

National Water-Quality Assessment Project

# **A Method for Addressing Differences in Concentrations of Fipronil and Three Degradates Obtained by Two Different Laboratory Methods**

Open-File Report 2017–1056

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



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By Charles G. Crawford and Jeffrey D. Martin

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## Foreword

Sustaining the quality of the Nation's water resources and the health of our diverse ecosystems depends on the availability of sound water-resources data and information to develop effective, science-based policies. Effective management of water resources also brings more certainty and efficiency to important economic sectors. Taken together, these actions lead to immediate and long-term economic, social, and environmental benefits that make a difference to the lives of the almost 400 million people projected to live in the United States by 2050.

In 1991, Congress established the National Water-Quality Assessment (NAWQA) to address where, when, why, and how the Nation's water quality has changed, or is likely to change in the future, in response to human activities and natural factors. Since then, NAWQA has been a leading source of scientific data and knowledge used by national, regional, state, and local agencies to develop science-based policies and management strategies to improve and protect water resources used for drinking water, recreation, irrigation, energy development, and ecosystem needs (<https://water.usgs.gov/nawqa/applications/>). Plans for the third decade of NAWQA (2013–23) address priority water-quality issues and science needs identified by NAWQA stakeholders, such as the Advisory Committee on Water Information and the National Research Council, and are designed to meet increasing challenges related to population growth, increasing needs for clean water, and changing land-use and weather patterns.

The U.S. Geological Survey (USGS) has been measuring pesticide concentrations in the Nation's streams and rivers for many years. These data are used by many organizations outside the USGS including the U.S. Environmental Protection Agency for assessing the effect of pesticide use on aquatic ecosystems. As technology has improved, the methods of measuring pesticide concentrations have changed. Knowing how pesticide concentrations determined by various methods differ and how to reconcile these differences is important for accurately evaluating pesticide trends and assessing changes in any effects on aquatic ecosystems through time. This report addresses a method change for the insecticide fipronil. All NAWQA reports are available online (<https://water.usgs.gov/nawqa/bib/>).

We hope this publication will provide you with insights and information to meet your water-resource needs and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters. The information in this report is intended primarily for those interested or involved in resource management and protection, conservation, regulation, and policymaking at the regional and national levels.

Dr. Donald W. Cline  
Associate Director for Water  
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## Conversion Factors

International System of Units to U.S. customary units

Multiply	By	To obtain
Volume		
liter (L)	33.82	ounce, fluid (fl. oz)
microliters ( $\mu\text{L}$ )	$0.3382 \times 10^{-4}$	ounce, fluid (fl. oz)
Mass		
microgram ( $\mu\text{g}$ )	$0.3527 \times 10^{-7}$	ounce, avoirdupois (oz)
nanogram (ng)	$0.3527 \times 10^{-10}$	ounce, avoirdupois (oz)

## Abbreviations

DAI	direct aqueous-injection
EPA	U.S. Environmental Protection Agency
GC/MS	gas chromatography/mass spectrometry
LC-MS/MS	liquid chromatography tandem mass spectrometry
$\mu\text{g/L}$	microgram per liter
$\mu\text{L}$	microliter
$\text{ng/L}$	nanogram per liter
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
OLS	ordinary least squares
USGS	U.S. Geological Survey



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## Abstract

In October 2012, the U.S. Geological Survey (USGS) began measuring the concentration of the pesticide fipronil and three of its degradates (desulfinylfipronil, fipronil sulfide, and fipronil sulfone) by a new laboratory method using direct aqueous-injection liquid chromatography tandem mass spectrometry (DAI LC–MS/MS). This method replaced the previous method—in use since 2002—that used gas chromatography/mass spectrometry (GC/MS). The performance of the two methods is not comparable for fipronil and the three degradates. Concentrations of these four chemical compounds determined by the DAI LC–MS/MS method are substantially lower than the GC/MS method. A method was developed to correct for the difference in concentrations obtained by the two laboratory methods based on a methods comparison field study done in 2012. Environmental and field matrix spike samples to be analyzed by both methods from 48 stream sites from across the United States were sampled approximately three times each for this study. These data were used to develop a relation between the two laboratory methods for each compound using regression analysis. The relations were used to calibrate data obtained by the older method to the new method in order to remove any biases attributable to differences in the methods. The coefficients of the equations obtained from the regressions were used to calibrate over 16,600 observations of fipronil, as well as the three degradates determined by the GC/MS method retrieved from the USGS National Water Information System. The calibrated values were then compared to over 7,800 observations of fipronil and to the three degradates determined by the DAI LC–MS/MS method also retrieved from the National Water Information System. The original and calibrated values from the GC/MS method, along with measures of uncertainty in the calibrated values and the original values from the DAI LC–MS/MS method, are provided in an accompanying data release.

## Introduction

The U.S. Geological Survey (USGS) has been measuring pesticide concentrations in the Nation's streams and rivers (herein collectively referred to as streams) for many years. Water samples are analyzed for pesticides by the USGS National Water Quality Laboratory (NWQL) using methods developed by the NWQL's Methods Research and Development team. The pesticide fipronil and several degradates were added to the list of pesticides analyzed in filtered water samples in 2002. From 2002 until 2012, a method based on gas chromatography/mass spectrometry (GC/MS) was the most common means of analysis of water samples for fipronil (Madsen and others, 2002). In October 2012, a new laboratory method for pesticides that included fipronil and several degradates (Sandstrom and others, 2015) was introduced and most analyses from then on used the new method. The new laboratory method is direct aqueous-injection (DAI) liquid chromatography tandem mass spectrometry (LC-MS/MS). The new DAI LC–MS/MS method has several advantages over the older GC/MS method, including small sample volumes and no sample preparation or extraction procedures (Sandstrom and others, 2015, p. 46).

Both the GC/MS and DAI LC–MS/MS laboratory methods provide concentrations for multiple pesticides; however, the performance of the methods for specific pesticides varies. While the methods provide comparable results for many compounds, this is not so for fipronil and some of its degradates included in the methods. Concentrations produced by the DAI LC–MS/MS method are substantially lower than the old method.

## Purpose and Scope

This report describes the differences in concentrations obtained by the GC/MS and DAI LC–MS/MS laboratory methods for four chemical compounds. The four chemical compounds are the pesticide fipronil and three of its degradates—desulfinylfipronil, fipronil sulfide, and fipronil sulfone (hereafter referred to as “compounds”). Differences

between the methods are determined based on the results of a field study done in 2012. A statistical approach for relating the data from the two laboratory methods is described. Finally, this approach is used to remove differences in concentrations of the four compounds due to the method change in over 16,000 stream samples collected between 2002 and 2016 and analyzed by means of the GC/MS laboratory method.

## Description of Laboratory Methods

The most widely used method for determination of pesticides in filtered water by the USGS over the last two decades was GC/MS. In this method, pesticides are isolated from 1-liter filtered water samples by solid-phase extraction and analyzed by capillary-column GC/MS with selected-ion monitoring (Zaugg and others, 1995). Results from the GC/MS method are reported in micrograms per liter ( $\mu\text{g/L}$ ). The original version of the GC/MS method is known as NWQL schedule 2001. The same laboratory method, but with samples having solid-phase extraction done in the field rather than the laboratory, is known as NWQL schedule 2010. Two other NWQL schedules (2003 and 2033) that differ only in the numbers of pesticides included were also used at various times. Schedule 2003 was most commonly used for fipronil and its degradates, followed by schedules 2033, 2001, and 2010. Hereafter, these four schedules are referred to as the “old” method.

The new DAI LC–MS/MS (Sandstrom and others, 2015) requires only a 20-milliliter filtered sample, unlike the old method that required one liter. Other than filtering, no sample preparation procedures (such as extraction) are required, so differences in bias and variability with the old method were expected. Results from the DAI LC–MS/MS method are reported in nanograms per liter ( $\text{ng/L}$ ). The DAI LC–MS/MS method is known as NWQL schedule 2437 and has been used

as the primary laboratory method for fipronil and its degradates since October 2012. Hereafter, schedule 2437 is referred to as the “new” method. A list of all the schedules is given in table 1.

## Data Used for This Study

Two groups of data were used for this investigation. The first were data from a methods comparison field study done specifically to compare method performance for a number of pesticides determined by the two methods. These data were used to develop a relation between the concentrations of the four compounds determined by both the old and new laboratory methods. The second group of data was from stream samples obtained from the USGS National Water Information System (NWIS). The NWIS is the database for hydrologic data collected by the USGS (U.S. Geological Survey, 2017a). Results from the old method were converted to  $\text{ng/L}$  to be consistent with those obtained by the new method.

## Methods Comparison Field Study

A methods comparison field study (hereafter “field study”) was done to document performance of the new method in a variety of stream-water matrices and to quantify any potential changes in measurement bias or variability that could be attributed to changes in laboratory methods (Martin and others, in press). Among the goals of the field study were to (1) summarize performance (bias and variability of pesticide recovery) of the new method in a variety of stream-water matrices; (2) compare performance of the new method to that of the old method in a variety of stream-water matrices; and (3) compare pesticide detections and concentrations measured by the new method to those of the old methods in a variety of stream-water matrices.

**Table 1.** Description of National Water Quality Laboratory schedules and method codes used to analyze fipronil and degradates.

