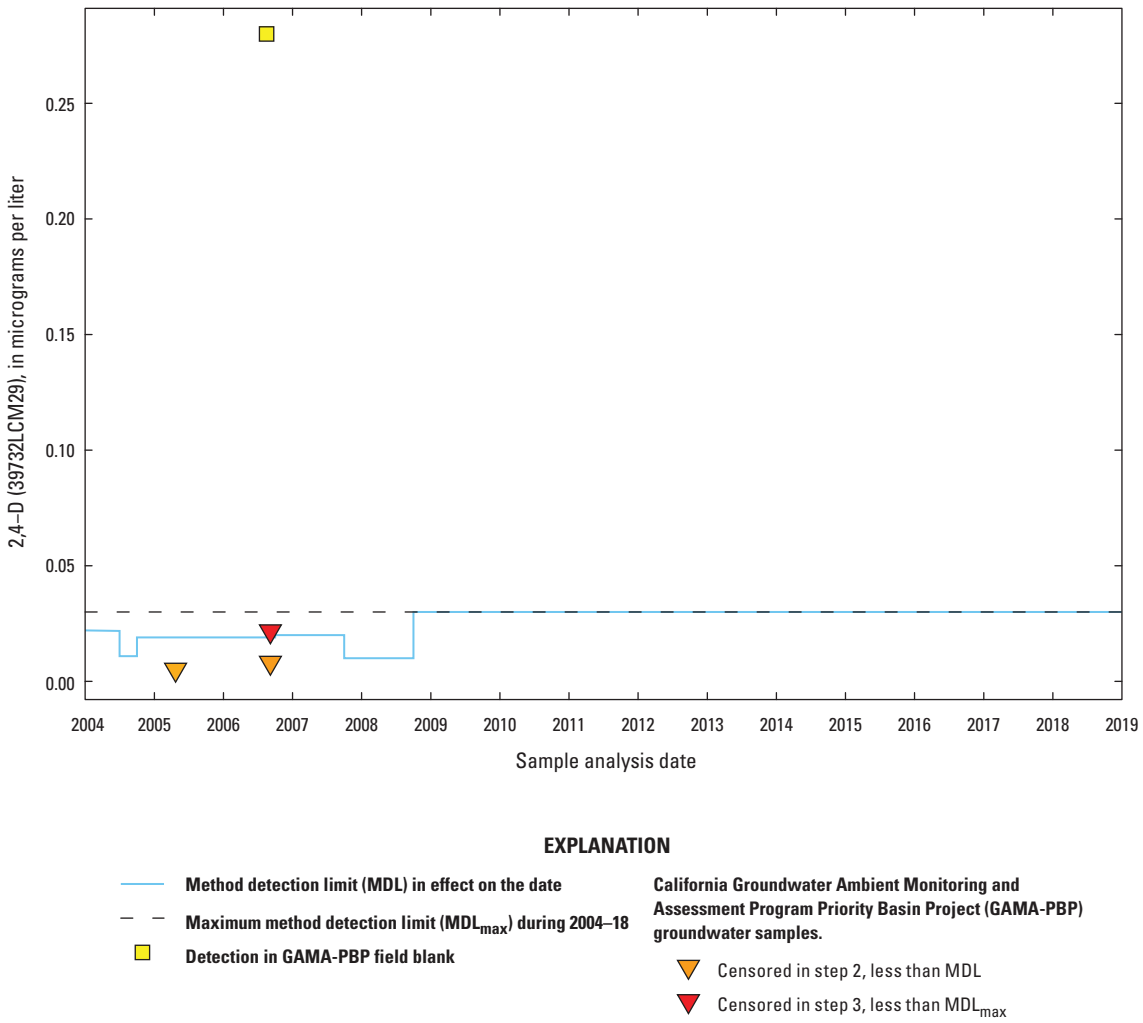

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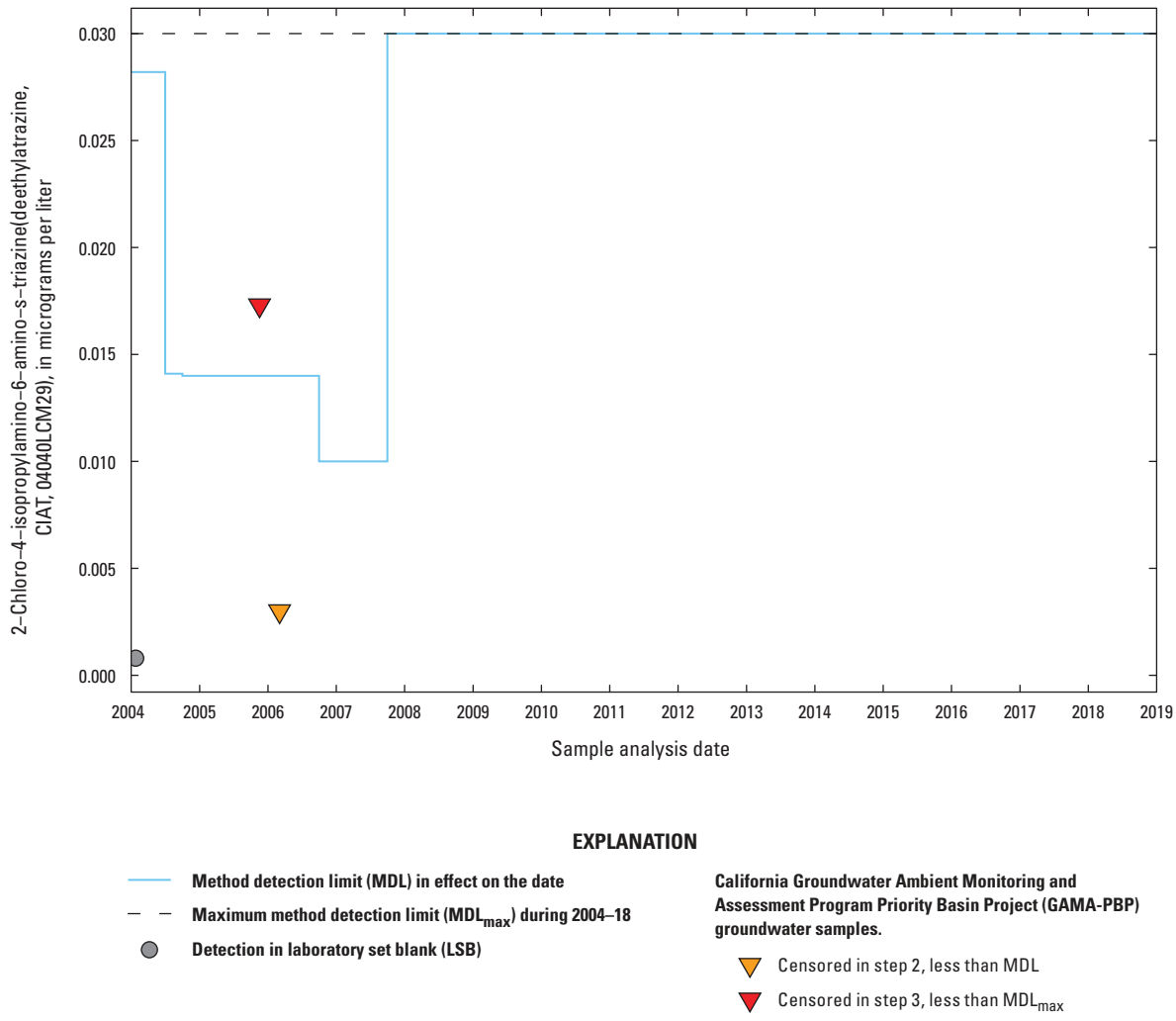

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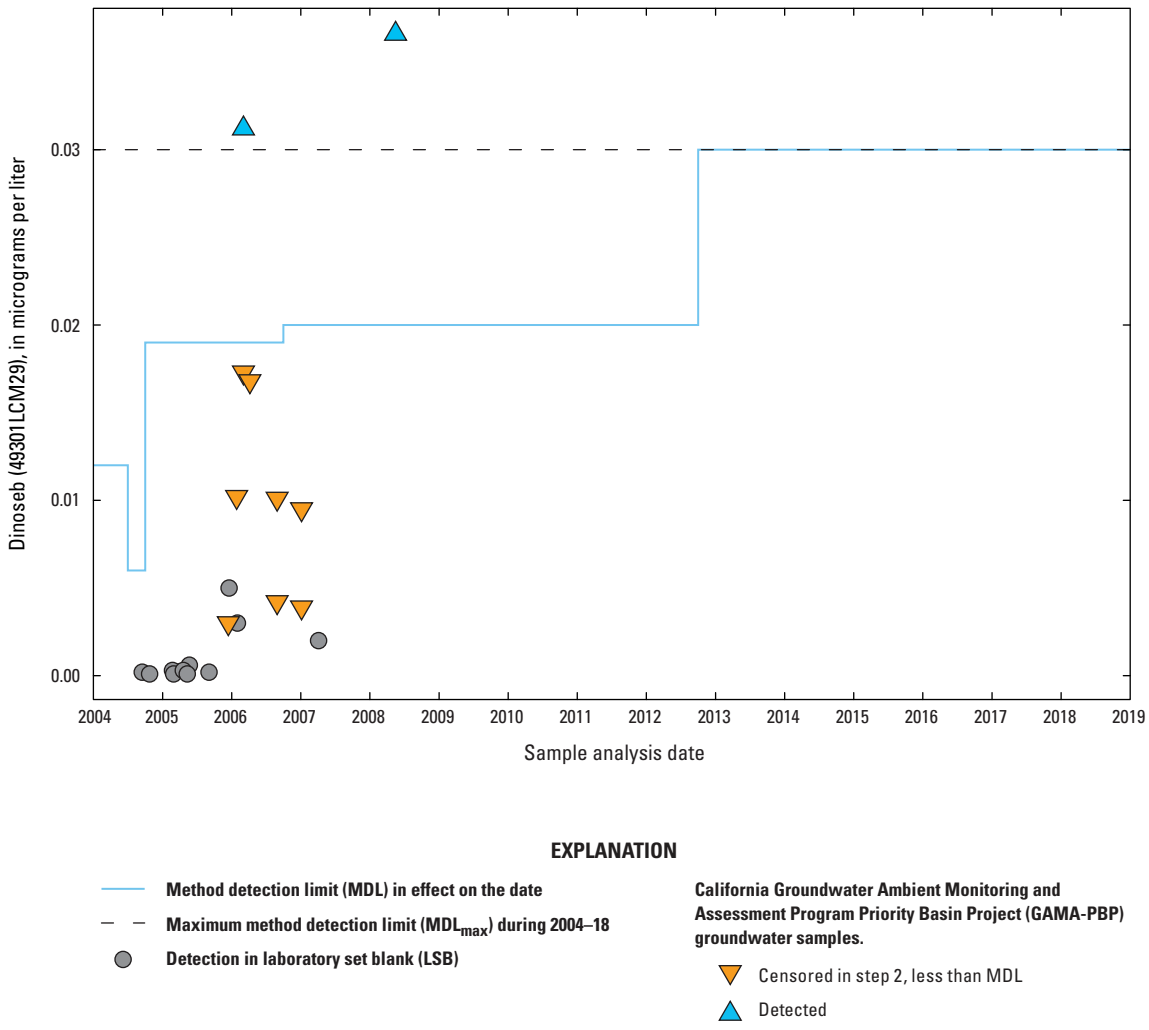

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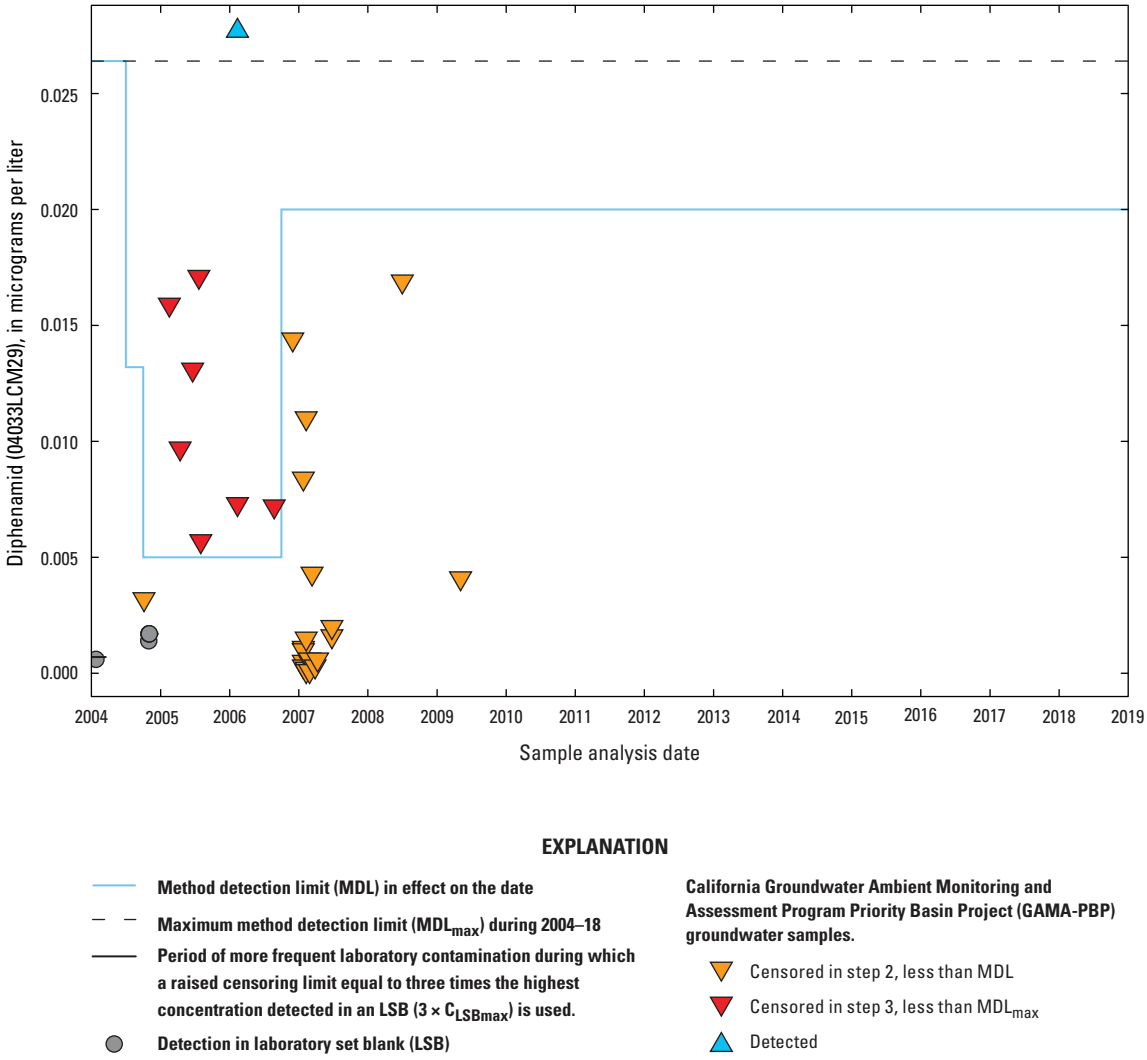

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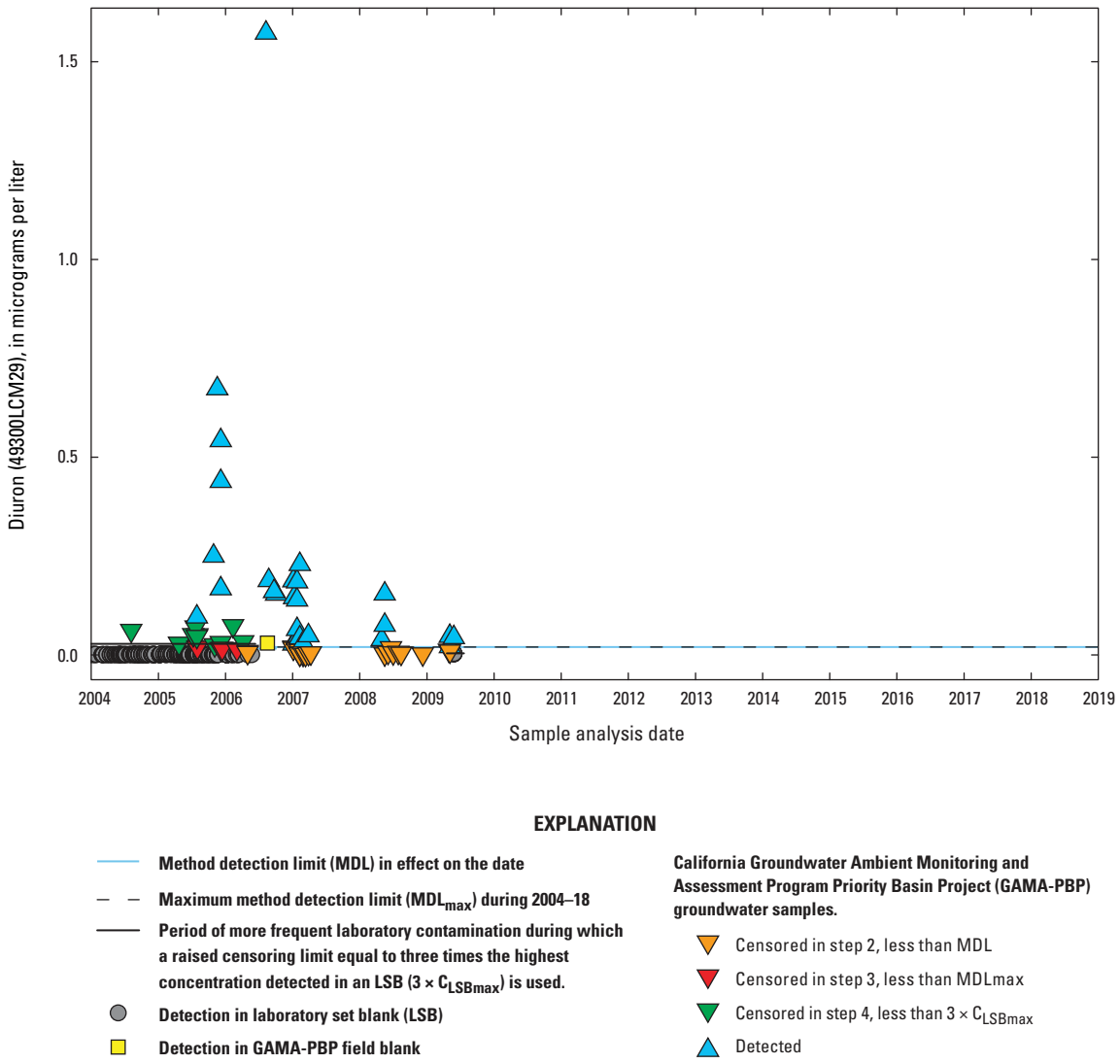

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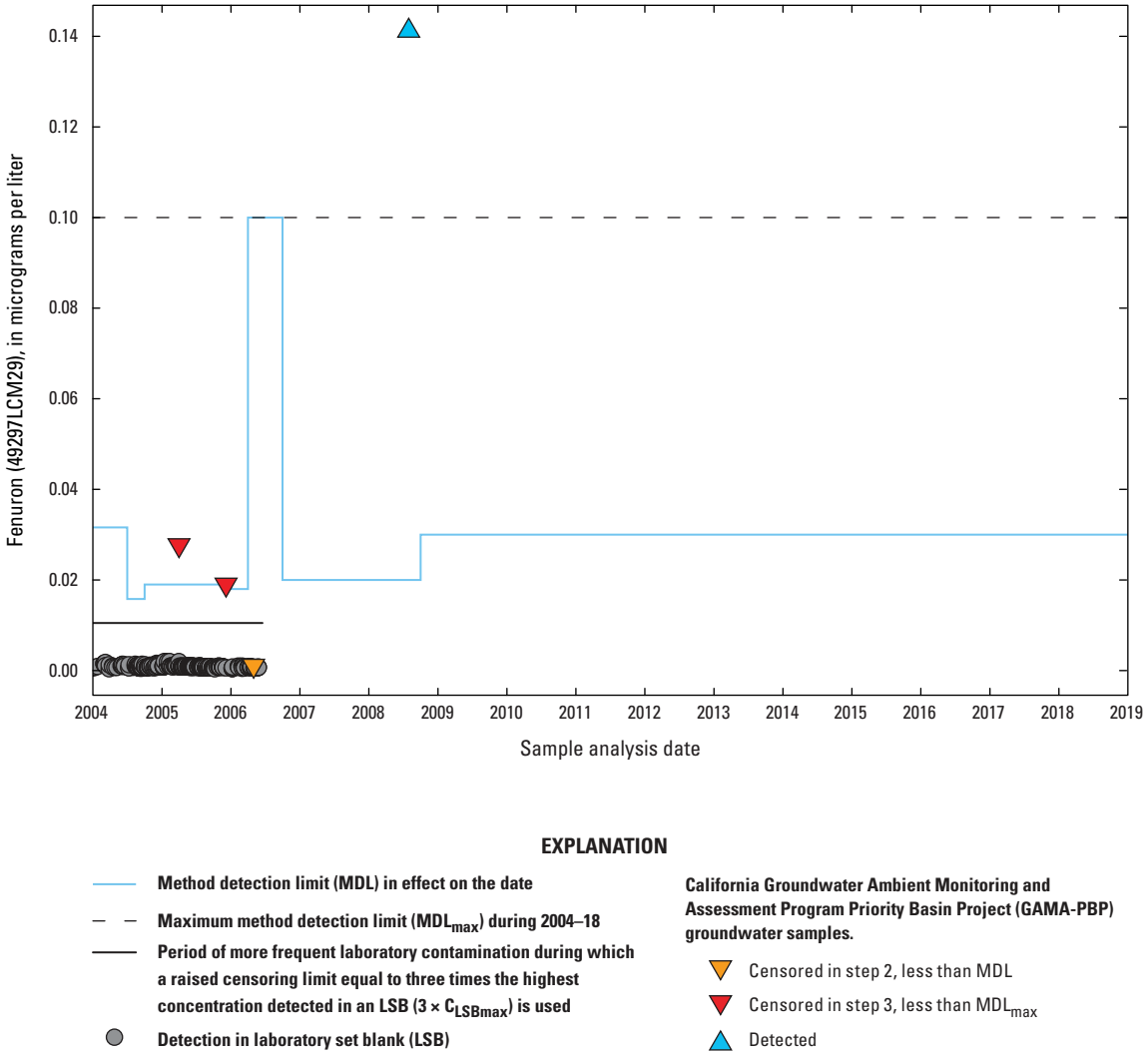

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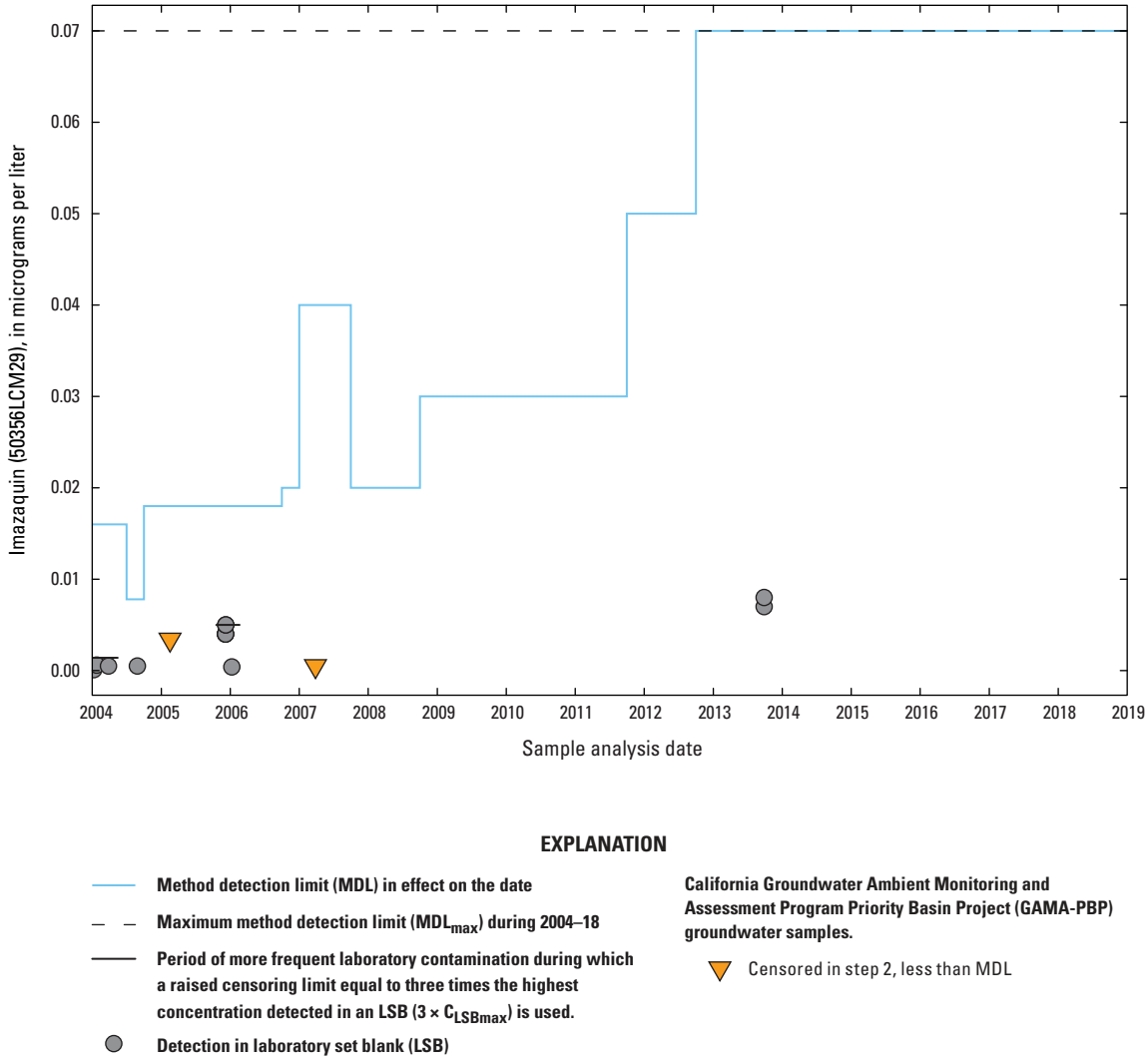

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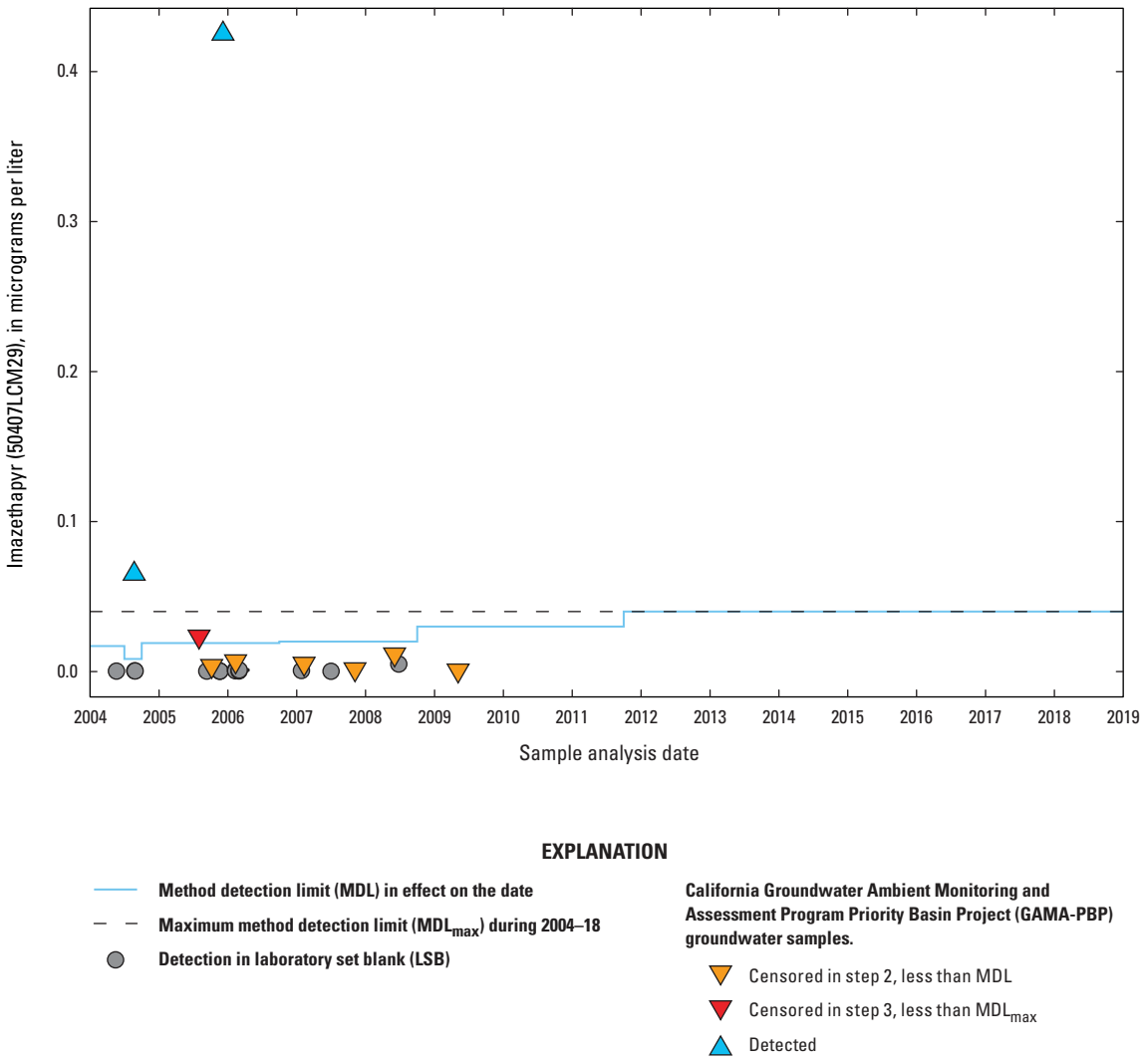

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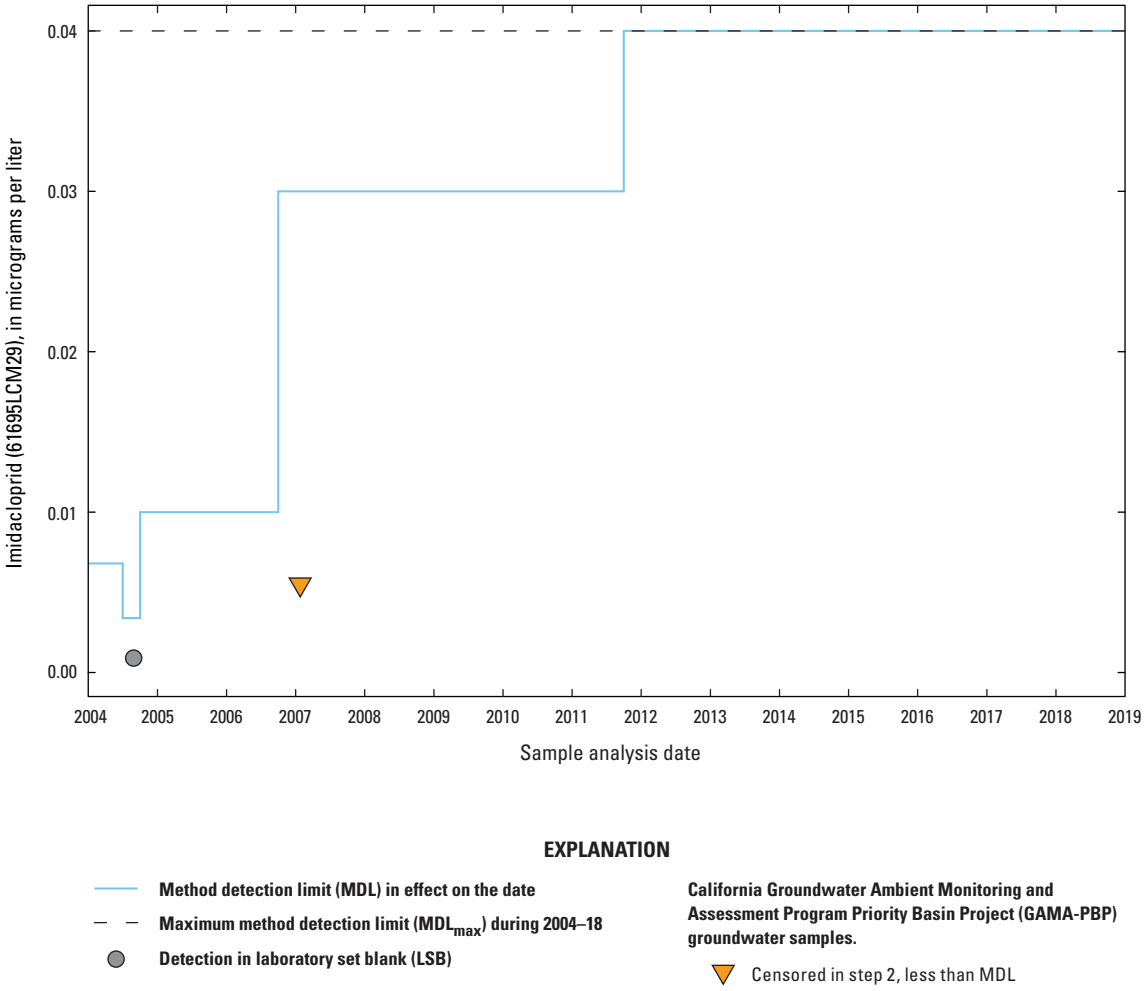

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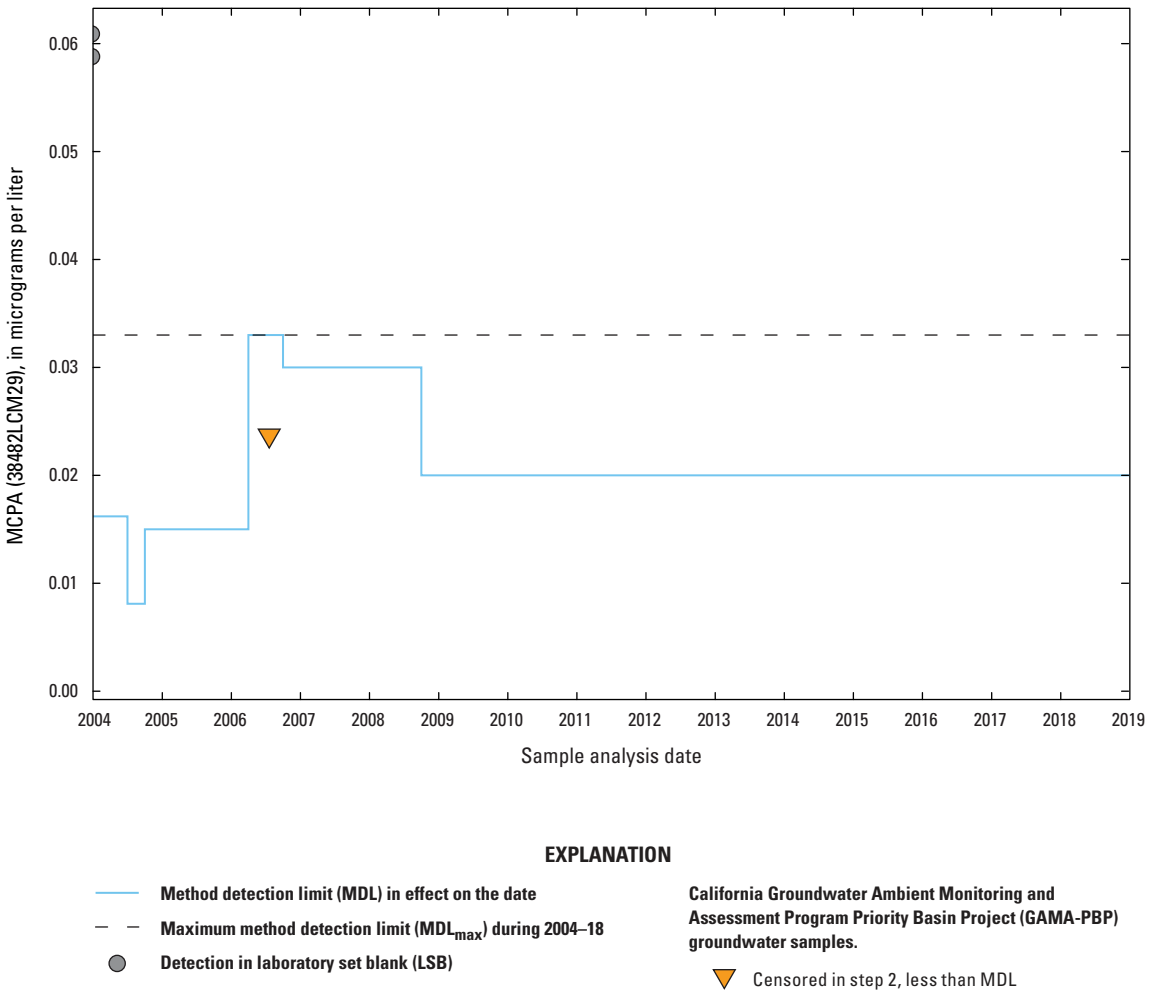

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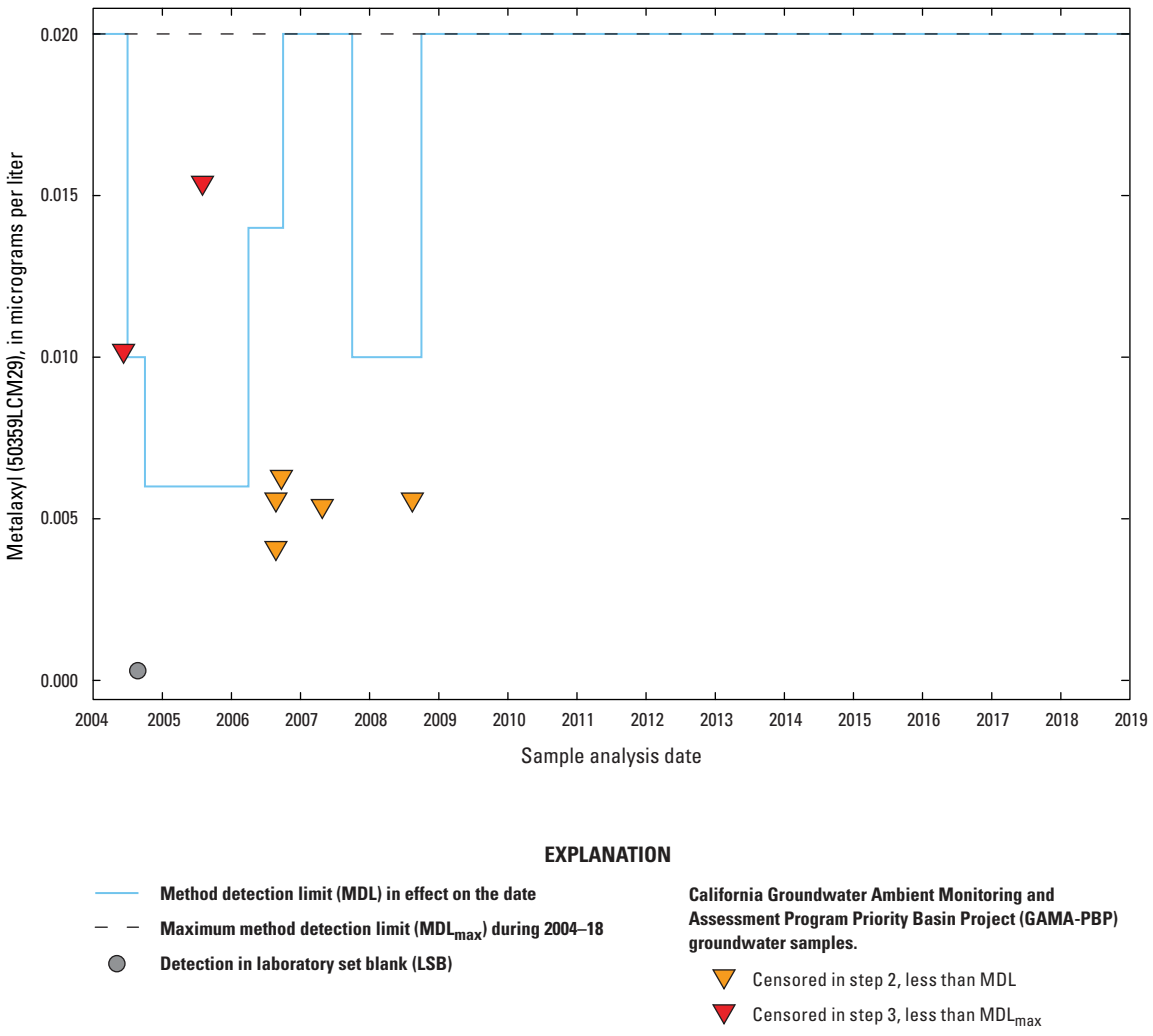