[NWQL, National Water Quality Laboratory; GC/MS, gas chromatography/mass spectrometry; DAI LC-MS/MS, direct aqueous-injection liquid chromatography tandem mass spectrometry]

NWQL schedule number	Analytical method	NWQL method code	Sample preprocessing	Reporting units	Designation for this report
2001	GC/MS	GCM31	extraction done in the laboratory	micrograms per liter	old method
2010	GC/MS	GCM30	extraction done in the field	micrograms per liter	old method
2003	GC/MS	GCM29	extraction done in the laboratory	micrograms per liter	old method
2033	GC/MS	GCM29	extraction done in the laboratory	micrograms per liter	old method
2437	DAI LC-MS/MS	LCM60	no extraction required	nanograms per liter	new method

Stream-water samples were collected at 48 sites in the USGS monitoring network during June–September 2012. Stream sites were located across the United States and included sites in agricultural and urban land-use settings, as well as sites on major rivers and reference sites (Martin and others, in press). Most sites were sampled on three dates (site visits) for a total of 150 site visits.

For each site visit, a single large-volume water sample was collected and processed into an environmental sample and a field matrix spike for both the old and new method. A method-specific spike solution (100 microliters [ $\mu\text{L}$ ]) was added to each field matrix spike sample. Spiking typically increased the concentration of pesticides by approximately 0.1  $\mu\text{g/L}$  in schedule 2033 samples and by 250  $\text{ng/L}$  (0.25  $\mu\text{g/L}$ ) in schedule 2437 samples. The two sets of samples were then analyzed, one by schedule 2033 and one by schedule 2437.

Several factors affected the field study data available for use in this investigation. These include problems with the field matrix spikes used for recovery correction, as well as samples where one of the compounds evaluated for this study was not detected by the method used.

## Recovery Correction

Recovery is the ratio of a measured concentration divided by a theoretical or “expected” concentration and is a principal measure of laboratory method performance. Field matrix recovery was determined by adding a method-specific spike solution to an aliquot of water for each sample. Recovery for that spiked sample was then determined by subtracting the concentrations of pesticides in an associated unspiked sample of stream water (the environmental concentration). High environmental concentrations of pesticides result in invalid estimates of recovery for some matrix spikes. In the presence of high environmental concentrations, the additional concentration from spiking may be indistinguishable from the normal laboratory variability of measurements. Recoveries calculated from matrix spikes under these conditions may be much higher or lower (even negative) than is typical for the method. Samples with calculated recoveries where environmental concentrations were greater than three times the expected concentration were not used in this study. Eleven samples were discarded under this criterion for fipronil while 10 were discarded for each of the three degradates.

A summary of recoveries for the usable field matrix spikes for the four compounds is given in table 2. Recoveries for samples analyzed by the old method were generally greater than 100 percent with median recoveries ranging from 110 to 144 percent for the four compounds. Fipronil had the highest recovery for the old method, which was typically about 20 percent higher than the three degradates. In contrast, recoveries in samples analyzed by the new method were similar across compounds and, with median recoveries ranging from 85 to 91 percent.

As recovery varies among methods and through time, it is important to adjust for recovery when comparing the results from two different laboratory methods. Correspondingly, all stream samples in the field study with detected pesticide concentrations were adjusted for recovery using the concentration measured in the associated field matrix spike. Stream samples were corrected for recovery by dividing the concentration reported by the laboratory by percent recovery in the field matrix spike. The percent recovery of the field matrix spike was computed as 100 times the ratio of the measured concentration in the field matrix spike (with the stream concentration subtracted from the measured concentration in the spike sample) divided by the concentration expected from the amount of chemical added during the spike preparation. That is,  $R = 100 * ([C_{\text{spiked}} - C_{\text{unspiked}}] / C_{\text{expected}})$ , where  $R$  is pesticide recovery in percent,  $C_{\text{spiked}}$  is the measured concentration of the pesticide in the field matrix spike,  $C_{\text{unspiked}}$  is the measured concentration of the pesticide in the unspiked field sample, and  $C_{\text{expected}}$  is the expected concentration of the pesticide in the field matrix spike based on the amount of pesticide added. Thus, if the laboratory reported a concentration of 10  $\text{ng/L}$  in a stream sample but the recovery in the associated field matrix spike was 80 percent (the ratio was 0.80), the recovery-corrected concentration in the stream sample would be 12.5  $\text{ng/L}$ . If the field matrix spike for that same stream sample had a recovery of 125 percent (the ratio was 1.25), the recovery-corrected concentration would be 8  $\text{ng/L}$ . Hereafter, all references to concentrations from the field study refer to recovery-corrected concentrations.

Trends in recovery of field matrix spikes for fipronil as obtained by the old and new method are shown in figure 1. Recoveries for the new method had pronounced differences over the 4 months of the method comparison study, as illustrated by the cyclical pattern of the lowess (locally weighted scatterplot smooth [Cleveland, 1979]) curve drawn through the data. (The function lowess from the R statistical computing software [R Core Team, 2016] was used to draw the lowess curves in this report. Version 3.2.2 of R was used.) Recoveries for the old method did not show a similar cyclical pattern. However, this method had greater variability in recovery at any given point in time than did the new method. Patterns of field matrix-spike recovery for the three fipronil degradates were similar to that observed for fipronil, except the variability in recovery by the old method was not as large.

Recoveries for the old method during the study period were anomalous relative to the longer term average. Figure 2 shows variation in recovery of fipronil analyzed by the new and old methods in blind samples for a 5-year period, centered on the time of the method comparison study. These blind samples were submitted to the NWQL by the USGS Branch of Quality Systems (U.S. Geological Survey, 2017b). Blind samples are quality-control samples whose composition and origin are unknown by the analyzing laboratory. They are disguised to be indistinguishable from routine water samples sent to the laboratory and are intended to provide for a realistic measure of bias in laboratory procedures. Recoveries of fipronil in

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Table 2. Summary of recovery of field matrix spikes for fipronil and three degradates.

Pesticide	Number of samples	Mean	Minimum	25th percentile	Median	75th percentile	Maximum
Schedule 2437							
Fipronil	138	93.1	66.0	83.8	90.3	99.2	126.9
Desulfinylfipronil	139	87.3	62.6	80.2	84.9	91.5	118.8
Fipronil sulfide	139	92.3	67.9	84.2	91.0	98.6	124.2
Fipronil sulfone	139	86.8	62.2	77.5	85.7	94.1	115.5
Schedule 2033							
Fipronil	138	144.6	99.3	129.6	143.8	158.9	195.3
Desulfinylfipronil	139	117.2	91.9	110.6	117.6	123.1	164.0
Fipronil sulfide	139	119.5	90.1	110.6	119.5	126.3	175.7
Fipronil sulfone	139	110.7	71.9	103.2	109.5	117.1	150.1

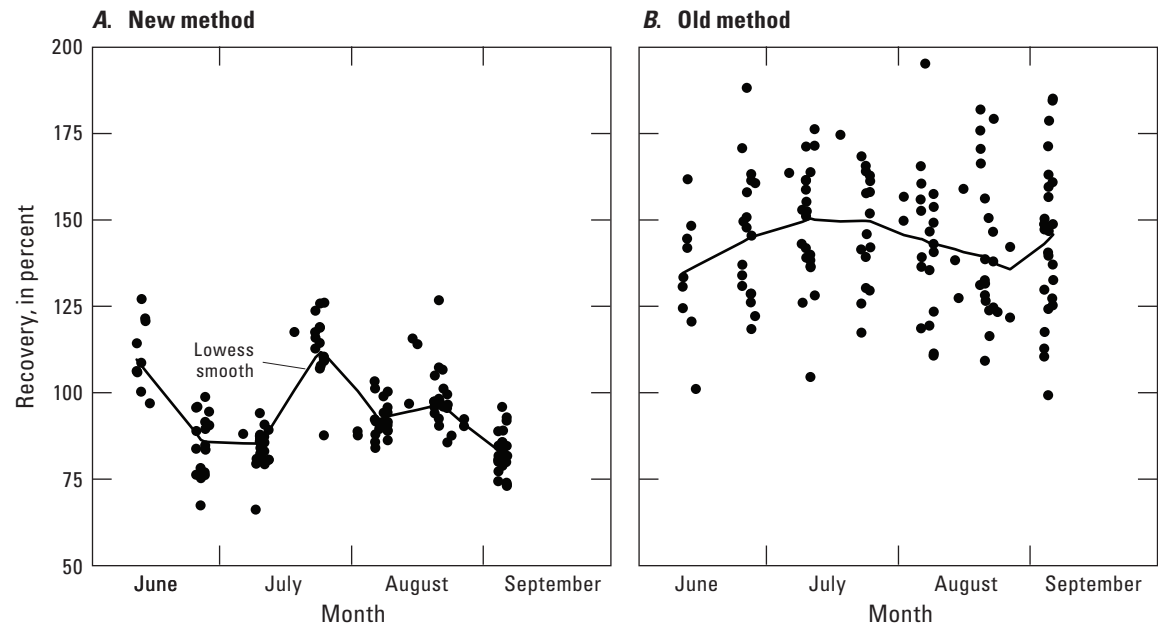
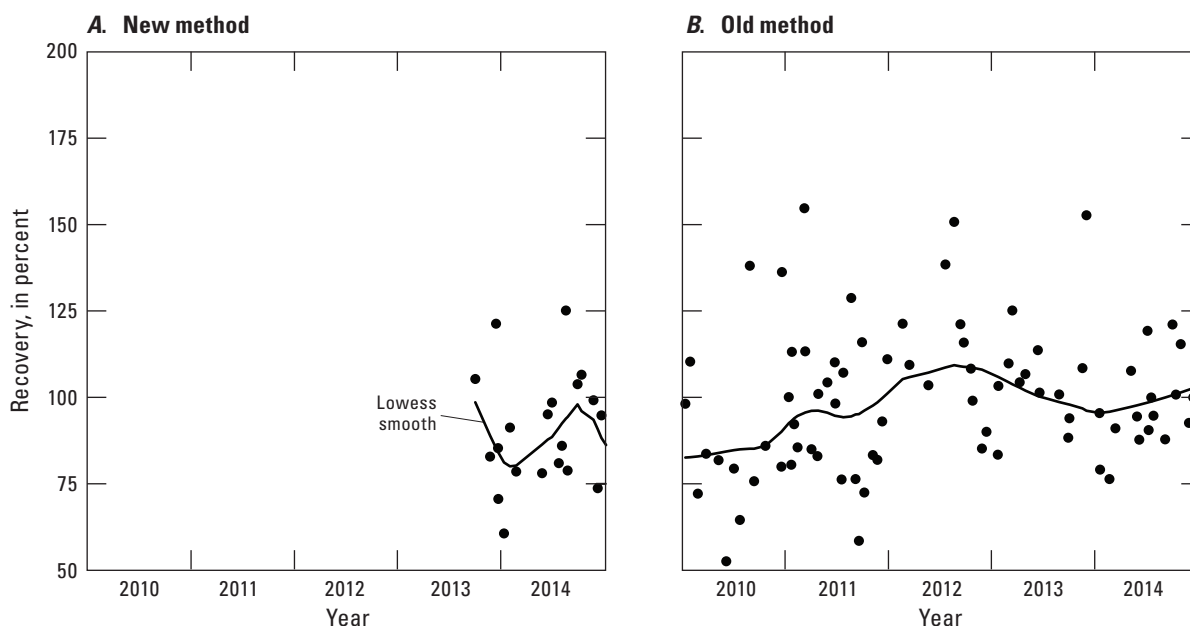