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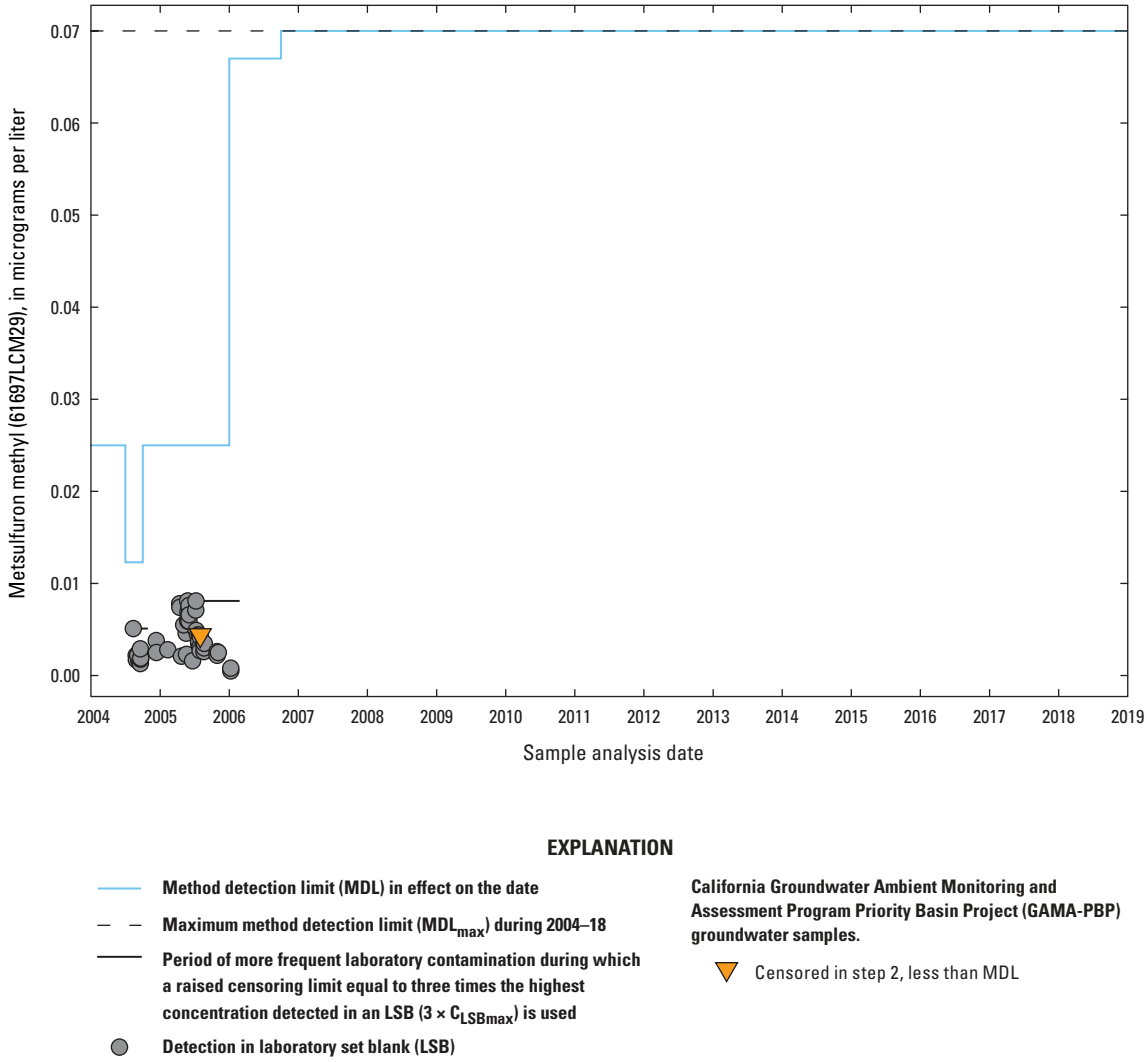

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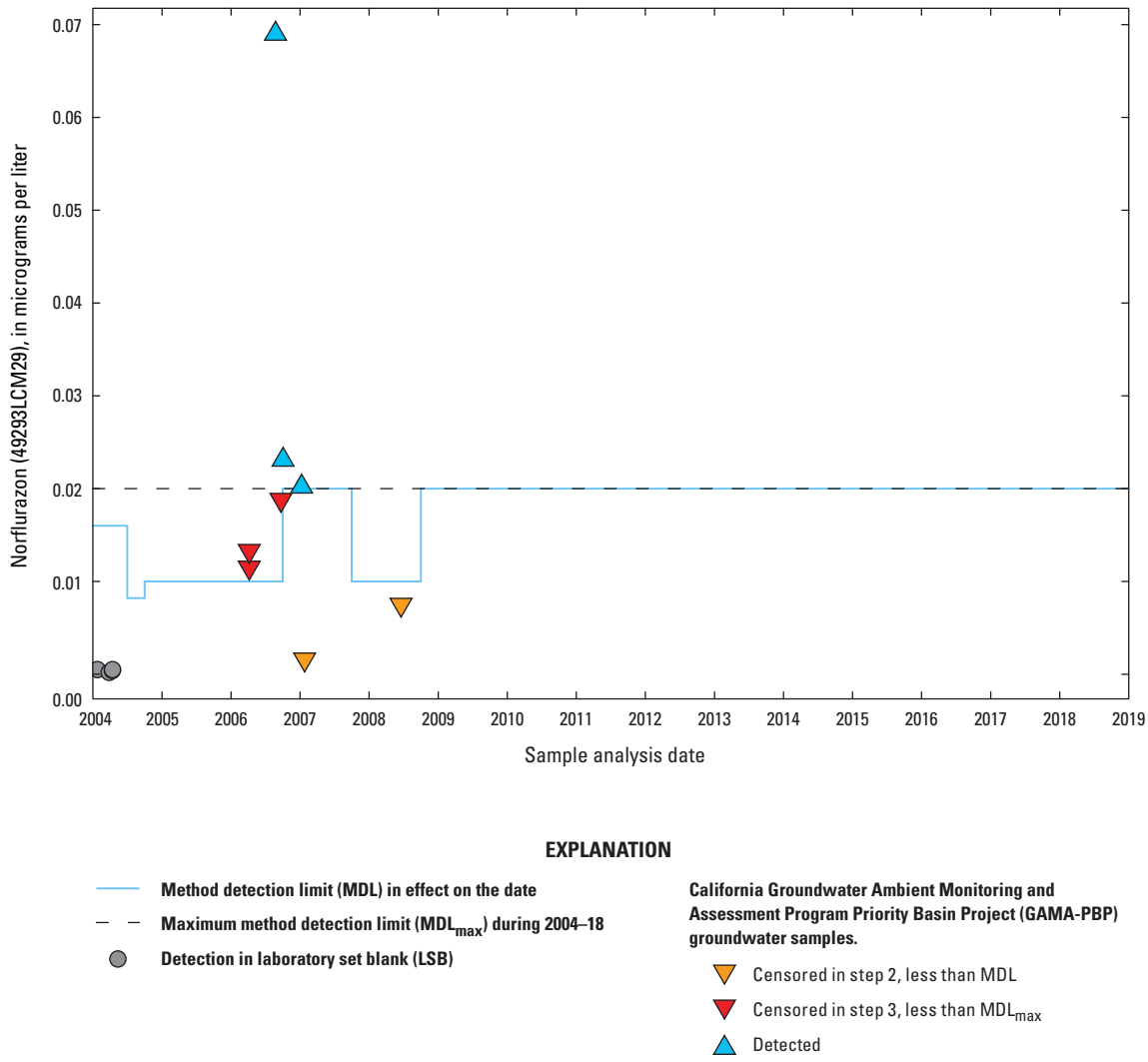

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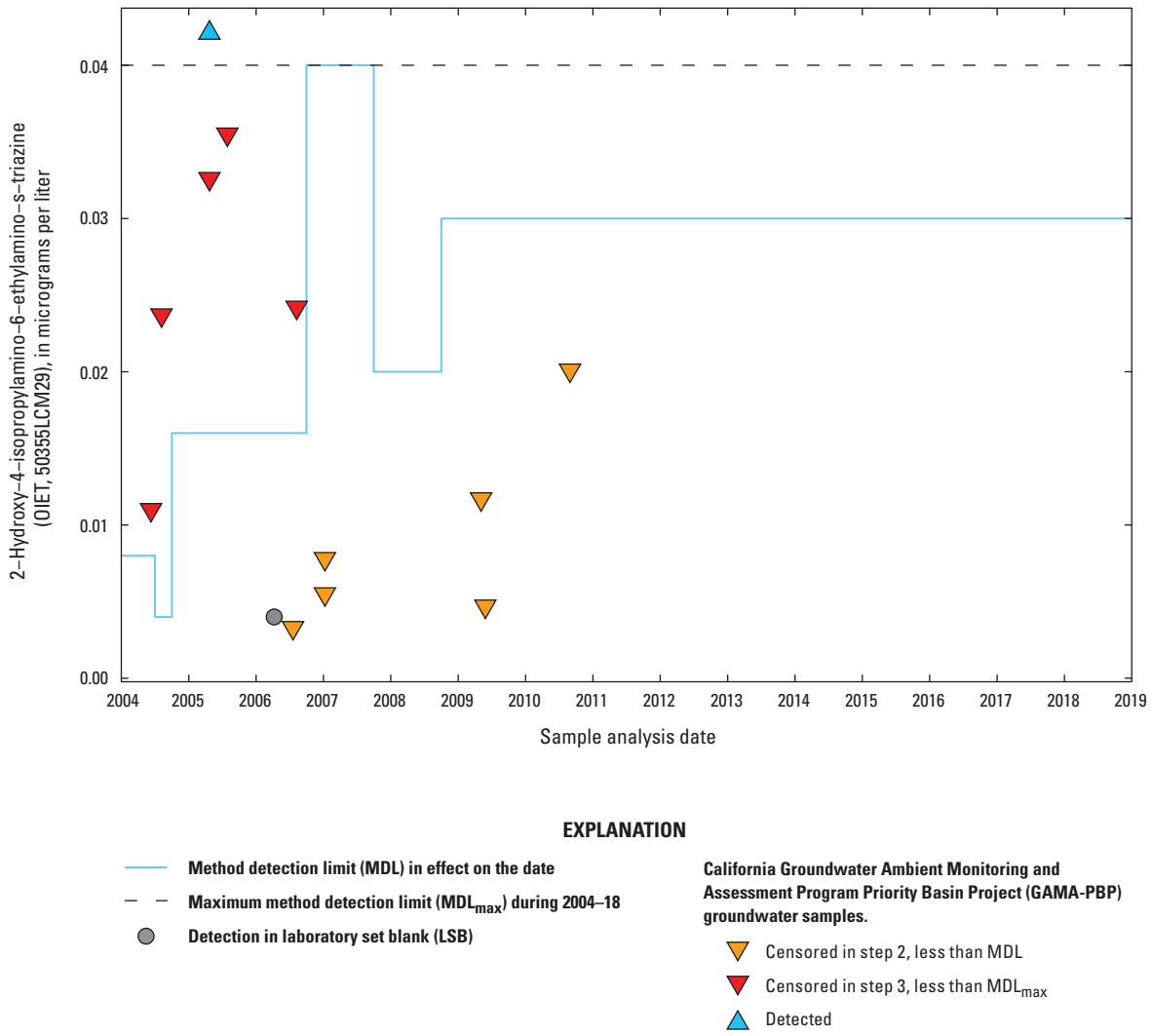

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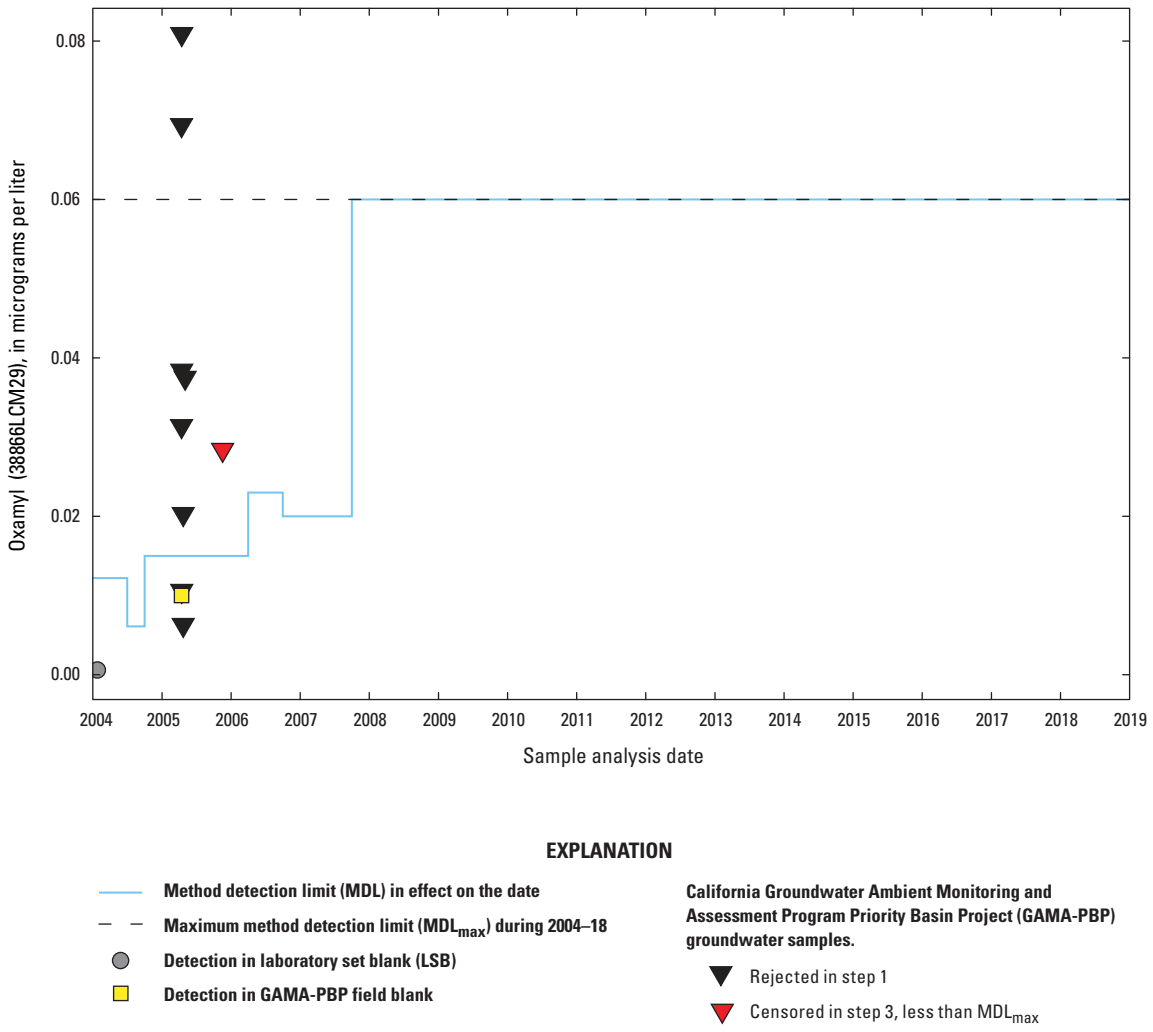

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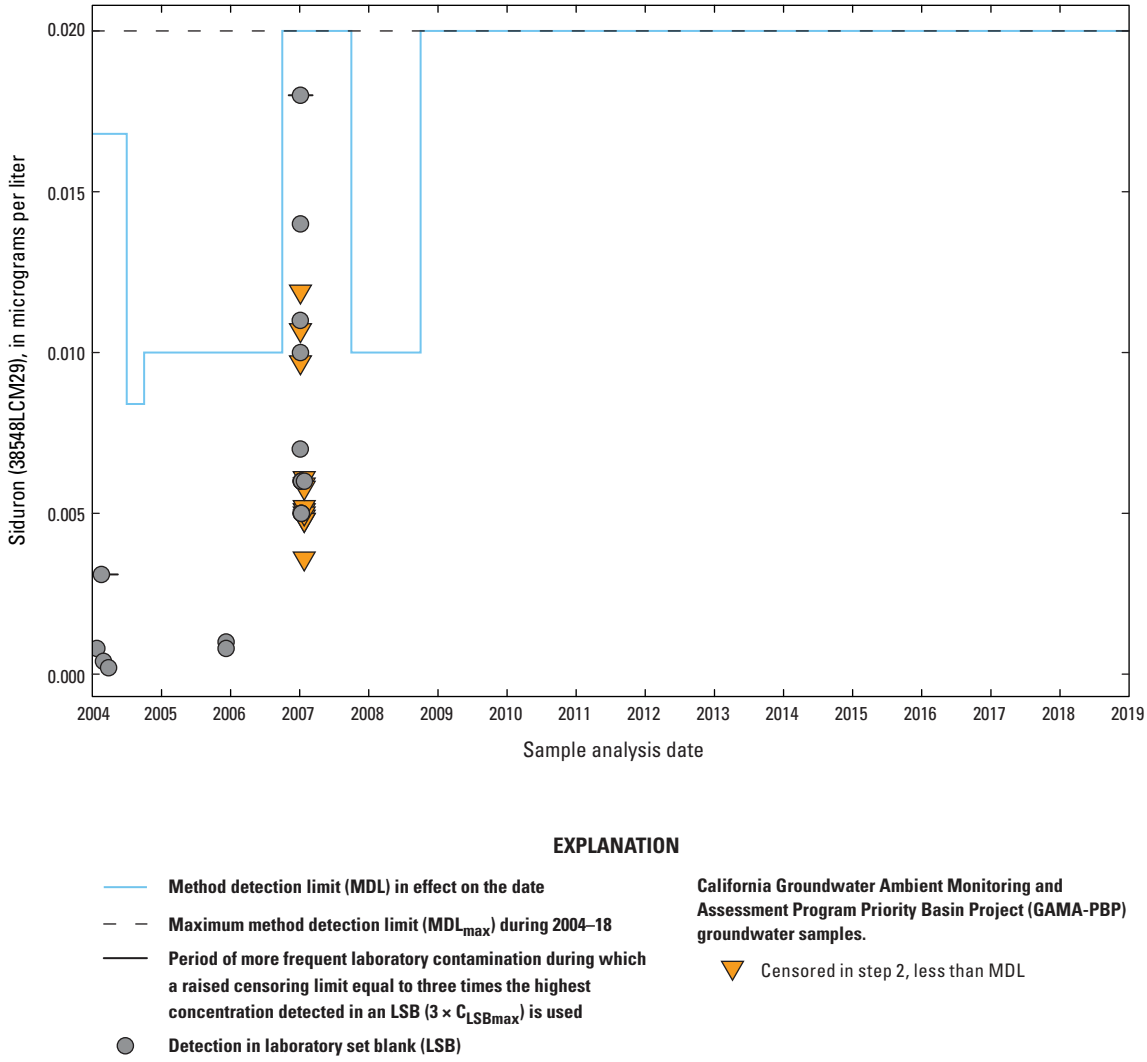

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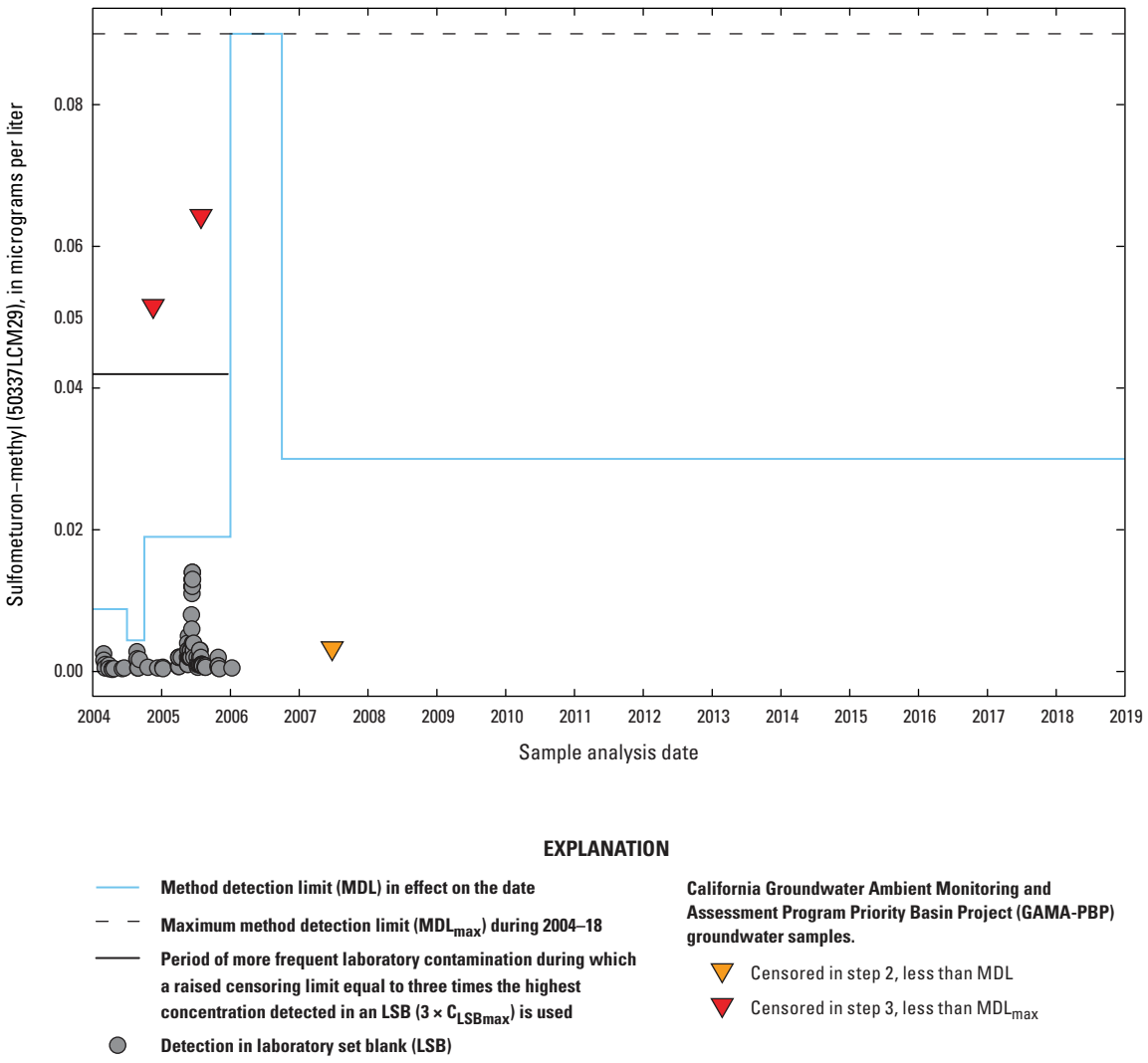

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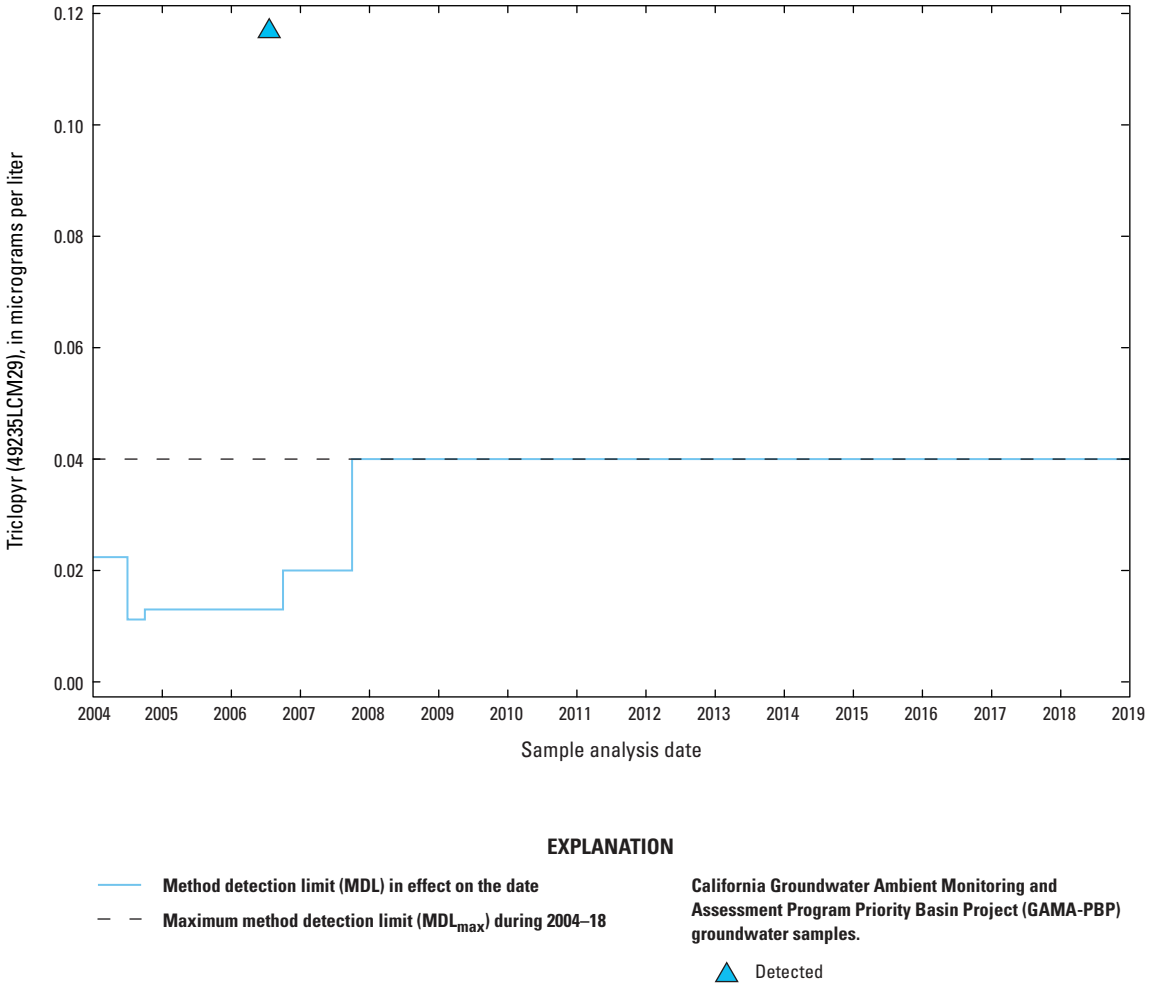

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Step 3: Evaluating the History of Method Detection Limits Used During 2004–18 to Select One Method Detection Limit as the Study Reporting Limit for the Entire Dataset and Censoring Results Having Concentrations Less Than That Reporting Limit

As discussed in the section on GAMA-PBP data-quality objectives, use of a single reporting limit for each constituent, rather than multiple censoring limits, facilitates comparisons on an equivalent basis through time. The simplest choice of a single reporting limit would be the highest MDL (MDL_{max}) established by the NWQL during July 2004−August 2018. This section presents an evaluation of the history of MDLs established during that period and describes the GAMA-PBP's justification for using the MDL_{max} as the preferred reporting limit for the dataset.

The same analytical methods were used for the entire period 2004−2018 (schedule 2003, 2032, or 2033 and schedule 2060); however, the MDLs for many constituents changed for reasons including improvements or degradation in instrumentation, changes in the types and quantity of data used to calculate the MDLs, and transient contamination conditions in the laboratory. Depending on the type of change, if any, observed in the MDLs during the entire period of the dataset (2004−18), it may be appropriate to use the highest MDL (MDL_{max}) as the censoring limit for the entire dataset (for example, Fram and Belitz, 2011; Fram and others, 2012).

The MDLs in use between July 2004 and August 2018 for pesticide constituents on schedules 2003, 2032, or 2033, or on schedule 2060 are listed in the USGS data release published concurrently with this report (Lor and others, 2019) and are summarized in table 2. Sample collection for the GAMA-PBP began in May 2004, and the NWQL began analyzing GAMA-PBP samples in July 2004. The evaluation described in this report was done in September 2018, hence the date of August 2018 for retrieval of MDL information. The GAMA-PBP plans to continue to collect data for pesticide constituents on schedule 2003, 2032, or 2033 beyond the publication date of this report; MDLs for schedules 2003, 2032, or 2033 continue to be monitored, and an update to this report is intended to be published if there are substantial changes to those MDLs in the future. The GAMA-PBP ceased collecting data for pesticide constituents on schedule 2060 in February 2011.

Data for detection limits, laboratory reporting levels, and reporting level types used during 2001−18 are listed in Lor and others (2019). The reporting level types were the IRL, LRL, and MRL. For IRLs and LRLs, the MDL or LT-MDL was usually half of the IRL or LRL, although not always exactly half because of rounding. During the period addressed in this report (2004−18), the reporting level for seven constituents was an MRL for at least some of the time. The primary reason for assigning an MRL was chronic contamination in laboratory set blanks (LSBs); the MRL is used as a censoring limit for reporting detections and, therefore, functions as an MDL for the purpose of reporting (see Medalie and others, 2019, for more discussion). Schedules 2003, 2032, and 2033 usually had the same MDLs and the same number of changes in MDLs for each constituent; for some constituents, schedule 2033 had a higher maximum MDL and a greater number of changes than did schedule 2003 or 2032. In those cases, the schedule 2033 MDLs were selected to represent the constituents.

Of the 142 constituents in the 2 analytical methods, 135 had at least 1 change in MDL between July 2004 and August 2018, and a majority had at least 3 changes in MDL (fig. 5*A*; table 2). About 75 percent of the 415 changes in MDLs were to increase the MDL concentration (fig. 5*B*). Overall, MDL concentrations increased between July 2004 and August 2018: 125 constituents had a higher MDL in August 2018 than in July 2004 (table 2). The changes were not evenly distributed in time: about 80 percent of the changes were in Federal fiscal years 2005–09 (fig. 5*B*).

A possible explanation for the overall increase in MDLs is that as more data are gathered to establish MDLs, the MDLs become more representative of the true long-term capability in the analytical method. A similar pattern of increasing MDLs through time was observed for pharmaceutical constituents on NWQL schedule 9003/2080 (Fram and Belitz, 2011). In that case, the MDLs increased most when the NWQL switched the method from a research method using interim MDLs and IRLs to a production method using LT-MDLs and LRLs. Interim MDLs were calculated using the original EPA procedure based on seven low-level spikes (U.S. Environmental Protection Agency, 1997). The LT-MDL calculation procedure is based on 24 low-level spikes collected over at least 6 months and is designed to more fully incorporate the inherent day-to-day variability in the method (Childress and others, 1999; U.S. Geological Survey, 2015). For the pesticide constituents on NWQL schedules 2003, 2032, or 2033, or on schedule 2060, 99 constituents changed from an IRL in July 2004 to an LRL by August 2018 (table 2), and 90 percent of the changes from IRL to LRL were in 2005 and 2006, of which 80 percent were to a higher MDL (fig. 5*B*). Thus, change in the procedures used to calculate MDLs contributed substantially to the overall increase in MDLs between July 2004 and August 2018.

Table 2. Summary of method detection limits during July 2004–August 2018, detection frequencies in laboratory set blanks during January 2002–May 2016, and detection frequencies in U.S. Geological Survey Branch of Quality Systems Organic Blind Sample Program (OBSP) unspiked blanks January 2001–September 2017 for pesticide constituents on National Water Quality Laboratory (NWQL) schedules 2003, 2032, or 2033, or on schedule 2060.

[The constituent identification code is the concatenation of the 5-digit numeric U.S. Geological Survey (USGS) parameter code unique that identifies a constituent or property and the 5-digit alphanumeric USGS method code that indicates the analytical method used to measure it. NWQL schedule 2003/2033 uses method codes GCM35, GCM39, GCM14, GCM29, and GCM40; NWQL schedule 2060 uses method code LCM29. **Constituents**: CIAT, 2-Chloro-4-isopropylamino-6-amino-*s*-triazine; CEAT, 2-Chloro-6-ethylamino-4-amino-*s*-triazine; OIET, 2-Hydroxy-4-isopropylamino-6-ethylamino-*s*-triazine. **Other abbreviations**: MDL, method detection limit; OBSP, Organic Blind Sample Program; MDL_{max}, maximum method detection limit; RLTYP, reporting level type; IRL, interim reporting level; LRL, laboratory reporting level; MRL, method reporting limit; LSB, laboratory set blank; DLBLK-LSB, detection limit determined from LSBs; µg/L, microgram per liter; NWQL, National Water Quality Laboratory; —, none; nc, no changes; nd, no data]

Constituent identification code	Constituent name	Method detection limits and reporting level types[1]						Changes in MDLs[1]		Laboratory set blanks[2]			OBSP unspiked blanks[3]
		MDL in July 2004 (µg/L)	RLTYP in July 2004	MDL in August 2018 (µg/L)	RLTYP in August 2018	Federal fiscal year August 2018 MDL began	MDL_{max} during July 2004–August 2018 (µg/L)	Number of changes in MDL during July 2004–August 2018	Percentage of MDL changes that were increasing concentration	Detection frequency in LSBs during January 2001–May 2016 (percent)	Detection frequency in LSBs not in contamination periods[4] (percent)	DLBLK-LSB (µg/L)	Detection frequency in OBSP unspiked blanks (percent)
Constituents on NWQL schedule 2003, 2032, or 2033													
49260GCM33	Acetochlor	0.003	LRL	0.005	LRL	2009	0.005	1	100	0.02	0.02	—	—
46342GCM35	Alachlor	0.002	LRL	0.004	LRL	2009	0.004	2	100	0.02	0.02	—	—
39632GCM35	Atrazine	0.004	LRL	0.004	LRL	2004	0.004	0	nc	0.3	0.1	—	1.3
82686GCM35	Azinphos-methyl	0.02	LRL	0.06	LRL	2008	0.06	2	100	—	—	—	—
61635GCM39	Azinphos-methyl oxon	0.0117	IRL	0.021	LRL	2006	0.021	1	100	0.03	0.03	—	1.1
82673GCM35	Benfluralin	0.005	LRL	0.007	LRL	2009	0.007	3	67	12.5	1.3	0.0029	0.4
82680GCM35	Carbaryl	0.021	LRL	0.03	LRL	2010	0.1	3	67	0.02	0.02	—	1.8
82674GCM35	Carbofuran	0.01	LRL	0.03	LRL	2009	0.03	1	100	0.02	0.02	—	—
61618GCM39	2-Chloro-2',6'-diethylacetanilide	0.0021	IRL	0.005	LRL	2008	0.005	2	100	0.1	0.1	—	—
61633GCM39	4-Chloro-2-methylphenol	0.0013	IRL	0.004	LRL	2012	0.004	4	75	0.1	0.1	—	—
38933GCM35	Chlorpyrifos	0.003	LRL	0.005	IRL	2013	0.005	3	67	0.2	0.2	—	—
61636GCM39	Chlorpyrifos oxon	0.0099	IRL	0.04	IRL	2012	0.04	2	100	—	—	—	0.4
04041GCM35	Cyanazine	0.009	LRL	0.011	LRL	2010	0.02	3	67	0.05	0.05	—	—
61585GCM39	Cyfluthrin	0.0006	IRL	0.008	LRL	2008	0.026	2	50	—	—	—	—
61595GCM39	λ-Cyhalothrin	0.0009	IRL	0.007	LRL	2013	0.0071	4	75	—	—	—	—
61586GCM39	Cypermethrin	0.0011	IRL	0.01	LRL	2009	0.023	3	67	—	—	—	—
82682GCM35	DCPA (Dacthal)	0.002	LRL	0.0038	LRL	2010	0.0038	2	100	7.8	1.3	0.0014	—

Table 2. Summary of method detection limits during July 2004–August 2018, detection frequencies in laboratory set blanks during January 2002–May 2016, and detection frequencies in U.S. Geological Survey Branch of Quality Systems Organic Blind Sample Program (OBSP) unspiked blanks January 2001–September 2017 for pesticide constituents on National Water Quality Laboratory (NWQL) schedules 2003, 2032, or 2033, or on schedule 2060.—Continued

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Constituent identification code	Constituent name	Method detection limits and reporting level types[1]						Changes in MDLs[1]		Laboratory set blanks[2]			OBSP unspiked blanks[3]
		MDL in July 2004 (µg/L)	RLTYP in July 2004	MDL in August 2018 (µg/L)	RLTYP in August 2018	Federal fiscal year August 2018 MDL began	MDL_{max} during July 2004–August 2018 (µg/L)	Number of changes in MDL during July 2004–August 2018	Percentage of MDL changes that were increasing concentration	Detection frequency in LSBs during January 2001–May 2016 (percent)	Detection frequency in LSBs not in contamination periods[4] (percent)	DLBLK-LSB (µg/L)	Detection frequency in OBSP unspiked blanks (percent)
Constituents on NWQL schedule 2003, 2032, or 2033—Continued													
04040GCM35	Deethylatrazine (CIAT)	0.003	LRL	0.005	LRL	2013	0.007	4	75	0.1	0.1	—	—
62170GCM29	Desulfinylfipronil	0.006	LRL	0.006	LRL	2004	0.006	0	nc	0.5	0.2	—	1.7
62169GCM29	Desulfinylfipronil amide	0.015	LRL	0.015	LRL	2004	0.015	0	nc	0.1	—	—	—
39572GCM35	Diazinon	0.003	LRL	0.003	LRL	2004	0.003	0	nc	0.1	0.1	—	1.4
61638GCM14	Diazinon oxon	0.0021	IRL	0.006	LRL	2012	0.006	2	100	—	—	—	1.0
61625GCM39	3,4-Dichloroaniline	0.0015	IRL	0.003	LRL	2012	0.003	4	75	0.3	0.3	—	—
61627GCM39	3,5-Dichloroaniline	0.0017	IRL	0.003	LRL	2012	0.006	6	50	0.2	0.0	—	0.9
38775GCM39	Dichlorvos	0.0027	IRL	0.02	LRL	2017	0.02	3	100	—	—	—	—
38454GCM39	Dicrotophos	0.01589	IRL	0.04	LRL	2009	0.04	1	100	—	—	—	0.5
39381GCM35	Dieldrin	0.004	LRL	0.006	LRL	2016	0.006	1	100	3.8	0.9	—	0.4
82660GCM35	2,6-Diethylaniline	0.003	LRL	0.003	LRL	2004	0.003	0	nc	0.3	0.3	—	—
82662GCM40	Dimethoate	0.0011	IRL	0.005	LRL	2012	0.005	2	100	0.1	0.1	—	—
82677GCM35	Disulfoton	0.011	LRL	0.02	LRL	2008	0.02	2	50	—	—	—	—
61640GCM39	Disulfoton sulfone	0.0013	IRL	0.005	LRL	2013	0.007	3	67	—	—	—	2.8
34362GCM39	α-Endosulfan	0.0012	IRL	0.005	LRL	2016	0.0055	3	67	0.6	0.2	—	—
61590GCM39	Endosulfan sulfate	0.004	IRL	0.008	LRL	2011	0.011	3	67	—	—	—	—
82668GCM35	EPTC	0.002	LRL	0.0028	LRL	2011	0.0028	2	50	0.2	0.2	—	—
82346GCM40	Ethion	0.0008	IRL	0.005	LRL	2012	0.0082	5	60	0.1	0.1	—	0.4
61644GCM39	Ethion monoxon	0.0004	IRL	0.011	LRL	2006	0.011	1	100	0.03	0.03	—	2.1

Table 2. Summary of method detection limits during July 2004–August 2018, detection frequencies in laboratory set blanks during January 2002–May 2016, and detection frequencies in U.S. Geological Survey Branch of Quality Systems Organic Blind Sample Program (OBSP) unspiked blanks January 2001–September 2017 for pesticide constituents on National Water Quality Laboratory (NWQL) schedules 2003, 2032, or 2033, or on schedule 2060.—Continued

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Constituent identification code	Constituent name	Method detection limits and reporting level types[1]						Changes in MDLs[1]		Laboratory set blanks[2]			OBSP unspiked blanks[3]
		MDL in July 2004 (µg/L)	RLTYP in July 2004	MDL in August 2018 (µg/L)	RLTYP in August 2018	Federal fiscal year August 2018 MDL began	MDL_{max} during July 2004–August 2018 (µg/L)	Number of changes in MDL during July 2004–August 2018	Percentage of MDL changes that were increasing concentration	Detection frequency in LSBs during January 2001–May 2016 (percent)	Detection frequency in LSBs not in contamination periods[4] (percent)	DLBLK-LSB (µg/L)	Detection frequency in OBSP unspiked blanks (percent)
Constituents on NWQL schedule 2003, 2032, or 2033—Continued													
82672GCM35	Ethoprop	0.002	LRL	0.008	LRL	2009	0.008	3	100	0.1	0.1	—	0.9
61620GCM39	2-Ethyl-6-methylaniline	0.0016	IRL	0.005	LRL	2011	0.005	2	100	0.1	0.1	—	—
61591GCM39	Fenamiphos	0.0147	IRL	0.015	LRL	2006	0.015	1	100	—	—	—	0.9
61645GCM39	Fenamiphos sulfone	0.0088	IRL	0.027	LRL	2006	0.027	1	100	0.03	0.03	—	1.4
61646GCM39	Fenamiphos sulfoxide	0.0086	IRL	0.04	LRL	2009	0.1	3	67	—	—	—	1.3
62166GCM29	Fipronil	0.008	LRL	0.009	LRL	2010	0.02	3	67	0.1	0.1	—	1.5
62167GCM29	Fipronil sulfide	0.006	LRL	0.008	LRL	2013	0.008	1	100	0.7	0.6	—	14.0
62168GCM29	Fipronil sulfone	0.012	LRL	0.012	LRL	2004	0.012	0	nc	0.3	0.3	—	13.4
04095GCM35	Fonofos	0.001	LRL	0.0024	LRL	2011	0.005	5	80	0.2	0.2	—	0.4
61649GCM39	Fonofos oxon	0.0008	IRL	0.0008	IRL	2004	0.0008	0	nc	—	—	—	nd
04025GCM39	Hexazinone	0.002	IRL	0.006	LRL	2012	0.013	3	67	—	—	—	—
61593GCM39	Iprodione	0.269	IRL	0.007	LRL	2009	0.269	3	33	0.1	0.1	—	—
61594GCM39	Isofenphos	0.0011	IRL	0.007	LRL	2013	0.007	4	75	0.1	0.1	—	—
61652GCM39	Malaoxon	0.0075	IRL	0.011	LRL	2011	0.04	4	50	0.2	0.1	—	1.4
39532GCM35	Malathion	0.014	LRL	0.008	LRL	2010	0.014	3	33	—	—	—	—
61596GCM39	Metalaxyl	0.0021	IRL	0.007	LRL	2011	0.007	3	67	0.7	0.3	—	—
61598GCM39	Methidathion	0.0013	IRL	0.006	LRL	2011	0.006	4	75	—	—	—	—
61664GCM39	Methyl paraoxon	0.0096	IRL	0.007	LRL	2011	0.01	3	67	—	—	—	—
82667GCM35	Methyl parathion	0.008	LRL	0.004	LRL	2007	0.008	1	0	0.02	0.02	—	—