Figure 1. Variation in recovery of fipronil in field matrix spikes for A, new method and B, old method during the method comparison field study.



**Figure 2.** Variation in recovery of fipronil in blind quality assurance samples for *A*, new method and *B*, old method, 2010–2014.

blind samples analyzed by means of the old method during this 5-year period were highest during 2012. Blind samples for the new method were not submitted until after the time the method was introduced and are only available for the latter part of the 5-year period, as shown in figure 2. However, the data that are available are comparable to that seen during the period of the field study.

## Reporting Limits and Estimated Values

Analytical methods discussed in this report do not have specified “detection limits” for each pesticide analyte. Compounds detected and conclusively identified by retention time and mass spectral characteristics are quantified and reported (Zaugg and others, 1995, p. 19–21; Furlong and others, 2001, p. 37; Sandstrom and others, 2015, p. 17). Nondetections of pesticides (analyses that do not meet identification criteria based on retention time and mass spectral characteristics) are reported as less than the reporting level for that method and analyte (for example, less than [ $<$ ] 5 ng/L). The numerical values of the reporting levels are method- and analyte-specific and are based on estimates of the Long-Term Method Detection Level (Childress and others, 1999; Sandstrom and others, 2015, p. 21–22). Reporting levels may change through time, typically at the start of the water year, in response to changes in the ability of the method to quantify low-level concentrations in laboratory reagent-water spikes.

The frequency of detection ranged from 12–56 percent of samples for the four compounds analyzed by means of

the old method (table 3). Desulfinylfipronil was the most frequently detected of the four compounds by these schedules. The frequency of detection ranged from 12–24 percent for samples analyzed using the new method. Fipronil was the most frequently detected of the four compounds by the new method. When one of the compounds was detected by only one of the two methods, it was much more likely to have been detected by the old method than the new (table 3). Eighty-three percent of the samples falling into this category were detected by the old method but not by the new method. The exception was fipronil sulfone, for which an equal number of samples were detected by one method but not the other.

**Table 3.** Number of analyses and detections available for fipronil and three degradates.

Chemical	Fipronil	Desulfinyl-fipronil	Fipronil sulfide	Fipronil sulfone
Usable samples out of 150 total	138	139	139	139
Samples with detections by both old and new method	24	31	16	7
Samples without detections by either old or new method	86	60	83	112
Samples with detection by new method but not by old method	9	1	2	10
Samples with detection by old method but not by new method	19	47	38	10



Some concentration values were assigned an “E” remark code indicating greater uncertainty in the provided value. Typical reasons for the laboratory assigning an “E” remark code to pesticide data include: (1) the pesticide was detected at a concentration less than the reporting level, (2) the value was extrapolated above the calibration curve, (3) the sample was diluted to bring the concentration into the calibration range, (4) the typical performance of the analyte does not meet method-specific criteria, (5) moderate matrix interference conditions occurred, and (6) contamination was in associated blank samples. An “E” remark is assigned in this latter situation when  $3 \times C_b \leq C_s \leq 10 \times C_b$ , where  $C_b$  is the analyte concentration in the associated laboratory blank(s) and  $C_s$  is the analyte concentration in the sample. Reasons to assign “E” remark codes have changed through time as laboratory standard operating procedures change or as typical method performance changed. For example, all detections of pesticides less than the reporting limit, before approximately 2011, were remarked “E.” Subsequently detections less than the reporting level were not remarked “E” (U.S. Geological Survey, 2010).

Regarding this investigation, the important point about the “E” remark codes is that (at a selected period in time) an “E” remark code indicates greater (but unknown) amounts of uncertainty in the associated concentration value than concentrations of the same value that are not remarked “E.” Additional information on “E” remark codes and changes through time are provided in Childress and others (1999), Madsen and others (2002), U.S. Geological Survey (2010), and U.S. Geological Survey (2011). Two compounds detected by the old method during the field study had “E” remark codes (100 percent of fipronil detections and 13 percent of desulfinylfipronil detections). None of the concentrations detected by the old method for the other two degradates or for the four compounds by the new method had “E” remark codes.

All data from the field study are available (Martin and Baker, in press). Data for the four compounds included in this study are available separately (Crawford and Baker, 2017).

## National Water Information System

All fipronil data contained in NWIS were retrieved for use in this investigation. However, only data identified as having been analyzed by schedules 2001, 2003, 2010, 2033, or 2437 were retained. This was the vast majority of all data (about 93 percent). There were a small amount of data analyzed by other methods (typically associated with small research projects), while some samples were missing the codes identifying the method by which the analysis was done. In total, there were 16,639 samples analyzed for fipronil by means of schedule 2001, 2003, 2010, or 2033, and 7844 samples analyzed for fipronil by means of schedule 2437. As with the field study, many of the fipronil concentrations retrieved from NWIS were either not detected

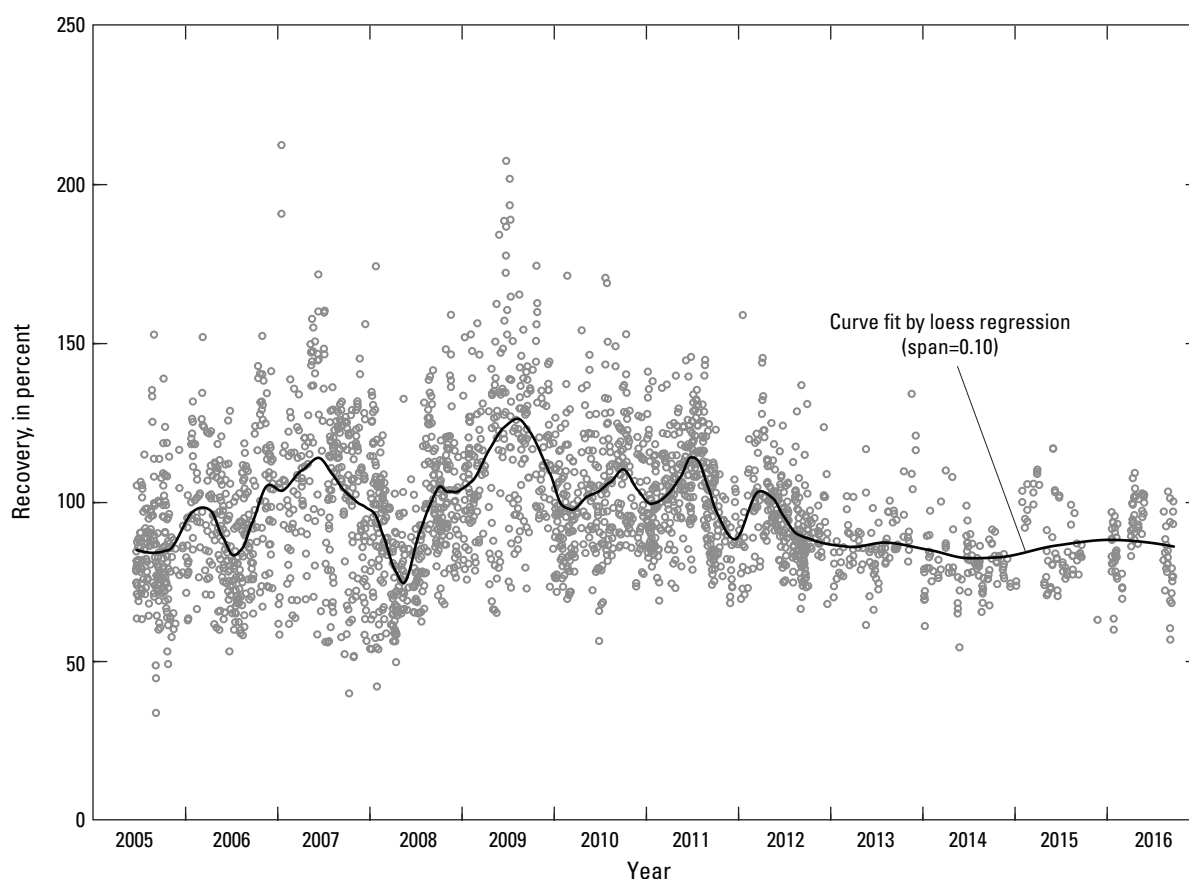
or estimated. The frequency of detection ranged from 11–26 percent of samples for the four compounds analyzed by means of the old method. Desulfinylfipronil was the most frequently detected of the four compounds by the old method. The frequency of detection for the four compounds ranged from 10–23 percent for samples analyzed by means of the new method. Fipronil was the most frequently detected of the four compounds by the new method. Some of the data from NWIS for the four compounds also had “E” remark codes. For the old laboratory method, the majority of detected samples had “E” remark codes (from 70 to 99 percent). For the new laboratory method, the percentage of “E” remarked samples was much lower, ranging from 9 to 19 percent. The higher percentage of “E” remarked values in the old method partially reflects the USGS policy; in effect, prior to 2011, where all detections less than the reporting limit were given an “E” remark code (U.S. Geological Survey, 2010).