Table 2. Summary of method detection limits during July 2004–August 2018, detection frequencies in laboratory set blanks during January 2002–May 2016, and detection frequencies in U.S. Geological Survey Branch of Quality Systems Organic Blind Sample Program (OBSP) unspiked blanks January 2001–September 2017 for pesticide constituents on National Water Quality Laboratory (NWQL) schedules 2003, 2032, or 2033, or on schedule 2060.—Continued

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Constituent identification code	Constituent name	Method detection limits and reporting level types[1]						Changes in MDLs[1]		Laboratory set blanks[2]			OBSP unspiked blanks[3]
		MDL in July 2004 (µg/L)	RLTYP in July 2004	MDL in August 2018 (µg/L)	RLTYP in August 2018	Federal fiscal year August 2018 MDL began	MDL_{max} during July 2004–August 2018 (µg/L)	Number of changes in MDL during July 2004–August 2018	Percentage of MDL changes that were increasing concentration	Detection frequency in LSBs during January 2001–May 2016 (percent)	Detection frequency in LSBs not in contamination periods[4] (percent)	DLBLK-LSB (µg/L)	Detection frequency in OBSP unspiked blanks (percent)
Constituents on NWQL schedule 2003, 2032, or 2033—Continued													
39415GCM35	Metolachlor	0.006	LRL	0.01	LRL	2011	0.01	4	75	1.8	0.8	—	0.4
82630GCM35	Metribuzin	0.003	LRL	0.006	LRL	2010	0.014	4	50	0.02	0.02	—	—
82671GCM35	Molinate	0.002	LRL	0.004	LRL	2013	0.004	4	75	1.2	0.2	—	—
61599GCM39	Myclobutanil	0.0011	IRL	0.005	LRL	2008	0.017	2	50	0.1	0.1	—	—
49295GCM39	1-Naphthol	0.0363	IRL	0.025	LRL	2013	0.0363	3	33	0.9	0.7	—	3.6
61600GCM39	Oxyfluorfen	0.0016	IRL	0.005	LRL	2012	0.0085	5	60	1.3	0.6	—	—
82683GCM35	Pendimethalin	0.011	LRL	0.006	LRL	2008	0.011	2	0	0.2	0.2	—	—
82687GCM35	*cis*-Permethrin	0.003	LRL	0.005	LRL	2011	0.007	3	67	0.1	0.1	—	—
82664GCM35	Phorate	0.006	LRL	0.01	LRL	2009	0.027	4	50	—	—	—	—
61666GCM39	Phorate oxon	0.0083	IRL	0.013	LRL	2006	0.013	1	100	—	—	—	—
61601GCM39	Phosmet	0.0009	IRL	0.07	IRL	2013	0.1	5	60	1.0	—	—	—
61668GCM39	Phosmet oxon	0.0079	IRL	0.0079	LRL	2017	0.0079	0	nc	—	—	—	1.4
04037GCM35	Prometon	0.002	LRL	0.006	LRL	2009	0.006	1	100	0.4	0.2	—	—
04036GCM39	Prometryn	0.002	IRL	0.005	LRL	2012	0.005	2	100	0.2	0.2	—	0.9
82679GCM35	Propanil	0.005	LRL	0.005	LRL	2010	0.007	3	33	0.2	0.1	—	—
82685GCM35	Propargite	0.011	LRL	0.01	LRL	2009	0.02	3	33	0.05	0.05	—	—
79846GCM40	*cis*-Propiconazole	0.0006	IRL	0.004	LRL	2011	0.0064	3	67	—	—	—	nd
79847GCM40	*trans*-Propiconazole	0.0013	IRL	0.009	LRL	2012	0.017	4	50	—	—	—	nd
82676GCM35	Propyzamide	0.002	LRL	0.004	LRL	2013	0.004	2	50	0.02	0.02	—	—

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Constituent identification code	Constituent name	Method detection limits and reporting level types[1]						Changes in MDLs[1]		Laboratory set blanks[2]			OBSP unspiked blanks[3]
		MDL in July 2004 (µg/L)	RLTYP in July 2004	MDL in August 2018 (µg/L)	RLTYP in August 2018	Federal fiscal year August 2018 MDL began	MDL_{max} during July 2004–August 2018 (µg/L)	Number of changes in MDL during July 2004–August 2018	Percentage of MDL changes that were increasing concentration	Detection frequency in LSBs during January 2001–May 2016 (percent)	Detection frequency in LSBs not in contamination periods[4] (percent)	DLBLK-LSB (µg/L)	Detection frequency in OBSP unspiked blanks (percent)
Constituents on NWQL schedule 2003, 2032, or 2033—Continued													
04035GCM35	Simazine	0.002	LRL	0.003	LRL	2010	0.005	3	67	0.2	0.1	—	13.8
62852GCM14	Tebuconazole	0.002	IRL	0.01	LRL	2009	0.01	2	100	0.0	0.0	—	—
82670GCM35	Tebuthiuron	0.008	LRL	0.014	LRL	2010	0.014	2	100	0.04	0.04	—	—
61606GCM39	Tefluthrin	0.0012	IRL	0.007	LRL	2012	0.007	3	100	5.1	1.7	0.003	0.4
82675GCM35	Terbufos	0.009	LRL	0.009	LRL	2008	0.009	2	50	—	—	—	—
61674GCM39	Terbufos oxon sulfone	0.0176	IRL	0.022	LRL	2006	0.022	1	100	—	—	—	1.1
04022GCM39	Terbuthylazine	0.0045	IRL	0.004	LRL	2012	0.0045	3	33	0.2	0.2	—	0.5
82681GCM35	Thiobencarb	0.005	LRL	0.008	LRL	2009	0.008	1	100	0.1	0.1	—	2.1
61610GCM39	Tribuphos	0.0008	IRL	0.009	LRL	2010	0.018	2	50	0.1	0.1	—	3.3
82661GCM35	Trifluralin	0.005	LRL	0.009	LRL	2010	0.009	4	75	11.5	1.8	0.003	—
Constituents on NWQL schedule 2060													
49315LCM29	Acifluorfen	0.0033	IRL	0.04	LRL	2012	0.04	4	75	0.1	0.1	—	—
49312LCM29	Aldicarb	0.0198	IRL	0.06	LRL	2008	0.15	4	75	—	—	—	0.4
49313LCM29	Aldicarb sulfone	0.0098	IRL	0.04	LRL	2007	0.04	2	50	0.3	0.1	—	11.7
49314LCM29	Aldicarb sulfoxide	0.0041	IRL	0.04	LRL	2012	0.051	5	80	—	—	—	8.0
39632LCM29	Atrazine	0.0045	IRL	0.04	LRL	2012	0.04	3	67	0.4	0.4	—	0.5
50299LCM29	Bendiocarb	0.0126	IRL	0.02	LRL	2007	0.042	3	33	0.2	—	—	1.5
50300LCM29	Benomyl	0.0019	IRL	0.03	LRL	2009	0.03	4	75	0.1	0.1	—	—
61693LCM29	Bensulfuron-methyl	0.0079	IRL	0.03	LRL	2007	0.03	2	100	0.1	0.1	—	—

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Constituent identification code	Constituent name	Method detection limits and reporting level types[1]						Changes in MDLs[1]		Laboratory set blanks[2]			OBSP unspiked blanks[3]
		MDL in July 2004 (µg/L)	RLTYP in July 2004	MDL in August 2018 (µg/L)	RLTYP in August 2018	Federal fiscal year August 2018 MDL began	MDL_{max} during July 2004–August 2018 (µg/L)	Number of changes in MDL during July 2004–August 2018	Percentage of MDL changes that were increasing concentration	Detection frequency in LSBs during January 2001–May 2016 (percent)	Detection frequency in LSBs not in contamination periods[4] (percent)	DLBLK-LSB (µg/L)	Detection frequency in OBSP unspiked blanks (percent)
Constituents on NWQL schedule 2060—Continued													
38711LCM29	Bentazon	0.0055	IRL	0.03	LRL	2009	0.03	5	80	0.4	—	—	1.1
04029LCM29	Bromacil	0.0163	IRL	0.03	LRL	2009	0.03	4	50	—	—	—	—
49311LCM29	Bromoxynil	0.0085	IRL	0.06	LRL	2007	0.06	3	100	0.1	0.1	—	0.4
49310LCM29	Carbaryl	0.0142	IRL	0.02	LRL	2008	0.02	3	67	1.5	0.2	—	—
49309LCM29	Carbofuran	0.0028	IRL	0.02	LRL	2009	0.03	4	75	0.6	0.1	—	—
04038LCM29	CEAT	0.0052	IRL	0.04	LRL	2012	0.04	3	67	0.1	0.1	—	0.9
61188LCM29	Chloramben methyl ester	0.0089	IRL	0.1	LRL	2012	0.1	3	100	—	—	—	1.2
50306LCM29	Chlorimuron-ethyl	0.0048	IRL	0.04	LRL	2007	0.04	2	100	0.9	—	—	—
61692LCM29	*N*-(4-Chlorophenyl)-*N*'-methylurea	0.0121	IRL	0.05	LRL	2012	0.06	5	80	3.1	—	—	—
49305LCM29	Clopyralid	0.0069	IRL	0.07	LRL	2012	0.07	4	75	—	—	—	—
04031LCM29	Cycloate	0.0065	IRL	0.02	LRL	2009	0.03	4	75	0.3	—	—	0.4
39732LCM29	2,4-D	0.0109	IRL	0.03	LRL	2009	0.03	4	75	—	—	—	5.4
50470LCM29	2,4-D methyl ester	0.0043	IRL	0.2	MRL	2012	0.2	6	83	0.1	0.1	—	18.0
38746LCM29	2,4-DB	0.008	IRL	0.01	LRL	2005	0.01	1	100	—	—	—	3.0
49304LCM29	Dacthal (DCPA) monoacid	0.0058	IRL	0.02	LRL	2009	0.02	3	67	—	—	—	0.4
04040LCM29	Deethylatrazine (CIAT)	0.0141	IRL	0.03	LRL	2008	0.03	3	33	0.1	0.1	—	—

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Constituent identification code	Constituent name	Method detection limits and reporting level types[1]						Changes in MDLs[1]		Laboratory set blanks[2]			OBSP unspiked blanks[3]
		MDL in July 2004 (µg/L)	RLTYP in July 2004	MDL in August 2018 (µg/L)	RLTYP in August 2018	Federal fiscal year August 2018 MDL began	MDL_{max} during July 2004–August 2018 (µg/L)	Number of changes in MDL during July 2004–August 2018	Percentage of MDL changes that were increasing concentration	Detection frequency in LSBs during January 2001–May 2016 (percent)	Detection frequency in LSBs not in contamination periods[4] (percent)	DLBLK-LSB (µg/L)	Detection frequency in OBSP unspiked blanks (percent)
Constituents on NWQL schedule 2060—Continued													
38442LCM29	Dicamba	0.0064	IRL	0.05	LRL	2013	0.05	5	80	—	—	—	—
49302LCM29	Dichlorprop	0.0069	IRL	0.02	LRL	2009	0.02	4	75	—	—	—	0.8
49301LCM29	Dinoseb	0.006	IRL	0.03	LRL	2013	0.03	3	100	0.8	0.6	—	0.4
04033LCM29	Diphenamid	0.0132	IRL	0.02	LRL	2007	0.02	2	50	0.4	—	—	—
49300LCM29	Diuron	0.0075	IRL	0.02	LRL	2007	0.02	3	100	19.9	—	—	—
49297LCM29	Fenuron	0.0158	IRL	0.03	LRL	2009	0.1	5	60	20.2	—	—	—
61694LCM29	Flumetsulam	0.0057	IRL	0.04	LRL	2012	0.04	3	100	3.2	0.2	—	3.3
38811LCM29	Fluometuron	0.0155	IRL	0.02	LRL	2007	0.02	2	50	0.1	0.1	—	—
49308LCM29	3-Hydroxy carbofuran	0.0029	IRL	0.03	LRL	2012	0.03	4	100	0.1	0.1	—	0.4
50356LCM29	Imazaquin	0.0078	IRL	0.07	LRL	2013	0.07	7	86	0.9	0.9	—	—
50407LCM29	Imazethapyr	0.0084	IRL	0.04	LRL	2012	0.04	4	100	1.0	0.5	—	0.8
61695LCM29	Imidacloprid	0.0034	IRL	0.04	LRL	2012	0.04	3	100	0.1	0.1	—	—
38478LCM29	Linuron	0.0072	IRL	0.02	LRL	2009	0.02	4	50	—	—	—	0.4
38482LCM29	MCPA	0.0081	IRL	0.02	IRL	2009	0.033	4	50	—	—	—	0.5
38487LCM29	MCPB	0.0077	IRL	0.2	MRL	2012	0.2	5	60	—	—	—	—
50359LCM29	Metalaxyl	0.01	IRL	0.02	LRL	2009	0.02	5	60	0.1	0.1	—	0.5
38501LCM29	Methiocarb	0.004	IRL	0.02	LRL	2007	0.02	3	100	—	—	—	—
49296LCM29	Methomyl	0.0022	IRL	0.06	LRL	2008	0.06	4	75	—	—	—	—
61697LCM29	Metsulfuron-methyl	0.0123	IRL	0.07	LRL	2007	0.07	3	100	3.6	0.3	—	0.4

Table 2. Summary of method detection limits during July 2004–August 2018, detection frequencies in laboratory set blanks during January 2002–May 2016, and detection frequencies in U.S. Geological Survey Branch of Quality Systems Organic Blind Sample Program (OBSP) unspiked blanks January 2001–September 2017 for pesticide constituents on National Water Quality Laboratory (NWQL) schedules 2003, 2032, or 2033, or on schedule 2060.—Continued

[The constituent identification code is the concatenation of the 5-digit numeric U.S. Geological Survey (USGS) parameter code unique that identifies a constituent or property and the 5-digit alphanumeric USGS method code that indicates the analytical method used to measure it. NWQL schedule 2003/2033 uses method codes GCM35, GCM39, GCM14, GCM29, and GCM40; NWQL schedule 2060 uses method code LCM29. **Constituents**: CIAT, 2-Chloro-4-isopropylamino-6-amino-*s*-triazine; CEAT, 2-Chloro-6-ethylamino-4-amino-*s*-triazine; OIET, 2-Hydroxy-4-isopropylamino-6-ethylamino-*s*-triazine. **Other abbreviations**: MDL, method detection limit; OBSP, Organic Blind Sample Program; MDL_{max}, maximum method detection limit; RLTYP, reporting level type; IRL, interim reporting level; LRL, laboratory reporting level; MRL, method reporting limit; LSB, laboratory set blank; DLBLK-LSB, detection limit determined from LSBs; µg/L, microgram per liter; NWQL, National Water Quality Laboratory; —, none; nc, no changes; nd, no data]

Constituent identification code	Constituent name	Method detection limits and reporting level types[1]						Changes in MDLs[1]		Laboratory set blanks[2]			OBSP unspiked blanks[3]
		MDL in July 2004 (µg/L)	RLTYP in July 2004	MDL in August 2018 (µg/L)	RLTYP in August 2018	Federal fiscal year August 2018 MDL began	MDL_{max} during July 2004–August 2018 (µg/L)	Number of changes in MDL during July 2004–August 2018	Percentage of MDL changes that were increasing concentration	Detection frequency in LSBs during January 2001–May 2016 (percent)	Detection frequency in LSBs not in contamination periods[4] (percent)	DLBLK-LSB (µg/L)	Detection frequency in OBSP unspiked blanks (percent)
Constituents on NWQL schedule 2060—Continued													
49294LCM29	Neburon	0.006	IRL	0.01	LRL	2007	0.01	1	100	0.5	0.2	—	—
50364LCM29	Nicosulfuron	0.0065	IRL	0.16	LRL	2012	0.16	3	100	0.1	0.1	—	—
49293LCM29	Norflurazon	0.0082	IRL	0.02	LRL	2009	0.02	4	75	0.3	—	—	—
50355LCM29	OIET	0.004	IRL	0.03	LRL	2009	0.04	4	75	0.1	0.1	—	nd
49292LCM29	Oryzalin	0.0088	IRL	0.02	LRL	2007	0.02	3	67	0.2	—	—	0.8
38866LCM29	Oxamyl	0.0061	IRL	0.06	LRL	2008	0.06	4	75	0.1	0.1	—	0.8
49291LCM29	Picloram	0.0099	IRL	0.05	LRL	2012	0.06	3	67	—	—	—	0.9
49236LCM29	Propham	0.0048	IRL	0.02	LRL	2008	0.03	3	67	0.4	0.1	—	—
50471LCM29	Propiconazole	0.0105	IRL	0.03	LRL	2013	0.03	5	40	0.1	0.1	—	—
38538LCM29	Propoxur	0.004	IRL	0.03	LRL	2009	0.03	2	100	0.1	0.1	—	—
38548LCM29	Siduron	0.0084	IRL	0.02	LRL	2009	0.02	4	75	1.3	0.2	—	—
50337LCM29	Sulfometuron-methyl	0.0044	IRL	0.03	LRL	2007	0.09	3	67	7.0	0.1	—	—
82670LCM29	Tebuthiuron	0.0031	IRL	0.03	LRL	2009	0.03	3	100	1.4	0.2	—	—
04032LCM29	Terbacil	0.0049	IRL	0.023	LRL	2012	0.023	4	100	—	—	—	0.4
49235LCM29	Triclopyr	0.0112	IRL	0.04	LRL	2008	0.04	3	100	—	—	—	—

[1]Information from Lor and others (2019).

[2]Data from Riskin and others (2019).

[3]Data from U.S. Geological Survey Quality Systems Branch Organic Blind Sample Project https://qsb.usgs.gov/OBSP/index.html.

[4]Periods of more frequent laboratory contamination (table 3).

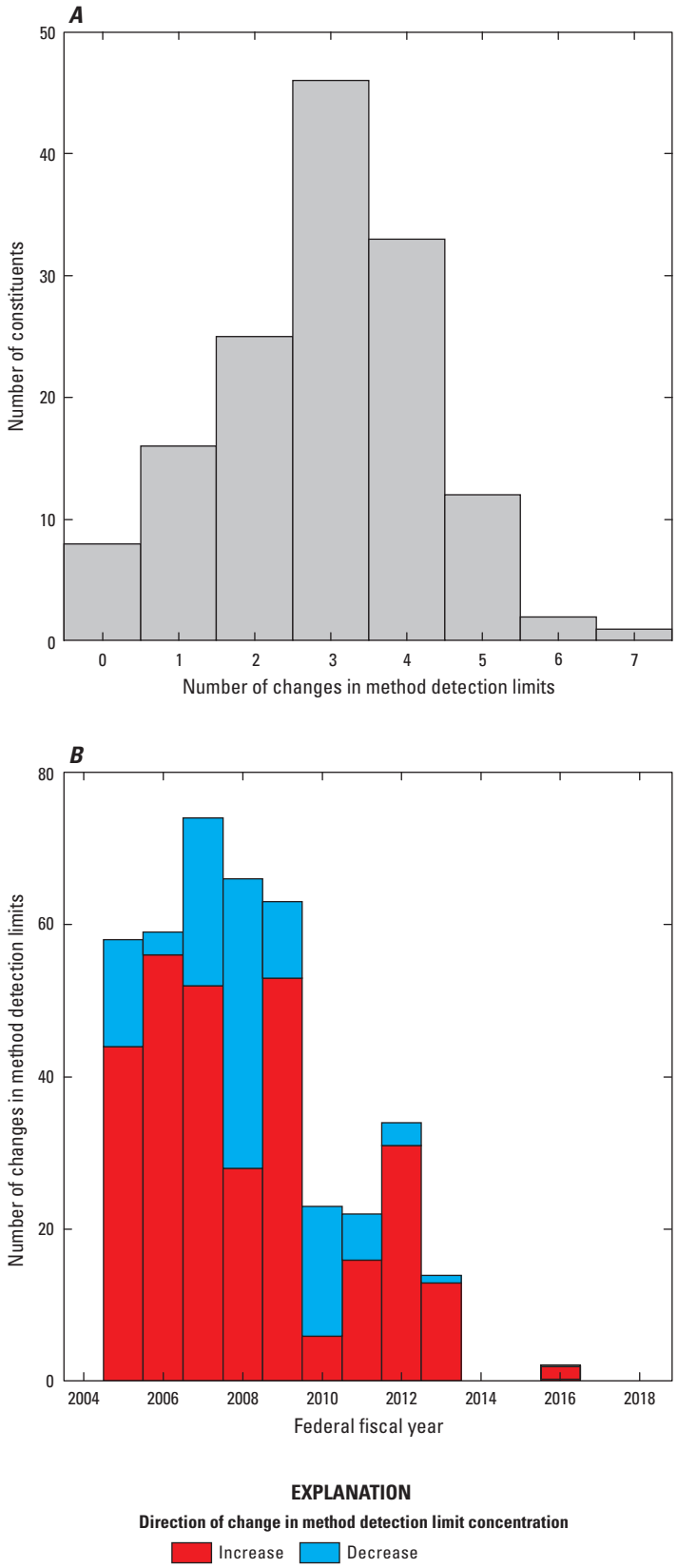

Figure 5. The number of changes in method detection limit for *A*, the 143 pesticide constituents on U.S. Geological Survey National Water Quality (NWQL) schedules 2003, 2032, or 2033, or on schedule 2060 from July 2004 through August 2018, and *B*, the direction of those changes for each Federal fiscal year.