As with data from the field study, it was also necessary to adjust the data retrieved from NWIS for recovery before further processing. It is unusual to have a field matrix spike associated with each stream sample as was done for the field study. Thus, a different approach for adjusting the NWIS data for recovery was needed. Periodic field matrix spikes are submitted to the NWQL for analysis as part of USGS monitoring programs. These data were not processed and available within the time constraints of this investigation. However, as part of its routine operating procedure, the NWQL prepares and analyzes a spiked blank-water sample (a laboratory “reagent” spike) with every set of samples run through the analytical instrument. These data were available and obtained from the NWQL for use in correcting the NWIS data for recovery. Laboratory reagent spike data were obtained for schedules 2001, 2003, 2033, and 2437 and processed separately. Laboratory reagent spike data from schedule 2001 were used to recovery correct the small amount of fipronil data analyzed by schedule 2010. The laboratory reagent spike data used for this study are available (Crawford and Baker, 2017).

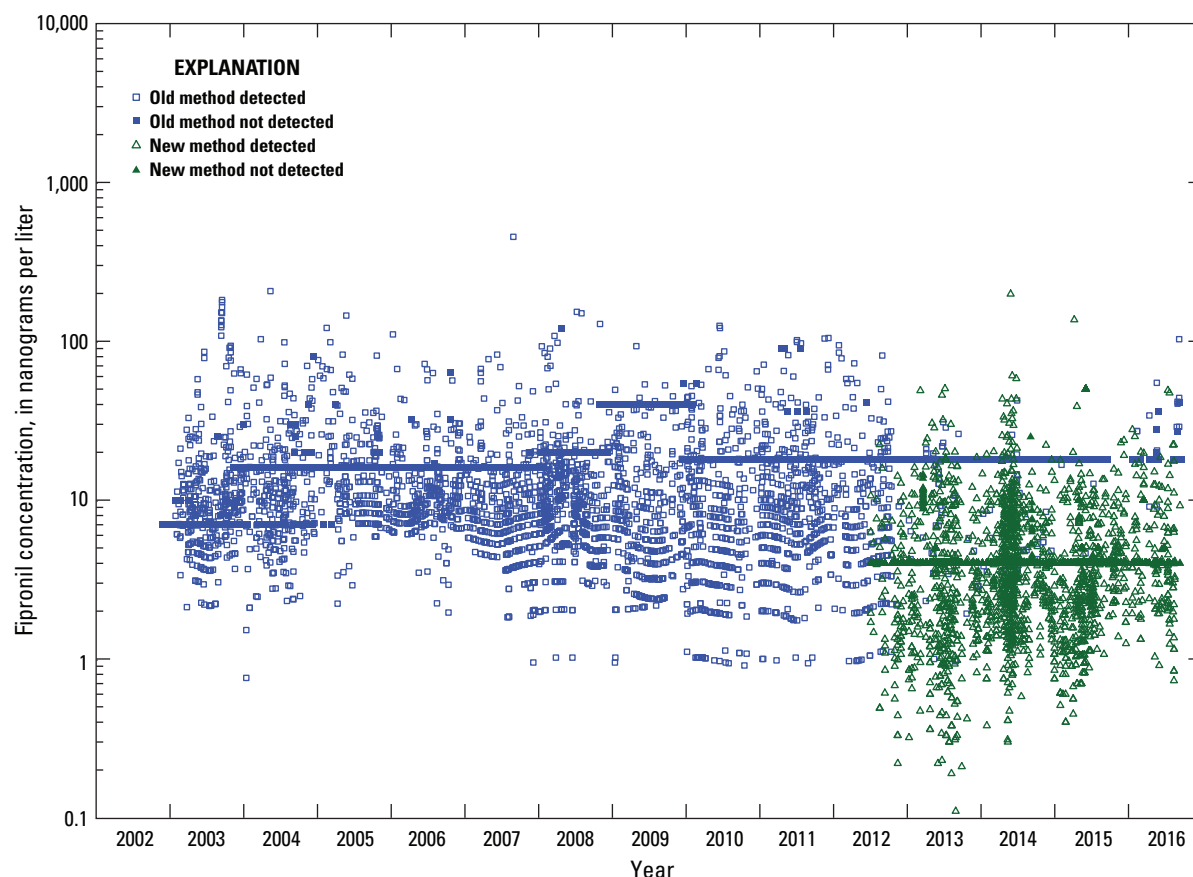
A procedure described by Martin and others (2009) was used for recovery correction. This procedure fits a smooth curve through the available spike recovery data using loess regression (Cleveland and Devlin, 1988). (The function *loess* from the R software package was used for this investigation.) Loess regression is similar to the lowess smoothing procedure previously mentioned but is a more general approach for fitting lines or surfaces to data. In loess regression, a parameter (the span) specifies what fraction of data is used to fit each data point. Larger values of the span parameter result in a smoother fit through the data while smaller values allow more flexibility in the shape of the curve. As was done by Martin and others (2009), a span of 0.1 was used for this investigation (indicating that the nearest 10 percent of all data were used for fitting each data point in the time series). Separate curves were fit to the laboratory spikes for fipronil and the three degradates for each of schedules 2001, 2003, 2033, and 2437. For each stream sample retrieved from

NWIS, an estimated recovery was obtained from the curve fit to the laboratory spikes for the date the stream sample was analyzed. As with the field study, the stream samples were divided by the estimated recovery ratio to obtain the recovery-corrected concentration. An example of a curve obtained by loess regression used for estimating recoveries

of fipronil for NWIS stream samples analyzed by schedule 2033 is shown in figure 3. Concentrations of fipronil obtained from NWIS and corrected for recovery using the procedure described above for all four schedules are shown in figure 4. Hereafter, all references to concentrations for data retrieved from NWIS refer to recovery-corrected concentrations.



**Figure 3.** Curve fit by loess regression through laboratory reagent spikes for fipronil analyzed by schedule 2033.



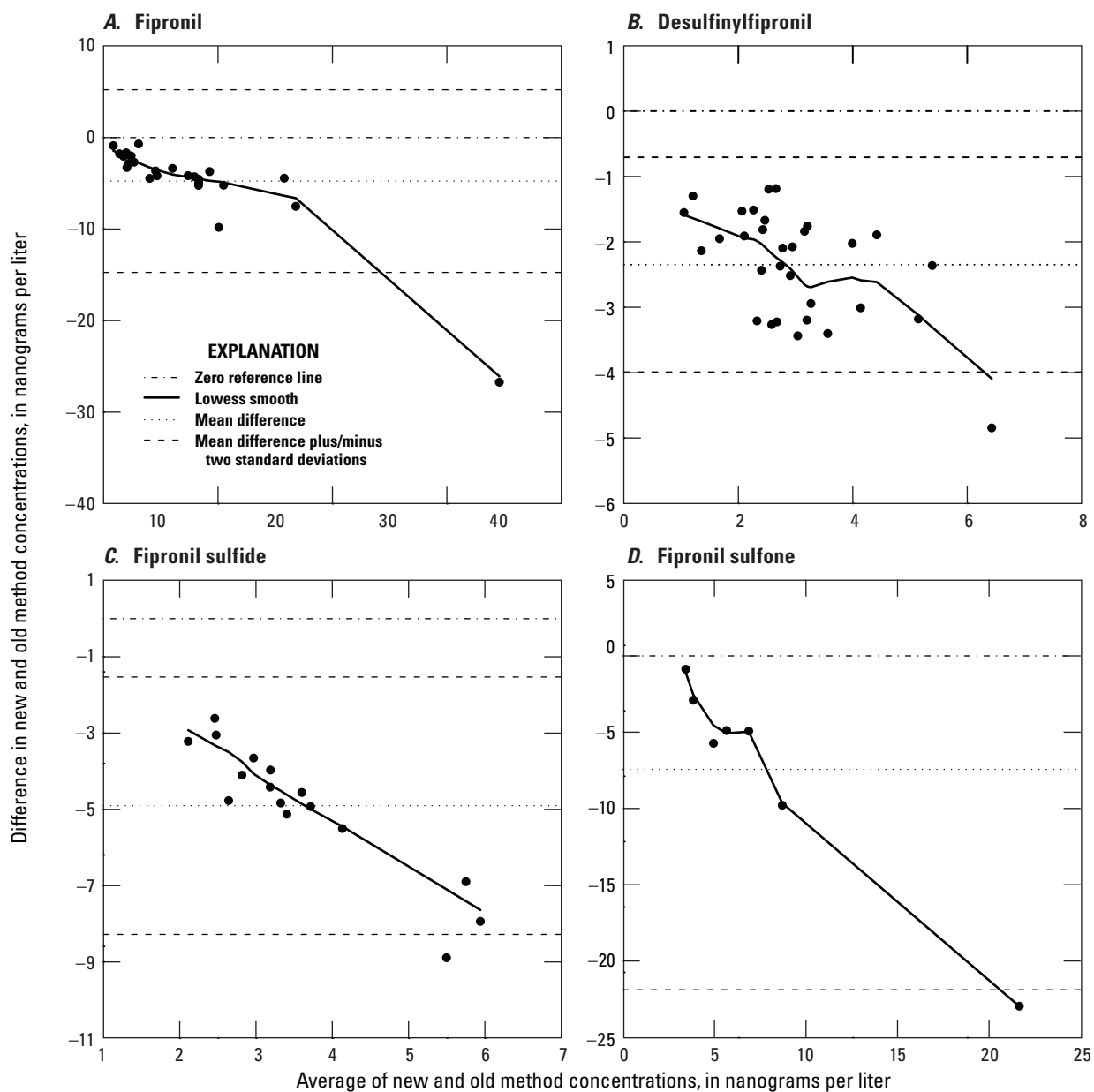
**Figure 4.** Relation of fipronil concentrations from the National Water Information System, as determined by the old and new laboratory methods and corrected for recovery, to time.

## Differences between the Laboratory Methods

One technique for evaluating differences in laboratory methods is the Bland-Altman plot (Bland and Altman, 1986). This approach plots the differences in concentrations obtained by two methods against the mean of the concentrations obtained by the two methods; however, its use is limited to detected concentrations only. Limits of agreement (Bland and Altman, 1999) defined as two times the standard deviation of the mean difference are also plotted. For two methods that are in perfect agreement, all points will fall on

a zero reference line. For two methods that are comparable, all points will fall along a zero reference line with random variability about that line and the limits of agreement will be small. Departures from this pattern indicate differences in the methods. Figure 5 shows Bland-Altman plots for fipronil and the three degradates used in this study. (The R package `BlandAltmanLeh` [Lehnert, 2015] was used to create the Bland-Altman plots in this report.) All four of the plots indicate substantial differences between the methods as illustrated by the downward slope of the lowest smooth drawn through the data. The downward slope is an indication of strong proportional bias (bias that increases as the concentration increases.)





**Figure 5.** Bland-Altman plots comparing concentrations analyzed by the old and new methods during the method comparison field study for *A*, fipronil; *B*, desulfinylfipronil; *C*, fipronil sulfide; and *D*, fipronil sulfone.

## Development of the Relation between Methods

The “calibration” approach described by Newell and others (1993) was used to develop the relation between methods for this investigation. This approach develops a relation between overlapping data obtained by one laboratory method to those obtained by another. This relation is then used to calibrate data obtained by the older method in order to remove any biases attributable to differences in the methods. Regression analysis (a statistical approach for estimating relations between two or more variables) is the commonly used approach for developing the relation between the methods. In addition, the intercept and slope from the regression provide information on the magnitude of the constant and proportional bias between the methods (Hartmann and others, 1997; Martinez and others, 1999). (Use of the term calibration in this context should not be confused with the calibration curve for the laboratory instrument used by the NWQL to measure concentrations in water samples.)

The data available from the field study for the four compounds included in this report had several characteristics that complicated the regression analysis completed for this investigation. First, the compounds from one or both laboratory methods were sometimes not detected (indicated by sample concentrations with a “<” remark code). Such values, commonly referred to as censored observations in the statistics literature, are only partially known. They thus provide less information than a sample for which a compound was detected. All that is known for these values is that the concentration is somewhere between zero and the reporting limit. Traditional regression analysis methods, and particularly those methods developed for obtaining relations between two laboratory methods, do not allow for censored observations. Second, the values from both laboratory methods have error associated with them. Most regression analysis methods assume that the explanatory variable (the variable used to predict the other, or response variable) is measured without error. Those that do allow for error in both the explanatory and response variables do not allow for censored observations. Finally, two of the compounds discussed in this report have outlier values. In statistics, an outlier is as an observation not consistent with others in the data or so different from the rest of the data as to make one concerned it originated from a different process (Ben-Gal, 2010). An outlier may be due to unusually high variability in a measurement or error in the collection and processing of a sample. The presence of outliers can distort the results of some statistical methods that require that certain assumptions about the distribution of data be met.

## Regression Methods

No single regression method was available that addressed all the complications in the available data previously described. An approach was used for this investigation that evaluated and compared several alternative regression methods, none of which are strictly appropriate for the data available. The methods evaluated include ordinary least squares (OLS) regression; Deming Regression (Deming, 1943); Passing-Bablok regression (Passing and Bablok, 1983); and tobit regression (Tobin, 1958). The first of these is not appropriate for use with censored data and is also not suitable for use with data having uncertainty in both the response and explanatory variables. OLS regression can, however, be used to obtain bounds of the regression slope for situations with uncertainty in the explanatory variable. Two of the methods are not appropriate for use with censored data but were specifically developed to address situations having data with uncertainty in both the response and explanatory variables (Deming and Passing-Bablok regression). Passing-Bablok regression was developed specifically for evaluating differences in two laboratory methods. The last one (tobit regression) can be used when the response variable has some censored observations but not when values of the explanatory variable are censored. Thus, the regression analysis methods evaluated for use in this study only included a subset of all data from the field study.

The function `lm` from the R statistical computing software (R Core Team, 2016) was used to perform the ordinary least squares regressions for this report. The function `deming` from the R package `deming`, version 1.0-1 (Therneau, 2014), was used to perform the Deming regressions. The function `pbreg` (using the method 1 option) from the R package `deming`, version 1.0-1 (Therneau, 2014), was used to perform the Passing-Bablok regressions. The function `survreg` from the R package `survival`, version 2.401 (Therneau, 2016), was used to perform the tobit regressions.

## Ordinary Least Squares Regression

OLS regression assumes explanatory variables are known with certainty (with no measurement error) and that all error in the model is associated with the response variable (Gillard, 2010). Measurement error in an explanatory variable results in the slope coefficient obtained from OLS regression being closer to zero than it, in fact, is. This situation is known as regression dilution (Frost and Thompson, 2000) or the errors-in-variables problem (Thomson and Willis, 1986).

Cochran (1968) has demonstrated that measurement errors in explanatory variables can result in a significant bias in the slope obtained by OLS regression under some circumstances, while being trivial under other circumstances. The degree of impairment depends upon the magnitude of the errors and how they affect the variances and covariances needed to obtain the regression solution. If the measurement error in the explanatory variable is small relative to the

overall range in the explanatory variable, then the error in the estimated slope will also be small (Draper, 1991). Cornbleet and Gochman (1979) suggest that if this ratio is greater than 0.2, the estimated slope from OLS regression will be severely biased. Further, if the variance of the explanatory variable is not zero, then the true value of the slope is unidentifiable (Leonard, 2011) and both the estimates of the slope and intercept coefficients are inconsistent (Gleser and others, 1987). (In statistics, identifiability is the property whereby it is theoretically possible to determine the true value of a parameter. Inconsistent estimates do not converge on the true value as sample sizes become very large.)

For slope coefficients that are unidentifiable due to measurement error, and assuming the measurement error is uncorrelated with model error, it has been demonstrated that the true value of the slope lies between that obtained from an OLS regression of the first variable and the second variable, and that obtained from the reverse regression of the same two variables (Erickson, 1993). The bounds on the slope are then obtained from the following two regression equations: (1)  $Y = a_1 + b_1 X$ , where  $Y$  and  $X$  are the first and second variables and  $a_1$  and  $b_1$  are the intercept and slope estimated from the first regression, and (2)  $X = a_2 + b_2 Y$ , where  $a_2$  and  $b_2$  are the intercept and slope from the second regression. Solving the second equation for  $Y$  yields  $Y = a_2/b_2 + (1/b_2)X$ , where  $a_2/b_2$  and  $1/b_2$  are the intercept and slope of the reverse regression. Thus, the true slope is bounded by  $b_1$  and  $1/b_2$ .