Another possible explanation for increases in MDLs through time is that the concentrations of the low-level spikes used to calculate the MDL may have increased during that time (Mark Sandstrom, U.S. Geological Survey National Water Quality Laboratory, written commun., Nov. 29, 2018). Calculation of an MDL from low-level spikes relies on the assumption that the concentration of the low-level spike is low enough to be within the range of concentrations for which the standard deviation of results from multiple analyses is the same as the standard deviation of results from multiple analyses of blanks (U.S. Environmental Protection Agency, 1997, 2016a; Childress and others, 1999; fig. 1). Standard deviation generally increases with concentration outside of this range. A greater standard deviation for the results from the low-level spikes would result in calculation of an MDL at a greater concentration. The NWQL may have increased the concentrations of low-level spikes used to calculate the MDL to minimize false negative non-detections in the dataset. The DQCALC procedure for calculating MDLs does not rely on the same assumption (ASTM International, 2007, 2010; U.S. Geological Survey, 2015), but as of August 2018 when information was compiled for this report, schedules 2003, 2032, or 2033, or on schedule 2060 had not been switched from the LT-MDL procedure for calculating MDLs to the DQCALC procedure.

Because the MDLs that were calculated annually generally increased from year to year, the NWQL reporting practice of applying new MDLs prospectively, not retrospectively to the past year, may result in data being reported with an MDL that is too low. In other words, the re-evaluation of MDLs is based on data collected during year 1, and the new MDL determined from those data is applied in year 2. If the MDL re-evaluation resulted in an increase in the MDL concentration, then the samples analyzed in year 2 are reported with the MDL from year 1, but the new MDL is not applied retrospectively to data collected during year 1, meaning that the data collected during year 1 remain reported with an MDL that is known to be too low. Establishing a study reporting limit equal to the highest MDL eliminated this problem for data analysis.

Based on the observation that the MDLs generally increased with time, the GAMA-PBP defined the maximum MDLs established by the NWQL between July 2004 and August 2018 as the step 3 censoring limit for results from all samples collected by the GAMA-PBP in 2004–18. For two-thirds of the constituents, the MDL_{max} is also the MDL that was in effect in August 2018 (table 2).

Among the 135 constituents with at least one change in MDL, there were a total of 415 changes in MDL. These changes were not evenly distributed in time; 61 percent of the changes were in 2004–07, another 38 percent were in 2008–11, and 1 percent was in 2012–17 (fig. 5*B*). This pattern indicates the MDL_{max} during 2004–18 is unlikely to be exceeded in subsequent years, and therefore, censoring limits equal to the MDL_{max} used during 2004–18 are likely to be valid in subsequent years, assuming no major changes in methodology or procedures at the NWQL.

Censoring the GAMA-PBP dataset with the MDL_{max} (step 3) resulted in a large change in the number of detections reported in GAMA-PBP samples, censoring an additional 16 percent of the original detections reported by the NWQL. A total of 438 detections of 44 constituents remaining after step 2 censoring were at concentrations less than MDL_{max} and were censored in step 3 (table 1). Step 3 included censoring of all remaining detections of 16 constituents (schedule 2003, 2032, or 2033 constituents 3,5-dichloroaniline, benfluralin, dichlorvos, dicrotophos, dimethoate, isofenphos, λ-cyhalothrin, trifluralin; schedule 2060 constituents atrazine, bensulfuron-methyl, deethylatrazine, 2,4-D, metalaxyl, *N*-(4-chlorophenyl)-*N'*-methylurea, oxamyl, sulfometuron-methyl; table 1; fig. 4). Note that schedule 2003, 2032, or 2033 is the preferred method for atrazine and deethylatrazine, although these compounds are also reported for schedule 2060.

Step 4: Defining Periods of Increased Frequency of Laboratory Contamination for Specific Constituents Based on Detections in Laboratory Set Blanks and Establishing Raised Reporting Limits for Those Periods

Using the MDL_{max} as the study reporting limit may not provide sufficient protection against the risk of false positive detections during periods of greater frequency of laboratory contamination for particular constituents. For schedules 2003, 2032, or 2033, and schedule 2060, samples are processed and analyzed in sets, each set consisting of eight environmental samples, one LSB, and one laboratory set spike (see Medalie and others, 2019). The LSB is reagent water that is processed and analyzed the same way that the environmental samples are; thus, the LSBs record a history of contamination during laboratory sample processing and analysis, if any. The NWQL has standard procedures for applying raised reporting levels to environmental samples analyzed in sets for which the LSB had a detection (U.S. Geological Survey, 2012). Although these procedures are successful for addressing contamination in individual sets, examination of LSBs from all sets analyzed during 2001–16 indicated that the LSBs also recorded contamination that was not addressed by this set-based censoring approach (Medalie and others, 2019). Medalie and others (2019) evaluated LSBs for 21 pesticide constituents on schedules 2003, 2032, or 2033, or on schedule 2060, many of which were selected for evaluation because they were more frequently detected in LSBs than most of the other constituents. For those 21 constituents, Medalie and others (2019) found that detections in LSBs were unevenly distributed through time, such that periods during which the LSBs had few to no detections were interspersed with periods during which a greater percentage of the LSBs had detections. These periods are referred to as "periods of episodic laboratory contamination" by Medalie and others (2019), but are called "periods of more frequent laboratory contamination" in this report to avoid using the potentially ambiguous term "episodic."

This study used a slightly modified version of the method of Medalie and others (2019) to identify periods of greater frequency of laboratory contamination and a modified version of the NWQL's standard set-based censoring protocol (U.S. Geological Survey, 2012) to define and apply raised censoring limits during those periods. This study used the dataset of LSBs for schedules 2001/2003, 2032, or 2033 and 2060 analyzed during January 2001–May 2016 (Riskin and others, 2019), the same LSB dataset as used by Medalie and others (2019).

Medalie and others (2019) based their method for determining time periods of greater frequency of laboratory contamination on the 21-sample LSB moving average detection frequency approach of Fram and Belitz (2011). To adjust for the variable length of time represented by 21 sequential LSBs, Medalie and others (2019) used a variable-sample (11 to 21) moving average. The variable-sample moving average was not used in this study.

NWQL schedules 2001, 2003, 2032, and 2033 all use the same analytical method, but include quantitation of different combinations of analytes and are, therefore, analyzed in separate sets. Medalie and others (2019) found differences in the frequency of LSB contamination among the four schedules, such that for unknown reasons the frequency of contamination was greatest using schedule 2033, and therefore, they evaluated the LSBs from the four schedules separately. For this study, the 5,842 LSBs from the 4 schedules were combined into 1 population, and this larger combined dataset had fewer of the large gaps in time between LSBs that contributed to the variable time spans observed by Medalie and others (2019) in the four separate populations. Because the publicly available data in NWIS include method codes, but not analytical schedules, it would be difficult, although not impossible, to determine if results with the same method code were analyzed under the same or different schedules. For that reason, it seemed reasonable to combine the LSBs from the four schedules. Note that combining these datasets may underestimate laboratory contamination for samples analyzed under schedule 2033 and overestimate contamination for samples analyzed under schedule 2003.

For the 5,815 LSBs analyzed with schedules 2001, 2003, 2032, or 2033, the median length of time represented by 21 sequential LSBs was 15 days (10th percentile was 8 days, and the 90th percentile was 34 days). For the 1,890 LSBs analyzed with schedule 2060, the median length of time represented by 21 sequential LSBs was 44 days (10th percentile was 21 days, and the 90th percentile was 93 days). For both datasets, the lengths of time represented by 21 sequential LSBs increased substantially starting in 2013, when the NWQL began analyzing pesticide constituents by a new method, schedule 2437 (Sandstrom and others, 2015). For both datasets, the frequency of detections in the LSBs was greater during the earlier years; after 2007, there were relatively few constituents for which detection frequencies were greater than 10 percent in any of the sets of 21 sequential LSBs. Therefore, censoring data on the basis of detections in LSBs would be less likely in the later years, and the length of time represented by the 21 sequential LSBs becomes moot.

The rest of the procedure followed Medalie and others (2019). The center of a period of more frequent laboratory contamination was identified by 7 sequential 21-sample moving windows during which detection frequency in the LSB results was greater than 10 percent, and the length of the period was defined as the total sequence of 21 LSBs for which there were non-zero detection frequencies on either side of the center, plus 10 calendar days on each end. If two such periods were separated by fewer than 60 calendar days, they were merged into one period.

The NWQL's analytical procedures include a standard protocol for censoring detections in environmental samples in response to detections in LSBs (U.S. Geological Survey, 2012). If the measured concentration in the sample is less than three times the concentration measured in the LSB in the same set and less than or equal to the LRL, then the result for the sample is reported as a non-detection relative to the LRL. If the measured concentration in the sample is less than three times the concentration measured in the LSB in the same set but greater than the LRL, then the result for the sample is reported as a non-detection relative to the measured concentration in the sample. In this protocol, the NWQL uses the LRL or three times the concentration in the LSB as a raised censoring limit applied to environmental samples analyzed in the same set as the contaminated LSB. The GAMA-PBP adapted the NWQL's set-based censoring protocol (U.S. Geological Survey, 2012) to create a censoring protocol for use during the identified times of more frequent laboratory contamination. The raised censoring limit was defined as three times the highest concentration detected in any LSB analyzed during the contamination period ($3 \times C_{LSBmax}$), and this raised censoring limit was applied to all samples analyzed during the period of increased frequency of detections in LSBs.

All 142 constituents were evaluated, and 52 constituents had at least 1 period of greater frequency of laboratory contamination between January 2001 and May 2016 (table 3). The majority of these periods were during 2001–07: of the 114 contamination periods identified, 41 percent had end dates prior to July 2004, and another 25 percent had end dates between July 2004 and December 2006. Only 34 of the constituents had at least 1 period of greater frequency of laboratory contamination during the time GAMA-PBP samples were analyzed (starting July 2004). For the convenience of data users, all identified contamination periods for all constituents are listed in table 3, even though many are not relevant for the GAMA-PBP dataset. Note that the periods listed in table 3 may not be the same as those listed in Medalie and others (2019) because of the differences in procedures used to identify the periods.

For the GAMA-PBP dataset, a total of 74 detections of 14 constituents during periods of more frequent laboratory contamination were of concentrations less than $3 \times C_{LSBmax}$; however, only 25 detections of 6 constituents were censored on this basis (DCPA, atrazine, metolachlor, dieldrin, and simazine on schedule 2003, 2032, or 2033; diuron on schedule 2060; fig. 4; table 1). These 25 detections were censored using raised reporting limits equal to $3 \times C_{LSBmax}$ and are classified as non-detections by the GAMA-PBP (table 1). Step 4 included censoring of all remaining detections of one constituent (schedule 2003, 2032, or 2033 constituent DCPA). The other 49 detections had already been censored in steps 2 or 3 because the concentrations were less than the MDL at the time of analysis or less than the MDL_{max}, respectively. The fact that so many of the detections at concentrations less than $3 \times C_{LSBmax}$ are also less than the MDL_{max} indicates that simply censoring at the MDL_{max} would successfully eliminate most of the detections reported at concentrations less than $3 \times C_{LSBmax}$ during periods of more frequent laboratory contamination.

Table 3. Periods of more frequent laboratory contamination for pesticide constituents on U.S. Geological Survey National Water Quality Laboratory (NWQL) schedules 2001, 2003, 2032, or 2033 or on schedule 2060, maximum concentration measured in laboratory set blanks during the period, and raised censoring limit defined for use with data from samples analyzed during that period, January 2001–May 2016.

[The constituent identification code is the concatenation of the 5-digit numeric USGS parameter code that identifies a constituent or property and the 5-digit alphanumeric USGS method code that indicates the analytical method used to measure it. **Abbreviations**: µg/L, microgram per liter; mm/dd/yyyy, month/day/year; $3 \times C_{LSBmax}$, three times the maximum concentration measured in an LSB during the period]

Constituent identification code	Constituent name	Start date of contamination period (mm/dd/yyyy)	End date of contamination period (mm/dd/yyyy)	Maximum concentration in an LSB (µg/L)	$3 \times C_{LSBmax}$ (µg/L)
Constituents on NWQL schedule 2003, 2032, or 2033					
39632GCM35	Atrazine	04/13/2008	05/19/2008	0.003	0.009
82673GCM35	Benfluralin	06/24/2001	11/25/2001	0.0028	0.0084
82673GCM35	Benfluralin	09/22/2002	11/05/2002	0.0051	0.0153
82673GCM35	Benfluralin	04/28/2003	08/09/2003	0.0045	0.0135
82673GCM35	Benfluralin	10/04/2004	11/07/2004	0.007	0.021
82673GCM35	Benfluralin	03/12/2005	12/12/2010	0.0186	0.0558
82673GCM35	Benfluralin	02/23/2014	06/06/2014	0.0019	0.0057
82682GCM35	DCPA (Dacthal)	05/08/2005	11/23/2008	0.004	0.012
82682GCM35	DCPA (Dacthal)	05/17/2009	11/06/2010	0.0042	0.0126
62170GCM29	Desulfinylfipronil	08/07/2005	09/17/2005	0.005	0.015

Table 3. Periods of more frequent laboratory contamination for pesticide constituents on U.S. Geological Survey National Water Quality Laboratory (NWQL) schedules 2001, 2003, 2032, or 2033 or on schedule 2060, maximum concentration measured in laboratory set blanks during the period, and raised censoring limit defined for use with data from samples analyzed during that period, January 2001–May 2016.—Continued

[The constituent identification code is the concatenation of the 5-digit numeric USGS parameter code that identifies a constituent or property and the 5-digit alphanumeric USGS method code that indicates the analytical method used to measure it. **Abbreviations**: µg/L, microgram per liter; mm/dd/yyyy, month/day/year; $3 \times C_{LSBmax}$, three times the maximum concentration measured in an LSB during the period]

Constituent identification code	Constituent name	Start date of contamination period (mm/dd/yyyy)	End date of contamination period (mm/dd/yyyy)	Maximum concentration in an LSB (µg/L)	$3 \times C_{LSBmax}$ (µg/L)
Constituents on NWQL schedule 2003, 2032, or 2033—Continued					
62170GCM29	Desulfinylfipronil	07/06/2009	09/12/2009	0.006	0.018
62170GCM29	Desulfinylfipronil	05/23/2015	08/02/2015	0.0032	0.0096
62169GCM29	Desulfinylfipronil amide	01/06/2004	02/16/2004	0.0032	0.0096
39572GCM35	Diazinon	11/29/2002	01/24/2003	0.0038	0.0114
39572GCM35	Diazinon	07/01/2003	08/25/2003	0.0031	0.0093
61627GCM39	3,5-Dichloroaniline	08/08/2010	10/04/2010	0.005	0.015
39381GCM35	Dieldrin	05/03/2005	07/04/2005	0.002	0.006
39381GCM35	Dieldrin	01/22/2006	04/08/2006	0.005	0.015
39381GCM35	Dieldrin	06/06/2008	08/28/2008	0.005	0.015
39381GCM35	Dieldrin	03/28/2009	08/10/2010	0.006	0.018
39381GCM35	Dieldrin	08/31/2011	10/19/2011	0.0039	0.0117
39381GCM35	Dieldrin	04/29/2013	12/15/2013	0.0046	0.0138
39381GCM35	Dieldrin	03/23/2014	10/31/2014	0.0053	0.0159
39381GCM35	Dieldrin	05/21/2015	08/29/2015	0.0069	0.0207
82660GCM35	2,6-Diethylaniline	08/02/2009	09/12/2009	0.002	0.006
34362GCM39	α-Endosulfan	07/04/2009	08/29/2009	0.006	0.018
34362GCM39	α-Endosulfan	02/13/2010	04/13/2010	0.0053	0.0159
34362GCM39	α-Endosulfan	05/13/2015	08/09/2015	0.0065	0.0195
62167GCM29	Fipronil sulfide	05/21/2015	08/02/2015	0.0037	0.0111
61652GCM39	Malaoxon	02/11/2008	03/22/2008	0.024	0.072
61596GCM39	Metalaxyl	02/13/2010	04/02/2010	0.0051	0.0153
61596GCM39	Metalaxyl	05/12/2013	01/28/2014	0.0039	0.0117
39415GCM35	Metolachlor	05/11/2005	01/17/2006	0.007	0.021
39415GCM35	Metolachlor	05/25/2008	08/15/2008	0.006	0.018
39415GCM35	Metolachlor	07/06/2009	09/12/2009	0.0104	0.0312
39415GCM35	Metolachlor	02/15/2010	03/28/2010	0.008	0.024
39415GCM35	Metolachlor	05/23/2015	08/02/2015	0.0072	0.0216
82671GCM35	Molinate	07/15/2007	03/22/2008	0.036	0.108
49295GCM39	1-Naphthol	09/05/2009	12/12/2009	0.003	0.009
61600GCM39	Oxyfluorfen	06/08/2005	08/28/2005	0.007	0.021
61600GCM39	Oxyfluorfen	09/23/2008	05/08/2009	0.007	0.021
61601GCM39	Phosmet	09/21/2003	04/13/2004	0.008	0.024
04037GCM35	Prometon	02/04/2014	06/19/2014	0.0031	0.0093
82679GCM35	Propanil	01/03/2004	02/22/2004	0.0043	0.0129
04035GCM35	Simazine	07/20/2007	10/04/2007	0.009	0.027
61606GCM39	Tefluthrin	03/20/2006	06/30/2006	0.005	0.015

Table 3. Periods of more frequent laboratory contamination for pesticide constituents on U.S. Geological Survey National Water Quality Laboratory (NWQL) schedules 2001, 2003, 2032, or 2033 or on schedule 2060, maximum concentration measured in laboratory set blanks during the period, and raised censoring limit defined for use with data from samples analyzed during that period, January 2001–May 2016.—Continued

[The constituent identification code is the concatenation of the 5-digit numeric USGS parameter code that identifies a constituent or property and the 5-digit alphanumeric USGS method code that indicates the analytical method used to measure it. **Abbreviations**: µg/L, microgram per liter; mm/dd/yyyy, month/day/year; $3 \times C_{LSBmax}$, three times the maximum concentration measured in an LSB during the period]