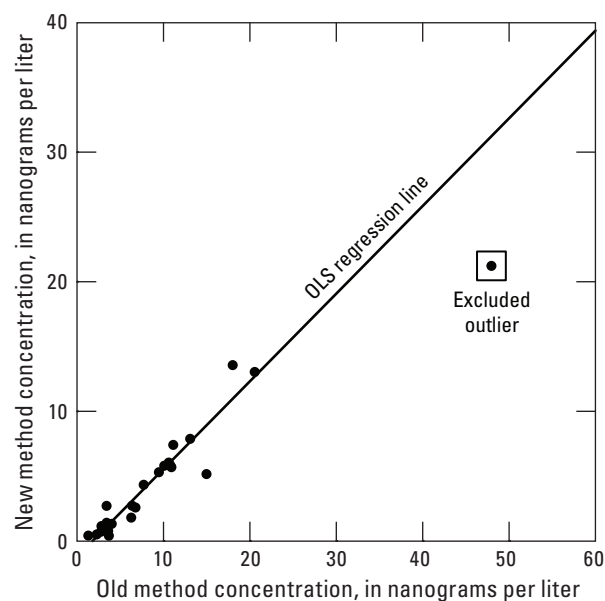
Another limitation of OLS regression is that it is susceptible to outliers. As OLS regression uses a squared deviation approach to model fitting, observations lying further from the overall pattern of the data can disproportionately pull the regression line toward that observation (Neter and others, 1985, p. 114). In method comparison studies, outliers can indicate serious errors due to contaminated samples, false measurements, or incorrectly calibrated instruments (Rauch and others, 2010). For this investigation, outliers in data used for OLS regression were identified using regression diagnostics as proposed by Belsley and others (1980). Only one observation for fipronil was identified as an outlier and excluded from the analysis (fig. 6).

Stöckl and others (1998) point out one important advantage of OLS regression for method comparison studies that is particularly important for this investigation. OLS regression provides an estimate of the standard deviation of the residual error about the regression line (the standard error of the regression). This statistic is useful for determining the amount of noise to add to recalibrated estimates of the old method to give them a distribution that is similar to that of estimates obtained via the new method.

## Deming Regression

Deming regression, also known as orthogonal regression, is another least squares regression method often used for comparing alternative laboratory methods (Linnet,

1993). This regression method minimizes residual error relative to both the response and explanatory variable (that is, perpendicular to the regression line). This is in contrast to OLS regression that minimizes error only relative to the response variable (that is, vertically with respect to the regression line). As such, the regression line obtained by Deming regression is considered to be symmetric with respect to the response and explanatory variable (Greene, 2013). (That is, coefficients obtained by the two regressions to bound the slope for OLS regression will be identical when Deming regression is used.) Deming regression assumes the ratio of the variances of the two methods is constant over the entire range of data (Linnet, 1998; Martin, 2000) or for generalized Deming regression, proportional (Linnet, 1990). Failing specific knowledge of this variance ratio, it is often assumed to be equal to one. However, Carroll and Ruppert (1996) have shown that if the variance ratio is not specified correctly (that is, if the assumption is not valid that the variance ratio is one), then orthogonal regression tends to overcorrect for measurement error. Like OLS regression, Deming regression is also susceptible to outliers (Shapiro and Brady, 1995; Fekria and Ruiz-Gazen, 2004). The outlier identified for OLS regression was also excluded from the data used to perform the Deming regression.



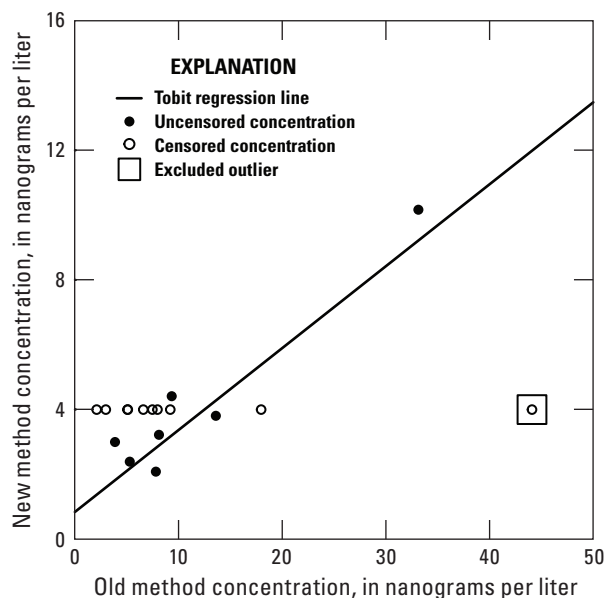
**Figure 6.** Relation of concentrations analyzed by the old and new methods and the ordinary least squares (OLS) regression line obtained for fipronil showing outlier observation excluded from the regression, fipronil sulfone.

## Passing-Bablok Regression

Passing-Bablok regression (Passing and Bablok, 1983) is a nonparametric regression method. It is similar to Theil-Sen regression (Theil, 1950; Sen, 1968; Helsel and Hirsch, 2002, p. 266). Passing and Bablok adapted the Theil procedure to take into account situations where there may be more than one observation with the same values of the explanatory variable but different values of the response variable (Bablok and Passing, 1985; Miller, 2012). This situation is not uncommon in laboratory method comparison studies. Passing-Bablok regression does not require knowledge of or assumptions about the measurement error in the response and explanatory variables. An estimate of the intercept and slope of the regression line is obtained from the median of the coefficients of the lines connecting each possible pair of observations in the dataset. Like Deming regression, Passing Bablok regression is symmetric; however, unlike Deming regression, it is robust against outliers (Linnet, 1993). No outlier values were excluded from the data used to perform Passing-Bablok regression.

## Tobit Regression

Tobit regression (Tobin, 1958) is a regression method for situations for which some of the values of the response variable are censored. Like OLS regression, tobit regression is also subject to regression dilution (Wang, 1998) and is susceptible to outliers (Escobar and Meeker, 1992). Outliers for tobit regression were identified visually. Only one observation for fipronil sulfone was identified as an outlier and excluded from the analysis (fig. 7). In addition, the one observation identified as an outlier for OLS regression was also excluded from the data to perform tobit regression. Like OLS regression, tobit regression also provides an estimate of the standard deviation of the residual error about the regression line. This estimate of the error for tobit regression is provided by the maximum likelihood scale parameter. However, the scale parameter is only an asymptotically unbiased estimate of the standard deviation of the error. An approximate method described by Aitkin (1981) was used to correct for this bias. When there are no censored data, the maximum likelihood method used to obtain parameter estimates for tobit regression provides coefficients identical to OLS regression but estimates of the standard error are still biased. The Aitkin method yields an estimate of the standard error for tobit regression identical to the standard error obtained by OLS regression when none of the observations are censored.



**Figure 7.** Relation of concentrations analyzed by the old and new methods and the tobit regression line obtained for fipronil sulfone showing outlier observation excluded from the regression.

## Regression Results

Coefficients for the regression of the new method concentration on the old method concentration for the four compounds obtained from the five different regression methods are given in table 4. For two of the compounds (fipronil and desulfinylfipronil), all estimates of the intercept from the five regression methods were less than zero, indicating a constant negative bias. (In laboratory method comparison studies, bias is typically separated into constant and proportional bias [Ludbrook, 1997; Magari, 2002]. Constant bias indicates that one method is consistently higher or lower than another method. Proportional bias indicates that the bias between methods is not constant but varies with concentration. One method may have one or both types of bias relative to another method.) For fipronil sulfone, the estimates of the intercept were always above zero, indicating a constant positive bias. For fipronil sulfide, the intercepts bracketed zero, indicating there is probably little or no constant bias between the two laboratory methods. All of the estimated regression slopes were less than one indicating that the new laboratory method had a proportional bias. That is, the bias between the methods was not constant but varied as the concentration increased. Had the coefficients from the OLS and reversed OLS regression bracketed one, it would have been an indication that the measurement error in the explanatory variable prevented detection of differences in the methods.

Coefficients of determination ( $R^2$ ) for the OLS and tobit regression equations are also shown in table 4. (They cannot be computed for the other three regression methods.) While the coefficient of determination cannot be used to select among regression methods (because the data used in the regressions are not the same), they can be used to infer a general sense of how good the relation is between the old and new laboratory methods for the four compounds. Accordingly, the relations for fipronil and fipronil sulfone are considered good (accounting for about 80 to 90 percent of the variation between the methods). The relation for desulfinylfipronil is considered fair (accounting for about 65 percent of

the variation between the methods). The relation for fipronil sulfide is considered poor (accounting for less than half the variation between the methods).

The estimated regression lines for the four compounds obtained from the five different regression methods are shown in figure 8. For fipronil and fipronil sulfone, all five of the regression lines are similar. For fipronil sulfide, all but the reverse OLS regression are similar. However, for desulfinylfipronil, there is a fair amount of difference in the regression lines. This is not surprising as the relation between the two laboratory methods for this compound had the largest variability of all the compounds.

**Table 4.** Coefficients obtained by several alternative regression methods for fipronil and three degradates.

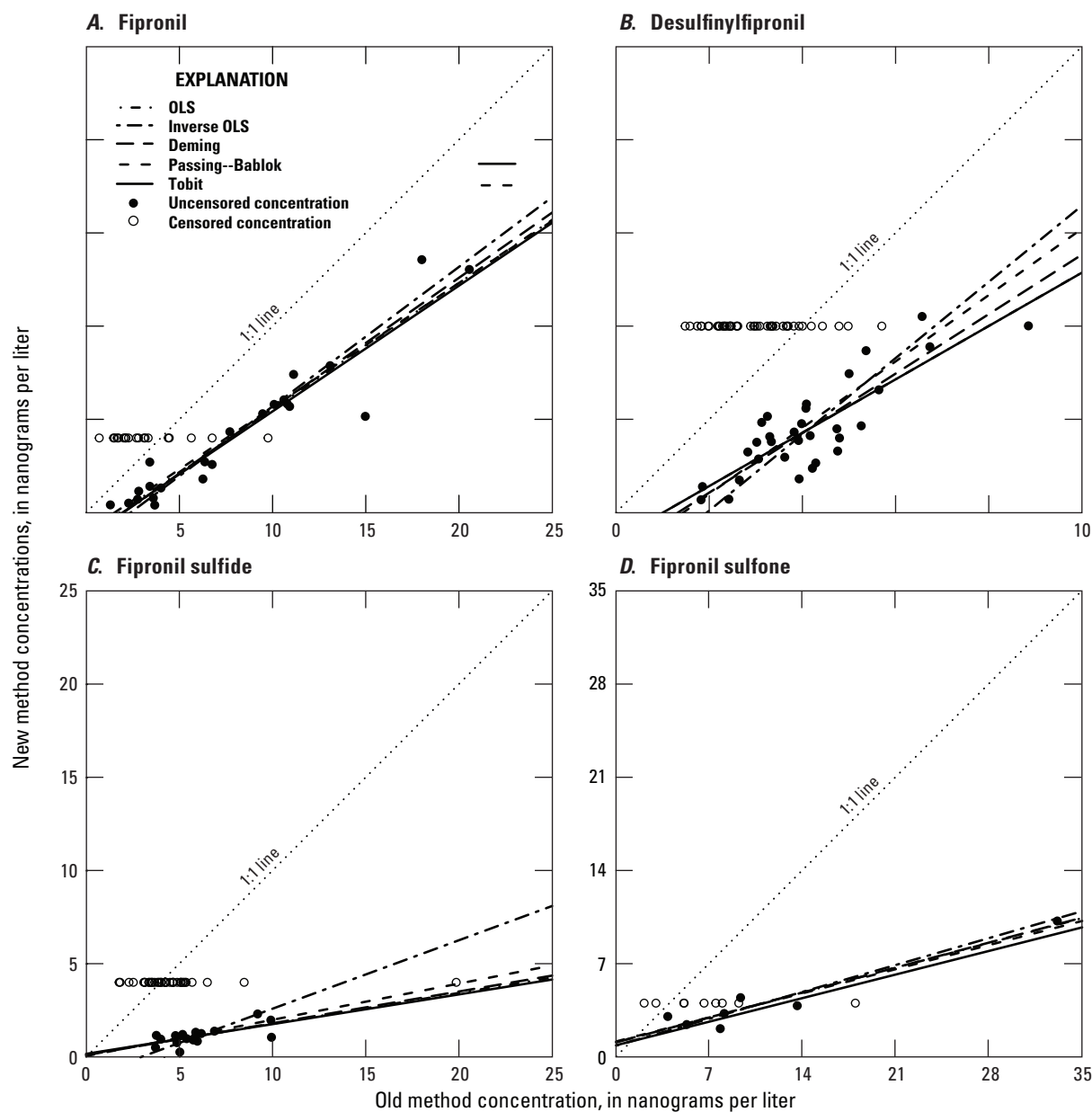
[OLS, ordinary least squares; NA, not applicable. The coefficient of determination for tobit regression was approximated using the method of Laitila (1993).]

Regression Method	Fipronil				Desulfinylfipronil			
	Number of samples used for regression	Intercept	Slope	Coefficient of determination ( $R^2$ )	Number of samples used for regression	Intercept	Slope	Coefficient of determination ( $R^2$ )
OLS	23	-1.2143	0.6765	0.90	31	-0.5788	0.5728	0.70
Reverse OLS	23	-1.7875	0.7482	NA	31	-1.5947	0.8179	NA
Deming	23	-1.3984	0.6995	NA	31	-0.8509	0.6385	NA
Passing-Bablok	24	-1.0191	0.6665	NA	31	-1.0278	0.7117	NA
Tobit	42	-1.3156	0.6742	0.88	78	-0.5780	0.5725	0.65

**Table 4.** Coefficients obtained by several alternative regression methods for fipronil and three degradates.  
degradates.—Continued

[OLS, ordinary least squares; NA, not applicable. The coefficient of determination for tobit regression was approximated using the method of Laitila (1993).]

Regression Method	Fipronil				Desulfinylfipronil			
	Number of samples used for regression	Intercept	Slope	Coefficient of determination ( $R^2$ )	Number of samples used for regression	Intercept	Slope	Coefficient of determination ( $R^2$ )
OLS	16	0.1298	0.1650	0.45	7	1.0697	0.2661	0.92
Reverse OLS	16	-1.0899	0.3673	NA	7	0.8122	0.2883	NA
Deming	16	0.0964	0.1705	NA	7	1.0526	0.2676	NA
Passing-Bablok	16	0.0451	0.1943	NA	7	1.1250	0.2585	NA
Tobit	54	0.1616	0.1595	0.38	16	0.8399	0.2529	0.81



**Figure 8.** Relation of concentrations analyzed by the old and new methods and the corresponding regression line obtained by five different regression methods for *A*, fipronil; *B*, desulfinylfipronil; *C*, fipronil sulfide; and *D*, fipronil sulfone.



## Application of the Regression Equations to NWIS Data

The regression equations obtained for the four compounds were applied to all of the data in NWIS with concentrations detected by the old method to obtain the “calibrated” old method concentrations. The regression equations could predict values smaller than any observed concentration in NWIS and had no constraint on predicting negative values. Consequently, any calibrated concentrations less than the 0.1 percentile of the observed concentrations in NWIS for a compound were set equal to the 0.1 percentile value. (For the observed concentrations, 99.9 percent are greater than the 0.1 percentile.) If a concentration of one of the four compounds available in NWIS was not detected by the old method (it had a “<” remark code), the reporting limit for the new method during the method comparison study (4 ng/L) was substituted as the calibrated value in lieu of using the regression equation. For three of the four compounds in the field study, when they were not detected by the old method, it was either not detected by the new method or had a detected concentration less than the reporting limit. Desulfinylfipronil had one of 64 samples in this category detected above the 4-ng/L reporting limit, but at a concentration of only 4.6 ng/L; the rest were either not detected or detected at concentrations below the reporting limit. Thus, substituting the reporting limit of the new method as the calibrated value when a compound was not detected by the old method was deemed reasonable.

Figure 9 shows the distribution of concentrations estimated by the five regression equations for the four compounds. All of the regression equations for the four compounds result in similarly distributed concentrations, with the exception of the reverse OLS regression for fipronil sulfide. Consequently, tobit regression was chosen to calibrate values detected by the old method to the new method for all four compounds because it allowed for the use of more of the available data than any of the other methods, and it provided an estimate of variance of the residual error about the regression line.

Fipronil concentrations from the NWIS data determined by the old laboratory method calibrated to the new laboratory method using tobit regression are shown in figure 10, along with concentrations determined by the new method. Some concentrations of fipronil in NWIS were outside the range of data used to develop the regression equation. Predicted concentrations for these observations have greater uncertainty than those that were in the range of the calibration data, as they are subject both to uncertainty in the regression fit as well as extrapolation error. These extrapolated values are highlighted in figure 10. With only one exception, the extrapolated values for fipronil fall within the range of concentrations determined by the new method. The percentage of detected calibrated concentrations that were extrapolated ranged from 1 percent (fipronil sulfide) to 13 percent (fipronil).