Constituent identification code	Constituent name	Start date of contamination period (mm/dd/yyyy)	End date of contamination period (mm/dd/yyyy)	Maximum concentration in an LSB (µg/L)	$3 \times C_{LSBmax}$ (µg/L)
Constituents on NWQL schedule 2003, 2032, or 2033—Continued					
61606GCM39	Tefluthrin	07/11/2007	08/19/2007	0.004	0.012
61606GCM39	Tefluthrin	01/27/2008	11/11/2008	0.006	0.018
61606GCM39	Tefluthrin	06/03/2009	11/11/2010	0.0062	0.0186
82661GCM35	Trifluralin	08/07/2001	11/02/2001	0.001	0.003
82661GCM35	Trifluralin	04/09/2002	06/03/2002	0.0025	0.0075
82661GCM35	Trifluralin	09/22/2002	10/28/2002	0.0047	0.0141
82661GCM35	Trifluralin	04/28/2003	08/05/2003	0.004	0.012
82661GCM35	Trifluralin	08/17/2004	11/07/2004	0.005	0.015
82661GCM35	Trifluralin	03/12/2005	11/14/2009	0.01	0.03
82661GCM35	Trifluralin	05/04/2010	12/10/2010	0.0108	0.0324
Constituents on NWQL schedule 2060					
49315LCM29	Acifluorfen	02/24/2002	05/17/2002	0.0258	0.0774
49313LCM29	Aldicarb sulfone	07/06/2001	08/30/2001	0.0015	0.0045
49313LCM29	Aldicarb sulfone	01/04/2005	04/12/2005	0.004	0.012
49314LCM29	Aldicarb sulfoxide	09/16/2003	01/17/2004	0.0004	0.0012
50299LCM29	Bendiocarb	09/17/2003	04/24/2004	0.0032	0.0096
61693LCM29	Bensulfuron-methyl	09/16/2003	01/01/2004	0.0003	0.0009
38711LCM29	Bentazon	12/08/2005	05/11/2006	0.003	0.009
49310LCM29	Carbaryl	06/05/2001	08/24/2001	0.0018	0.0054
49310LCM29	Carbaryl	12/19/2002	10/26/2004	0.0068	0.0204
49310LCM29	Carbaryl	01/04/2005	04/25/2005	0.0009	0.0027
49309LCM29	Carbofuran	12/12/2003	05/04/2004	0.0067	0.0201
50306LCM29	Chlorimuron-ethyl	10/05/2001	02/20/2002	0.0013	0.0039
50306LCM29	Chlorimuron-ethyl	04/13/2005	06/23/2005	0.01	0.03
61692LCM29	*N*-(4-Chlorophenyl)-*N*'-methylurea	06/05/2001	09/28/2001	0.0026	0.0078
61692LCM29	*N*-(4-Chlorophenyl)-*N*'-methylurea	08/22/2003	07/20/2005	0.0011	0.0033
61692LCM29	*N*-(4-Chlorophenyl)-*N*'-methylurea	11/27/2005	02/20/2006	0.0009	0.0027
04031LCM29	Cycloate	12/12/2003	04/24/2004	0.0091	0.0273
49301LCM29	Dinoseb	07/29/2003	01/04/2004	0.0028	0.0084
49301LCM29	Dinoseb	03/25/2005	06/05/2005	0.0006	0.0018
04033LCM29	Diphenamid	04/22/2002	09/10/2002	0.0125	0.0375
04033LCM29	Diphenamid	09/13/2003	03/17/2004	0.0007	0.0021
04033LCM29	Diphenamid	09/29/2004	12/12/2004	0.0017	0.0051
49300LCM29	Diuron	06/05/2001	06/12/2006	0.028	0.084
49300LCM29	Diuron	04/19/2009	07/21/2009	0.004	0.012
49297LCM29	Fenuron	06/05/2001	06/17/2006	0.0105	0.0315

Table 3. Periods of more frequent laboratory contamination for pesticide constituents on U.S. Geological Survey National Water Quality Laboratory (NWQL) schedules 2001, 2003, 2032, or 2033 or on schedule 2060, maximum concentration measured in laboratory set blanks during the period, and raised censoring limit defined for use with data from samples analyzed during that period, January 2001–May 2016.—Continued

[The constituent identification code is the concatenation of the 5-digit numeric USGS parameter code that identifies a constituent or property and the 5-digit alphanumeric USGS method code that indicates the analytical method used to measure it. **Abbreviations**: µg/L, microgram per liter; mm/dd/yyyy, month/day/year; $3 \times C_{LSBmax}$, three times the maximum concentration measured in an LSB during the period]

Constituent identification code	Constituent name	Start date of contamination period (mm/dd/yyyy)	End date of contamination period (mm/dd/yyyy)	Maximum concentration in an LSB (µg/L)	$3 \times C_{LSBmax}$ (µg/L)
Constituents on NWQL schedule 2060—Continued					
61694LCM29	Flumetsulam	08/02/2004	12/10/2004	0.01	0.03
61694LCM29	Flumetsulam	09/16/2005	06/05/2006	0.203	0.609
50356LCM29	Imazaquin	09/24/2001	03/28/2002	0.0014	0.0042
50356LCM29	Imazaquin	05/05/2003	05/15/2004	0.0014	0.0042
50356LCM29	Imazaquin	10/19/2005	02/19/2006	0.005	0.015
50407LCM29	Imazethapyr	01/07/2002	05/13/2002	0.0015	0.0045
50407LCM29	Imazethapyr	12/03/2002	03/13/2003	0.0002	0.0006
50407LCM29	Imazethapyr	10/17/2005	04/17/2006	0.001	0.003
38482LCM29	MCPA	02/24/2002	05/17/2002	0.02	0.06
50359LCM29	Metalaxyl	08/30/2003	12/30/2003	0.0043	0.0129
61697LCM29	Metsulfuron-methyl	07/15/2001	09/29/2001	0.032	0.096
61697LCM29	Metsulfuron-methyl	07/17/2004	10/24/2004	0.0051	0.0153
61697LCM29	Metsulfuron-methyl	03/07/2005	02/21/2006	0.0081	0.0243
49294LCM29	Neburon	06/05/2001	10/23/2001	0.0027	0.0081
49294LCM29	Neburon	12/19/2002	06/28/2003	0.0007	0.0021
49294LCM29	Neburon	09/15/2003	05/15/2004	0.0007	0.0021
49293LCM29	Norflurazon	12/19/2002	04/22/2003	0.0016	0.0048
49293LCM29	Norflurazon	09/20/2003	05/18/2004	0.0005	0.0015
49292LCM29	Oryzalin	12/12/2003	04/06/2004	0.036	0.108
49236LCM29	Propham	12/19/2002	04/22/2003	0.0047	0.0141
49236LCM29	Propham	08/25/2004	10/26/2004	0.0039	0.0117
50471LCM29	Propiconazole	06/19/2001	06/16/2002	0.0215	0.0645
38548LCM29	Siduron	07/23/2003	05/15/2004	0.0031	0.0093
38548LCM29	Siduron	11/04/2006	03/10/2007	0.018	0.054
50337LCM29	Sulfometuron-methyl	06/05/2001	09/05/2001	0.0033	0.0099
50337LCM29	Sulfometuron-methyl	05/04/2002	08/11/2002	0.0011	0.0033
50337LCM29	Sulfometuron-methyl	12/19/2002	05/22/2003	0.0015	0.0045
50337LCM29	Sulfometuron-methyl	08/22/2003	12/18/2005	0.014	0.042
82670LCM29	Tebuthiuron	06/05/2001	09/03/2001	0.0024	0.0072
82670LCM29	Tebuthiuron	01/09/2002	09/03/2002	0.0051	0.0153
82670LCM29	Tebuthiuron	05/05/2003	04/05/2004	0.0017	0.0051
82670LCM29	Tebuthiuron	07/19/2004	10/24/2004	0.0008	0.0024
82670LCM29	Tebuthiuron	11/28/2005	04/12/2006	0.0006	0.0018

Step 5: Evaluating Results From Field Blanks, Laboratory Set Blanks, and Blind Samples From the USGS Branch of Quality Systems to Determine If the Censoring Limits Established in Steps 3 and 4 Are Sufficient, and If Not, Calculating Alternative Method Detection Limits From the Results From the Blank Samples

MDLs generally are calculated from results from low-level spikes; however, for constituents for which contamination by laboratory processes is commonly detected, results from LSBs can be used to verify the MDLs calculated from low-level spikes or establish alternative MDLs (U.S. Geological Survey, 2015; U.S. Environmental Protection Agency, 2016a). If an MDL calculated from LSBs (called DLBLK, for detection level determined from blanks) has a higher concentration than an MDL calculated from low-level spikes, then the DLBLK shall be used as the MDL. The DLBLK procedure was developed for calculating MDLs from LSBs, but can also be used with field blanks (for example, Fram and others, 2012). A DLBLK calculated from field blanks represents an effective MDL for the purpose of data reporting by a project, but not as the MDL of the laboratory, because it also accounts for contamination during sample collection.

This study calculated DLBLKs following the method recommended by the NWQL for use with large datasets of blanks (U.S. Geological Survey, 2015). For a population of more than 100 blanks, the DLBLK is defined as the concentration of the 99th percentile ranked blank. This definition means that the detection frequency of blanks at concentrations greater than the DLBLK is no more than 1 percent, which is in accordance with the definition of an MDL. For a population of 20 to 100 blanks, the DLBLK is defined as the concentration of the second highest blank, which corresponds to the 95th to 99th percentile blank. The uncertainty in this estimate increases as the number of blanks in the population decreases, and this procedure for calculating DLBLKs should not be used if the population of blanks is less than 20.

Step 5 included evaluation of data from three types of blanks: LSBs analyzed outside of the periods of more frequent laboratory contamination identified in step 4, field blanks collected by the GAMA-PBP during 2004–18, and blanks submitted by the USGS Branch of Quality systems. If the DLBLK is greater than the MDL_{max} (step 3), then the DLBLK is used as the study reporting limit for the dataset.

Laboratory Set Blanks Not Analyzed During Periods of More Frequent Laboratory Contamination

The raised censoring limits established in step 4 are intended to account for laboratory contamination during identified times of more frequent laboratory contamination. Laboratory contamination may also be outside of those identified periods and may warrant calculation of DLBLKs (called DLBLK-LSB to distinguish it from other DLBLKs).

Nine pesticide constituents on schedule 2003, 2032, or 2033 (benfluralin, DCPA, dieldrin, metolachlor, molinate, oxyfluorfen, phosmet, tefluthrin, trifluralin) and ten pesticide constituents on schedule 2060 (carbaryl, diuron, fenuron, flumetsulam, imazethapyr, metsulfuron-methyl, *N*-(4-chlorophynyl)-*N*′-methylurea, siduron, sulfometuron-methyl, tebuthiuron) had detection frequencies greater than 1 percent in the LSBs (table 2) and, therefore, would have non-zero DLBLK-LSB values. All 19 of these pesticide constituents had one or more identified periods of more frequent laboratory contamination (table 3). The raised censoring limits established in step 4 already account for laboratory contamination during those periods. After excluding LSBs analyzed during those periods for each pesticide constituent, four pesticide constituents on schedule 2003, 2032, or 2033 (benfluralin, DCPA, tefluthrin, trifluralin) had detections frequencies greater than 1 percent in the remaining LSBs (table 2). The DLBLK-LSB values for those four constituents were less than the MDL_{max} values; therefore, the MDL_{max} was retained as the study reporting limit.

Field Blanks

For pesticide constituents, the GAMA-PBP used the DLBLK protocols recommended by the NWQL (U.S. Geological Survey, 2015), and DLBLKs calculated from field blanks are identified as DLBLK-FB. Note that there are multiple approaches for establishing censoring limits from field blank results, and selection of the most appropriate one may depend on the inferred mode of contamination, tolerance for probability of false positive detections due to field contamination, and number of field blanks analyzed. For example, Nowell and others (2011) defined censoring limits at 5 to 10 times the highest concentration measured in field blanks because they had relatively few field blanks and a low tolerance for risk of false-positive detections. Fram and others (2012) had a larger population of field blanks and defined censoring limits as either the highest concentration measured in a field blank or a value based on binomial probabilities and rank-order statistics.

The GAMA-PBP collected field blanks at approximately 10 percent of the sites where a groundwater sample was collected in 2004–18. There were 297 field blanks collected and analyzed for pesticide constituents on schedule 2003, 2032, or 2033 (9.9 percent of the 2,994 sites from which groundwater samples were collected and analyzed) and 89 field blanks collected and analyzed for pesticide constituents on schedule 2060 (10.6 percent of the 840 sites at which groundwater samples were collected and analyzed). Note that results from field blanks were not censored in steps 1–4, because the uncensored data are required for the DLBLK calculation protocols. There were a total of 24 detections of 14 pesticide constituents in field blanks (table 4). The detections were in field blanks collected between November 2004 and December 2008.

Six field blanks had a detection of at least one pesticide constituent on schedule 2003, 2032, or 2033. Atrazine was detected in four field blanks, simazine in two field blanks, and seven other constituents each were detected in one field blank (table 4). For a population of 297 field blanks, the DLBLK-FB is the concentration of the third highest field blank. Atrazine was the only pesticide constituent on schedule 2003, 2032, or 2033 detected in three or more field blanks. The DLBLK-FB value for atrazine (0.005 µg/L) was greater than the MDL_{max} (0.004 µg/L) (table 2). Applying the DLBLK-FB as the censoring limit for atrazine resulted in censoring 62 of the remaining detections of atrazine in GAMA-PBP groundwater samples (table 1; fig. 4).

At least one pesticide constituent was detected in nine field blanks on schedule 2060. Caffeine was detected in seven field blanks, and four other constituents were each detected in one field blank. Caffeine is not used as a pesticide, but is included on schedule 2060 because it is amenable to analysis by the same analytical method as pesticide constituents on schedule 2060. For a population of 89 field blanks, the DLBLK-FB is the concentration of the second highest field blank. Caffeine was the only constituent on schedule 2060 detected twice or more in field blanks. The DLBLK-FB value for caffeine was less than the MDL_{max} (table 2).

U.S. Geological Survey Branch of Quality Systems Blind Blanks

The third source of blank data evaluated in step 5 were the blind blanks from the USGS Branch of Quality Systems Organic Blind Sample Project (OBSP; https://bqs.usgs.gov/OBSP/index.html). The Branch of Quality Systems regularly submits OBSP samples to the NWQL for analysis of pesticide constituents on schedules 2003, 2032, or 2033, or on schedule 2060. The OBSP samples consist of reagent blank water to which a spike solution containing a known mixture of pesticide constituents have been added. Spike solutions containing different mixtures of pesticide constituents generally are obtained from commercial vendors. Blind blanks are not submitted as separate samples; instead, the pesticide constituents not listed as present in a spike solution are assumed to be absent. In this report, OBSP blanks are referred to as OBSP unspiked blanks to indicate that "blank" refers to the unspiked constituents in a spiked sample. The OBSP samples serve as third-party blind verification of laboratory performance of NWQL methods and are used by the NWQL to evaluate analyte recovery, to evaluate frequency of false positive detections and false negative non-detections, and to calculate the MDLs.

Instances of false positive detections and false negative non-detections in OBSP samples analyzed during October 2005–September 2017 for pesticide constituents on schedule 2033 and during January 2001–September 2014 for pesticide constituents on schedule 2060 were downloaded from the OBSP public Web page on January 25, 2019 (https://qsb.usgs.gov/OBSP/pickAyear4fc.html). The dataset included a median of 229 unspiked blank samples (10th to 90th percentile range of 203−264 samples) for each of the pesticide constituents.

Nineteen pesticide constituents on schedule 2003, 2032, or 2033 (1-napthol, atrazine, azinphos-methyl oxon, carbaryl, desulfinylfipronil, diazinon, disulfoton sulfone, ethion monoxon, fenaminphos sulfone, fenaminphos sulfoxide, fipronil, fipronil sulfide, fipronil sulfone, malaoxon, phosmet oxon, simazine, terbufos oxon sulfone, thiobencarb, tribufos) and ten pesticide constituents on schedule 2060 (2,4-D, 2,4-D methyl ester, 2,4-DB, aldicarb sulfone, aldicarb sulfoxide, bendiocarb, bentazon, caffeine, chloramben methyl ester, flumetsulam) had detection frequencies greater than 1 percent in OBSP unspiked blanks (table 2) and, therefore, would have non-zero DLBLK values. Of these 29 pesticide constituents, 2—desulfinylfipronil and flumetsulam—were detected at least once during a period of more frequent laboratory contamination identified in step 4. All other detections were outside of those identified times or were for pesticide constituents having no identified periods of more frequent laboratory contamination.

The frequency of false positive detections in the OBSP unspiked blanks was not correlated with the frequency of detections in the LSBs (fig. 6*A*) or with the frequency of detections in the original results for the GAMA-PBP samples (fig. 6*B*). The reasons for the lack of correlation between detection frequencies in the OBSP unspiked blanks and the other two sample types should be understood if the OBSP unspiked blank results are to be used to censor the GAMA-PBP data.

Table 4. Samples collected by the California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP) during 2004–18 for which pesticide constituents were detected in field blanks analyzed for pesticide constituents on U.S. Geological Survey National Water Quality Laboratory (NWQL) schedules 2003, 2032, or 2033, or on schedule 2060.

[297 field blanks were analyzed for pesticide constituents on schedule 2003/2032/2033; 89 field blanks were analyzed for pesticide constituents on schedule 2060, except for oxamyl, for which there were 83 field blanks. The constituent identification code is the concatenation of the 5-digit numeric USGS parameter code that identifies a constituent or property and the 5-digit alphanumeric USGS method code that indicates the analytical method used to measure it. **Comments**: < MDL, this concentration is less than the method detection limit (MDL) in effect at the time the field blank was analyzed (see discussion of step 2); < MDL_{max}, this concentration is less than the maximum MDL in effect during July 2004–August 2018 (see discussion of step 3); < 3 × C_{LSBmax}, this field blank was analyzed during a period of greater laboratory contamination for the constituent (table 3) and this concentration is less than three times the highest concentration in an LSB during the period (see discussion of step 4); DLBLK-FB, the detection limit defined from field blanks is equal to the concentration and the DLBLK-FB is either greater than (>) or less than (<) the MDL_{max} for this constituent (see discussion of step 5). **Other abbreviations**: USGS, U.S. Geological Survey; mm/dd/yyyy, month/day/year; hhmm, hour minute; µg/L, micrograms per liter; nc, no comment; CIAT, 2-Chloro-4-isopropylamino-6-amino-*s*-triazine]

USGS station identification number of site where field blank was collected	Collection date (mm/dd/yyyy)	Collection time (hhmm)	Analysis date (mm/dd/yyyy)	Constituent identification code	Constituent name	Concentration (µg/L)	Comment
Constituents on NWQL schedule 2003, 2032, or 2033							
383319122424301	09/14/2004	0838	11/15/2004	39632GCM35	Atrazine	0.005	nc
381400122020001	04/20/2005	1108	05/17/2005	82661GCM35	Trifluralin	0.005	< 3 × C_{LSBmax}, < MDL_{max}
381400122020001	04/20/2005	1108	05/17/2005	82673GCM35	Benfluralin	0.006	< 3 × C_{LSBmax}, < MDL_{max}
381400122020001	04/20/2005	1108	05/17/2005	82682GCM35	DCPA (Dacthal)	0.0016	< 3 × C_{LSBmax}, < MDL
384100121500001	05/19/2005	1258	06/09/2005	04040GCM35	Deethylatrazine (CIAT)	0.005	< MDL_{max}
384100121500001	05/19/2005	1258	06/09/2005	39415GCM35	Metolachlor	0.006	< 3 × C_{LSBmax}, < MDL_{max}
384100121500001	05/19/2005	1258	06/09/2005	39632GCM35	Atrazine	0.019	nc
384100121500001	05/19/2005	1258	06/09/2005	46342GCM35	Alachlor	0.004	nc
384100121500001	05/19/2005	1258	06/09/2005	49260GCM33	Acetochlor	0.006	nc
371100120090001	05/01/2006	1228	05/05/2006	04035GCM35	Simazine	0.004	< MDL_{max}
335000117000001	02/08/2007	1208	02/23/2007	04035GCM35	Simazine	0.004	< MDL_{max}
335000117000001	02/08/2007	1208	02/23/2007	39632GCM35	Atrazine	0.005	DLBLK-FB > MDL_{max}
344900118570001	09/22/2008	0948	12/02/2008	39632GCM35	Atrazine	0.008	nc
Constituents on NWQL schedule 2060							
382100121560001	03/23/2005	0938	04/01/2005	50305LCM29	Caffeine	0.012	DLBLK-FB < MDL_{max}
384200121190003	03/29/2005	1108	04/14/2005	38866LCM29	Oxamyl[1]	0.01	< MDL
381400122020001	04/20/2005	1108	05/03/2005	50305LCM29	Caffeine	0.01	< MDL_{max}
341000118220001	06/08/2005	1008	06/12/2005	50305LCM29	Caffeine	0.007	< MDL
364200119420002	10/18/2005	0808	10/28/2005	50305LCM29	Caffeine	0.005	< MDL
364355119484601	10/25/2005	0928	11/03/2005	50305LCM29	Caffeine	0.005	< MDL
364156119470001	11/15/2005	1108	12/06/2005	50305LCM29	Caffeine	0.011	< MDL_{max}
351800119180001	01/10/2006	1008	01/27/2006	50305LCM29	Caffeine	0.029	< MDL_{max}
384736121411501	08/03/2006	0938	08/17/2006	04029LCM29	Bromacil	0.11	nc
384736121411501	08/03/2006	0938	08/17/2006	39732LCM29	2,4-D	0.28	nc
384736121411501	08/03/2006	0938	08/17/2006	49300LCM29	Diuron	0.03	nc

[1]See discussion of step 1.

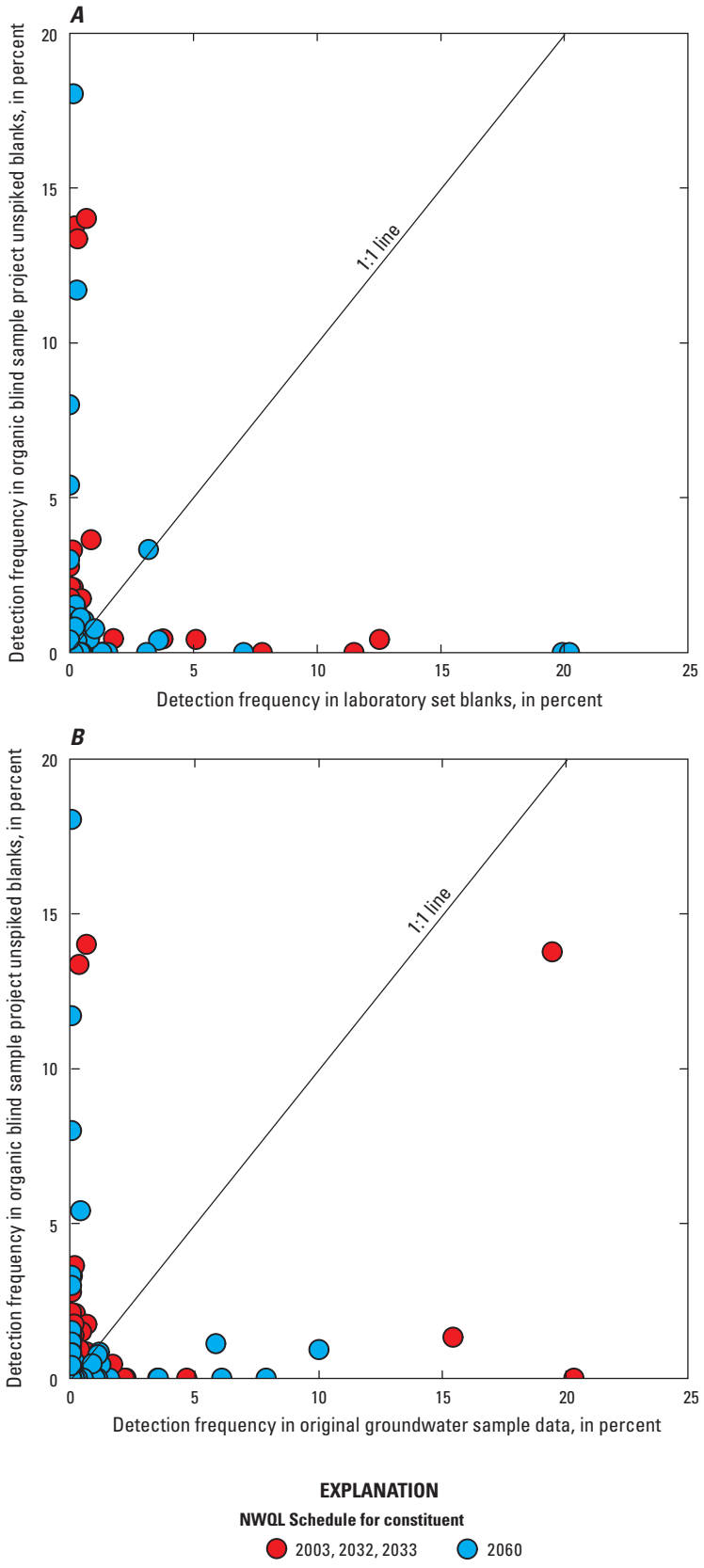

Figure 6. Comparison of detection frequencies in U.S. Geological Survey Branch of Quality Systems Organic Blind Sample Program (OBSP) unspiked blanks for pesticide constituents on National Water Quality Laboratory (NWQL) schedules 2003, 2032, or 2033, or on schedule 2060 compared with those in *A*, laboratory set blanks (LSBs) and *B*, original data from groundwater samples collected for the California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP). Each plotted point summarizes results for an individual analyte.

Application of set-based censoring may account for part of the lack of correlation. The NWQL treats OBSP unspiked blanks as they do other samples submitted for analysis in terms of analysis and reporting results. Following the set-based censoring protocols (U.S. Geological Survey, 2012), a detection of a pesticide constituent in an LSB may lead to censoring of detections of that constituent in samples analyzed in the same laboratory set. Such censoring would result in a higher detection frequency for the constituent in the LSBs (which are not censored) than in the reported results for the OBSP unspiked blanks and GAMA-PBP samples (which are censored). Medalie and others (2019) found that set-based censoring was applied to less than 1 percent of the samples analyzed for pesticide constituents on schedules 2003, 2032, or 2033, or on schedule 2060. Even if set-based censoring had been commonly used, however, it could not have explained why some constituents had much higher detection frequencies in the OBSP unspiked blanks than in the LSBs.

The relation between detection frequencies in the OBSP unspiked blanks and the GAMA-PBP samples indicates that the detections in the OBSP unspiked blanks may not be representative of the frequency of false positives for the analytical methods. In particular, it is difficult to explain higher detection frequencies in the OBSP unspiked blanks than in the GAMA-PBP samples. There were 29 pesticide constituents for which detection frequencies were between 1 and 20 percent in the OBSP unspiked blanks, and of those 29, just 3 pesticide constituents (simazine, atrazine, and bentazon) had detection frequencies greater than 1 percent in the original data for the GAMA-PBP samples (fig. 6*B*). Of these 29 constituents, only 1 had a detection frequency greater than 1 percent in the LSBs (flumetsulam), indicating that set-based censoring likely was not a factor. If detections in the OBSP unspiked blanks were representative of the frequency of false positive detections on schedules 2003, 2032, or 2033, or on schedule 2060, then one would expect the original data for the GAMA-PBP samples to have a similar pattern of false positive detections. The fact that most pesticide constituents frequently detected in the OBSP unspiked blanks were not detected in original data for the GAMA-PBP samples indicates that the way the OBSP unspiked blanks become contaminated with many pesticide constituents is not representative of factors that might affect the samples. Therefore, the OBSP unspiked blanks do not provide useful information about the frequency of false positive detections for schedules 2003, 2032, or 2033, or on schedule 2060 and are not used by the GAMA-PBP to calculate DLBLK values.

A likely source of pesticide constituents to the OBSP unspiked blanks is that the samples are not blanks for all unspiked constituents. The commercial spike mixtures used to make the OBSP spiked samples (blanks for the unspiked constituents) are certified to contain specified concentrations of the pesticide constituents in the spike mixture; however, they are not certified to contain zero concentration of all pesticide constituents not listed as components in the spike mixture. For this reason, procedures for creating blank samples for evaluating potential inadvertent contamination with constituents of interest during collection, processing, or analysis of water samples specify that these blank samples should consist of water certified to be free of the constituents of interest (for example, Zaugg and others, 1995; Lindley and others, 1996; Furlong and others, 2001; Sandstrom and others, 2001, 2015; Madsen and others, 2003). Single-blind interlaboratory comparison studies examine the frequency of false positives and false negatives for trace organic constituent analyses by sending the laboratories separate samples for blind blanks and blind spikes (for example, Vanderford and others, 2014). Schedules 2003, 2032, or 2033, or on schedule 2060 include many degradates of parent pesticide compounds. Some of the pesticide constituents frequently detected in the OBSP unspiked blanks are degradates of parent pesticide compounds (table 2) and may be present at low concentrations in the OBSP unspiked blanks as degradation products of spiked parent pesticide compounds. The presence of low concentrations of unspiked parent compounds is less easily understood.

GAMA Priority Basin Project Data Reporting

Data produced by the NWQL and stored in the USGS National Water Information System (NWIS) database are intended to be used by many projects ranging from research projects to projects driven by regulatory needs. Data-quality objectives can differ among these different types of projects. To serve all types of projects, it is current (2019) USGS policy to store original data produced by the NWQL in NWIS without applying any censoring for project-specific data-quality objectives (U.S. Geological Survey, 2017a).

This policy led to considerable confusion for some public users of the GAMA-PBP data, however, because data retrieved from NWIS Web (https://waterdata.usgs.gov/nwis) had more detections of pesticide constituents than the data for the same samples retrieved from the SWRCB's GAMA Groundwater Information System (http://gamagroundwater.waterboards.ca.gov/gama/gamamap/public) and the GAMA-PBP data viewer (https://ca.water.usgs.gov/projects/gama/water-quality-results/). In order to minimize this potential for confusion, all portals for retrieval of GAMA-PBP data should have the same data.

The default data available for retrieval from all portals should be the final data, after censoring to meet project data-quality objectives. The GAMA-PBP has a responsibility to report data that meet the stated project data-quality objectives. The GAMA-PBP data are used by California state agencies, local government and water agencies, non-governmental organizations, and members of the general public. These users expect that GAMA-PBP data publicly available from NWIS Web and other portals meet the stated data-quality objectives of the GAMA-PBP. In addition, censoring data to meet data-quality objectives requires access to data from field and laboratory quality-control samples. Such data are not available to the public from NWIS Web; therefore, the public would not have sufficient information to apply quality-control censoring to the original laboratory results.

Other projects have different data-quality objectives than the GAMA-PBP. For example, the USGS National Water Quality Program (NWQP) has a lower acceptable risk of false negative non-detections than does the GAMA-PBP and, therefore, classifies all results reported as detections by the NWQL as detections, including those with concentrations below the MDL. The USGS NWQP does national-scale assessments of pesticide constituents in the environment using data retrieved from NWIS. If different datasets in NWIS are censored to meet different project data-quality objectives, this may introduce bias to a national-scale assessment. In practice, however, the USGS NWQP national-scale assessments for pesticides generally have been based on data from sites sampled for the USGS NWQP, not on data from all sites in NWIS (for example, Gilliom and others, 2006; Toccalino and others, 2014).

The original data from the laboratory, prior to application of censoring to meet project data-quality objectives, should be preserved, but used with great caution because of the potential for conflicting conclusions reached from interpretations based on different versions of the data from the same samples.

As of 2019, the USGS NWIS database does not have the capability to store both the original value reported by the laboratory and the final value published by the GAMA-PBP that applies the quality-control censoring described in this report. In the interim, while this capability is being developed, the 1,031 results censored in steps 2–5 are blocked from release from the NWIS database. The original and final values for these 1,031 results are published in a USGS data release accompanying this report (Lor and others, 2019). The entire GAMA-PBP final dataset for May 2004–June 2018 pesticide constituents on schedules 2003, 2032, or 2033, or on schedule 2060 is publicly available in Lor and others (2019), through the USGS GAMA-PBP public web portal (https://ca.water.usgs.gov/projects/gama/water-quality-results/), and through the California SWRCB GAMA online groundwater information system (https://gamagroundwater.waterboards.ca.gov/gama/gamamap/public/).

This interim protocol meets three important criteria: (1) it adheres to USGS Fundamental Science Practices mandating public release of data (U.S. Geological Survey, 2017b); (2) it improves agreement between data publicly available from NWIS Web and data for the same samples retrieved from other public data portals; (3) it does not violate current (2019) USGS policy concerning changes to data in NWIS (U.S. Geological Survey, 2017a).

The final GAMA-PBP dataset for samples collected from May 2004 to June 2018, after censoring, had a total of 1,632 detections of 37 pesticide constituents. In the final GAMA-PBP dataset, 25 percent of the 3,001 samples analyzed had detections of one or more pesticide constituents.

Summary and Conclusions

The California Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP) is part of the California State Water Resources Control Board (SWRCB) GAMA Program and is being implemented as a cooperative project between the SWRCB and the U.S. Geological Survey (USGS). The purposes of the GAMA-PBP are to assess the quality of groundwater resources used for public and domestic drinking water supplies in the State of California, to monitor and evaluate changes in that quality, to investigate the human and natural factors controlling water quality, and to improve the availability of comprehensive groundwater-quality data and information. The GAMA-PBP includes analysis of pesticide constituents (parent pesticide compounds and degradates of those parent compounds) at the USGS National Water Quality Laboratory (NWQL) using analytical methods that have lower detection limits than are required for regulatory sampling. At these very low concentrations, pesticide constituents can be useful as sensitive tracers of the influence of human activities on groundwater. In addition, presence of these low concentrations may be of concern to State and local agencies.

Between May 2004 and May 2018, the GAMA-PBP submitted 2,994 groundwater samples to the NWQL for analysis of pesticide constituents on schedules 2003, 2032, or 2033 (65 to 84 constituents) and 840 groundwater samples for analysis of pesticide constituents on schedule 2060 (58 constituents). The original dataset reported by the NWQL to the USGS National Water Information System (NWIS) database contained a total of 2,688 detections of 78 pesticide constituents and 253,825 non-detections. In this original dataset, 33 percent of the 3,001 samples analyzed had reported detections of one or more pesticide constituents.

The GAMA-PBP commonly evaluates presence of pesticide constituents in groundwater by detection frequencies and commonly identifies differences among different study areas or changes through time in a given study area by comparison of detection frequencies. Therefore, the GAMA-PBP data-quality objectives for data for pesticide constituents address two primary data quality issues. First, the project establishes criteria for classifying laboratory results as detections or non-detections. These criteria are based on defining acceptable risk for false positive detections. Second, the project establishes criteria for accounting for changes in analytical methods or method performance through time.

To meet the project data-quality objectives, the GAMA-PBP developed a five-step process to assess and censor the data on the basis of quality-control considerations.

- **Step 1:** Reject results for which there was strong evidence that the samples were compromised by specific instances of contamination or other problems during collection or processing of the samples. Two cases requiring rejection of results were identified in samples collected for analysis of pesticide constituents on schedules 2003, 2032, or 2033, or on schedule 2060 during May 2004–May 2018. Eight detections of oxamyl were rejected because field quality-control data indicated samples were collected using field equipment contaminated with oxamyl. Oxamyl's physical properties indicate that it is highly unlikely to be present in groundwater. The eight wells yielded pre-modern age groundwater, had a median depth of 145 meters, and were not downgradient from registered field applications of oxamyl. Pesticide results for one groundwater sample were rejected entirely. This sample had the greatest number of detections (17) of any GAMA-PBP sample collected during 2004–18, and the combination of constituents was highly unusual, including 16 constituents not detected in any of the samples from the study and parent pesticide constituents not registered for use in California. The well yielded pre-modern age groundwater, further supporting the improbable nature of the detections. A total of 25 detections were rejected and assigned a data-quality indicator code of "Q" for "reviewed and rejected" in the NWIS database.

- **Step 2:** Censor data using the method detection limits (MDLs) in effect at the NWQL at the time the sample was analyzed. According to the U.S. Environmental Protection Agency (EPA) definition of MDL, detections at concentrations less than the MDL have greater than a 1 percent probability of being false positive detections. The GAMA-PBP data-quality objectives include that results reported as detections must have less than a 1 percent probability of being false positive detections. Therefore, although the NWQL reports numerical results for concentrations below the MDL for schedules 2003, 2032, or 2033, or on schedule 2060, the GAMA-PBP classifies these detections at concentrations less than the MDL as non-detections. A total of 506 detections at concentrations less than the MDL in effect at the time of analysis were censored. Step 2 is a subset of step 3, but is retained because it can be applied immediately, whereas step 3 required compilation of information about MDLs used during the entire period during which the GAMA-PBP samples were analyzed.

- **Step 3**: Censor the data using the highest MDL (MDL_{max}) established by the NWQL between July 2004 and August 2018. Concentrations of pesticide constituents detected in GAMA-PBP samples generally were low, nearly always less than one-tenth the concentrations of regulatory and non-regulatory health-based benchmarks; thus, the GAMA-PBPs evaluations of pesticides in groundwater are primarily based on detection frequencies. Evaluation of the history of MDLs used during July 2004–August 2018 indicated MDLs generally increased through time: 125 of the 142 pesticide constituents (87 percent) had a higher MDL in August 2018 than in July 2004, and the MDL was the MDL_{max} for 96 pesticide constituents (67 percent) in August 2018. One reason for increases in MDLs over time is the NWQL's practice of using a smaller, shorter term set of analyses for calculating the MDL when a laboratory method is first developed and using a larger, longer term set of analyses for calculating the MDL when the method transitions into full production. In addition, nearly all detections in laboratory set blanks (LSBs) were at concentrations less than MDL_{max}. These observations indicate that censoring at the MDL_{max} is necessary to meet the GAMA-PBP data-quality objective of limiting the risk of false positive detections to less than 1 percent. A total of 438 detections at concentrations less than the MDL_{max} were censored.

- **Step 4:** Identify periods of more frequent laboratory contamination and establish raised censoring limits for use during those times. These periods were defined using a moving-average detection-frequency approach, and the raised censoring limits corresponded to three times the highest concentration measured in an LSB during the period, analogous to the procedure used by the NWQL to define raised reporting levels for set-based censoring in response to detections in LSBs. Of the 114 periods identified during January 2001–May 2016 for 52 pesticide constituents, 67 percent were during 2001–06, indicating the frequency of laboratory contamination decreased substantially through time. A total of 25 detections in such time periods were censored. Another 49 detections in these time periods would have been censored by the raised censoring limits, but had already been censored in step2 or 3 because they had concentrations less than the MDL at the time of analysis or less than the MDL_{max}, respectively.
- **Step 5:** Evaluate LSBs analyzed outside of the step 4 periods, GAMA-PBP field blanks, and USGS Branch of Quality Systems Organic Blind Sample Program (OBSP) unspiked blind blanks to determine whether an alternative censoring limit is required because of contamination bias recorded in blanks. Detections from OBSP unspiked blanks were considered unrepresentative of the rate of false positive detections for the analytical method because pesticide constituents detected frequently in the OBSP unspiked blanks were rarely reported as detected in the original laboratory data for the GAMA-PBP samples. For LSBs and field blanks, the detection limit (DLBLK) was defined as the 99th-percentile concentration of the blanks, and if that concentration was greater than the MDL_{max}, the DLBLK was used as the censoring limit for the GAMA-PBP dataset. No data were censored on the basis of a DLBLK defined from LSBs analyzed outside of the step 4 periods, and a total of 62 detections of atrazine were censored on the basis of a DLBLK defined from GAMA-PBP field blanks.

After implementing these five quality-control censoring steps, the final GAMA-PBP dataset for the 3,001 samples analyzed for pesticide constituents on schedules 2003, 2032, or 2033, or on 2060 had 1,632 detections of 37 pesticide and pesticide degradate constituents. In the final GAMA-PBP dataset, 25 percent of the 3,001 samples analyzed had detections of one or more pesticide constituents.

The 37 pesticide constituents reported as detected in the final dataset for the 3,001 GAMA-PBP groundwater samples collected between May 2004 and May 2018 are listed by schedule:

Schedule 2003, 2032, or 2033	Schedule 2060
2,6-Diethylaniline	Bentazon
3,4-Dichloroaniline	Bromacil
Acetochlor	CEAT
Alachlor	Dinoseb
Atrazine	Diphenamid
Chlorpyrifos	Diuron
Deethylatrazine (CIAT)	Fenuron
Desulfinylfipronil	Imazethapyr
Diazinon	Norflurazon
Dieldrin	OIET
EPTC	Triclopyr
Fipronil	
Fipronil sulfide	
Hexazinone	
Metalaxyl	
Metolachlor	
Metribuzin	
Molinate	
Myclobutanil	
Pendimethalin	
Prometon	
Prometryn	
Propanil	
Simazine	
Tebuthiuron	
Terbuthylazine	

The 41 pesticide constituents reported as detected in the original dataset from the NWQL, but not in the final dataset published by the GAMA-PBP are listed by schedule:

Schedule 2003, 2032, or 2033	Schedule 2060
1-Naphthol	2,4-D
2-Ethyl-6-methylaniline	Atrazine
3,5-Dichloroaniline	Benomyl
Benfluralin	Bensulfuron-methyl
Carbaryl	Bromoxynil
Chlorpyrifos oxon	Chlorimuron-ethyl
cis-Permethrin	Deethylatrazine (CIAT)
cis-Propiconazole	Imazaquin
Cypermethrin	Imidacloprid
DCPA (Dacthal)	MCPA
Desulfinylfipronil amide	Metalaxyl
Dichlorvos	Metsulfuron-methyl
Dicrotophos	*N*-(4-Chlorophenyl)-*N*'-methylurea
Dimethoate	Oxamyl
Ethion	Siduron
Fipronil sulfone	Sulfometuron-methyl
Isofenphos	
λ-Cyhalothrin	
Oxyfluorfen	
Phorate	
Tefluthrin	
Thiobencarb	
trans-Propiconazole	
Tribufos	
Trifluralin	

The final GAMA-PBP dataset for pesticide constituents on schedules 2003, 2032, or 2033, or on schedule 2060 in samples collected by the GAMA-PBP in 2004–2018 is published in the USGS data release accompanying this report (Lor and others, 2019) and is available from the USGS GAMA-PBP public web portal (https://ca.water.usgs.gov/projects/gama/water-quality-results/) and from the SWRCB GAMA groundwater information system (https://gamagroundwater.waterboards.ca.gov/gama/gamamap/public/). The original and final values for the 1,031 results censored by the steps described in this report also are published in the USGS data release (Lor and others, 2019) accompanying this report.

As of 2019, the USGS NWIS database does not have the capacity to hold the original value from the laboratory and the final value published by the project. In the interim, the 1,031 results censored by the steps described in this report are blocked from release from the NWIS database to prevent the potentially confusing situation of two publicly available datasets for the GAMA-PBP samples that have different numbers of detections of pesticide constituents.

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