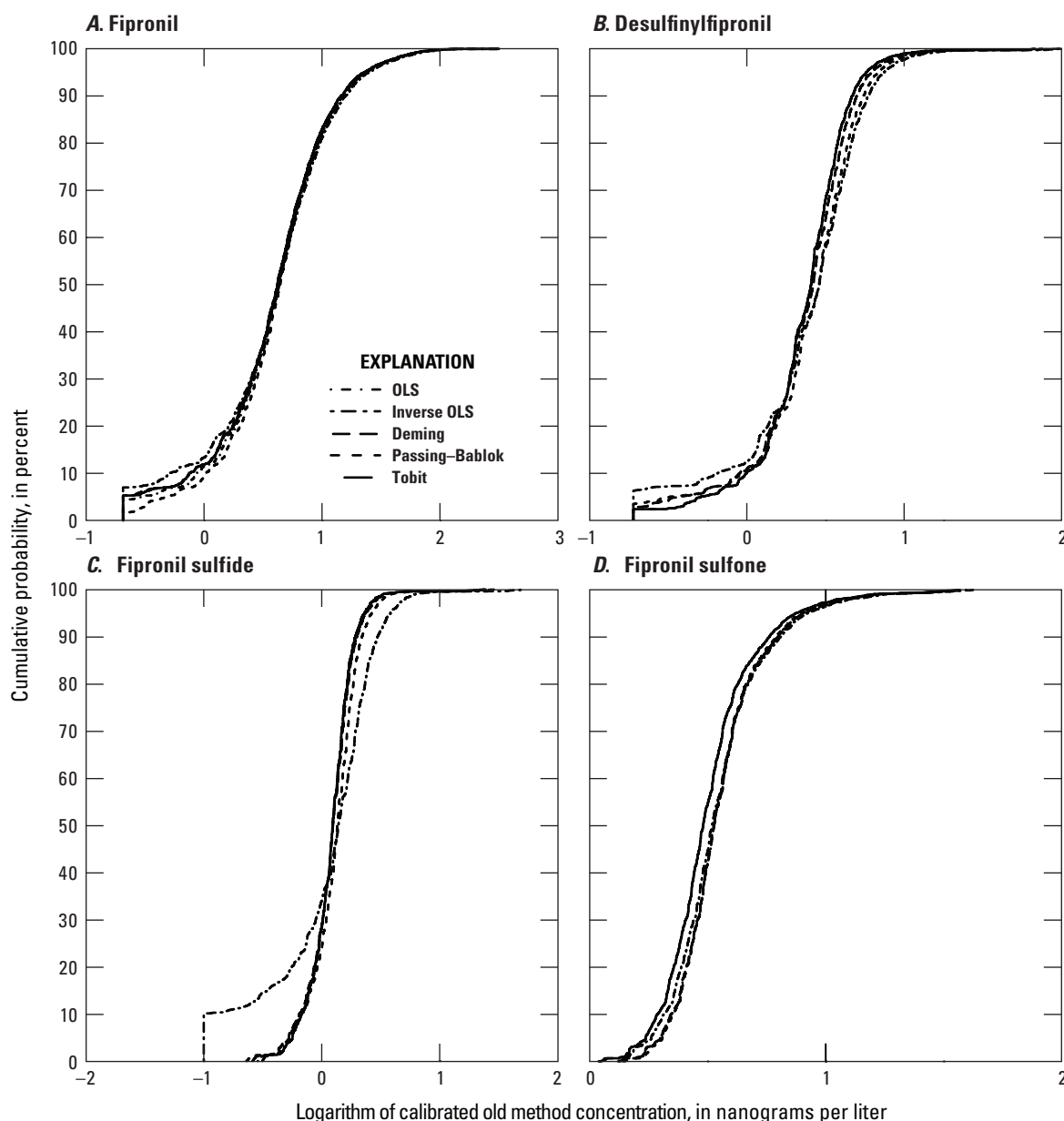
Values predicted by regression equations represent the mean value of the response variable expected for a given value of the explanatory variable. As such, these predicted values have much lower variance than the observed values of the response variable. The approach taken by Newell and others (1993) was used in this investigation to overcome this problem. They used the predicted value from the regression equation and added to it a residual value. Residual values were randomly chosen from a normal distribution, with zero mean and a variance equal to the variance of the predicted value plus the variance of the response variable. This quantity is equal to the variance of an individual predicted value (Neter and others, 1985, p. 80). For this study, the square of the standard error of prediction was used as the variance of the predicted value. The standard error provided by tobit regression was adjusted for degrees of freedom in a manner similar to Aitkin (1981). The square of the adjusted scale parameter from the tobit regression was used as the estimate of the variance of the response variable. The latter term is a constant while the former term varies with each possible value of the explanatory variable. This added residual value provides approximately the same amount of deviation about the regression line in the calibrated data as in the original data upon which the regression was derived, with an additional amount reflecting uncertainty in the regression. Examples of calibrated old method concentrations with random residuals added are shown in figure 11. Without the added random residuals, all of the data points shown in figure 11 would plot on the regression line. The calibrated concentrations of fipronil determined by the old laboratory method from NWIS (shown in figure 10) with added random residuals are shown in figure 12.

The fipronil data shown in figure 10 and figure 12 include all data from many sampling stations available in NWIS used for this investigation. The number of stations sampled and how often they were sampled has varied through time. The number of stations sampled before and after implementation of the new method in late 2012 and how frequently each was sampled are not the same. Consequently, figure 10 and figure 12 cannot be used to draw conclusions about trends in fipronil or how the calibrated data reflect trends through time. A better indication of how the calibrated data reflect this for individual sampling stations can be seen in the four examples shown in figure 13. The pronounced difference in concentrations of the four compounds obtained by the two laboratory methods is clearly seen in these examples. However, much, if not all, of the difference is removed after the concentrations determined by the old laboratory method are adjusted by the calibration approach.

The concentrations in samples for the four compounds determined by the two methods retrieved from NWIS, the calibrated values, and the calibrated values with added residual error are available in Crawford and Baker (2017). In addition to these values, 95-percent prediction intervals for the calibrated values are also provided, as well as the statistical values needed to compute different prediction intervals. A prediction interval provides the range within which the true

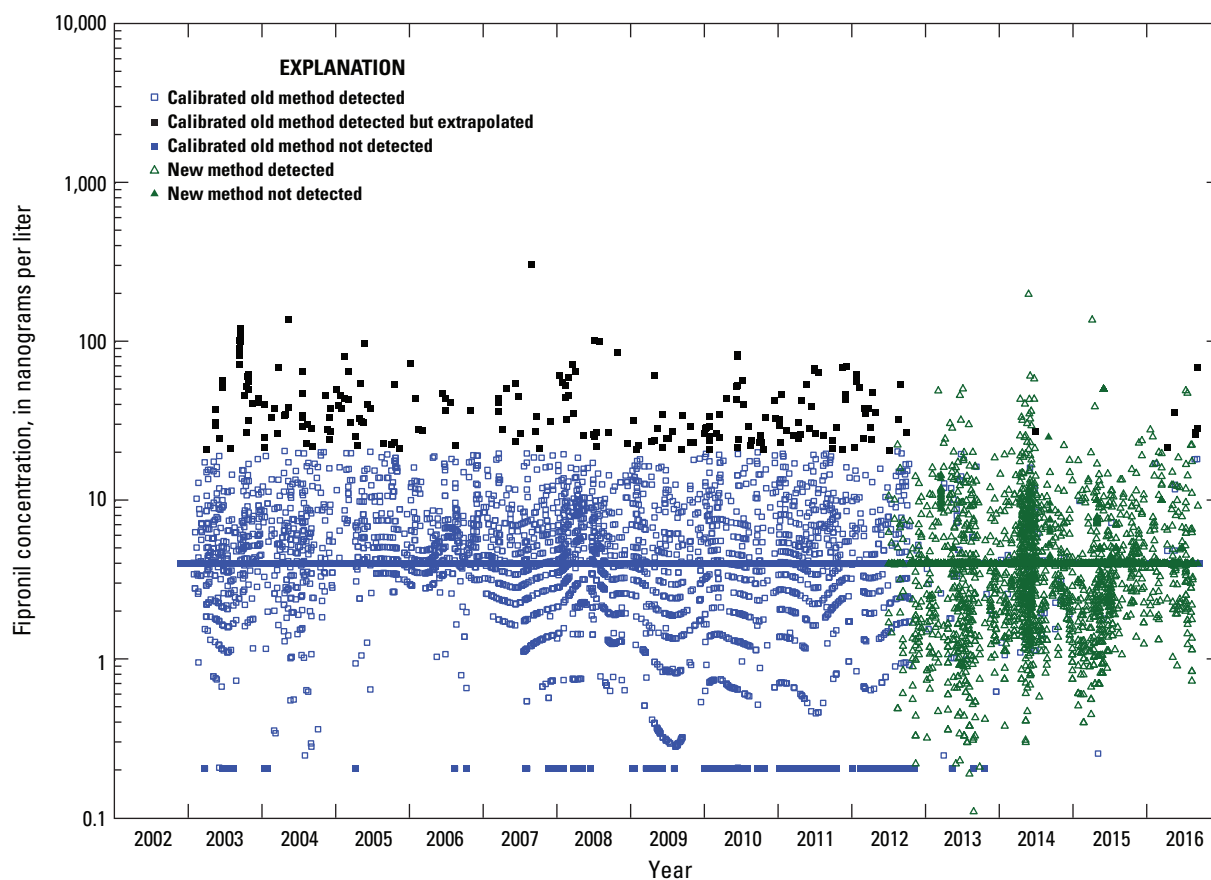
value of the response variable will lie, given the assumption that the regression equation truly describes the relation between the response and explanatory variables. It reflects both the uncertainty in the regression coefficients and variation in the response variable. However, these approximate intervals likely overstate the interval pertinent to the true concentration as the interval accounts for measurement error in the response variable. Exact prediction intervals for tobit regression are not available. Prediction intervals were approximated using normal theory and the t-distribution. That is, methods for OLS regression were used, which are only approximate when applied to tobit regression. The standard error of prediction

and scale parameters (adjusted as previously described) were used in the computation of the prediction intervals. This provides prediction intervals for tobit regression identical to those from OLS regression when there are no censored observations in the data. Prediction intervals computed in this manner for the tobit regression equations obtained for the four compounds are shown in figure 14. Note that prediction intervals for extrapolated values are especially approximate because the prediction intervals do not account for extrapolation uncertainty. That is, the prediction intervals for extrapolation values assume that the relation between the two methods is still linear in that region. We do not know this, however.

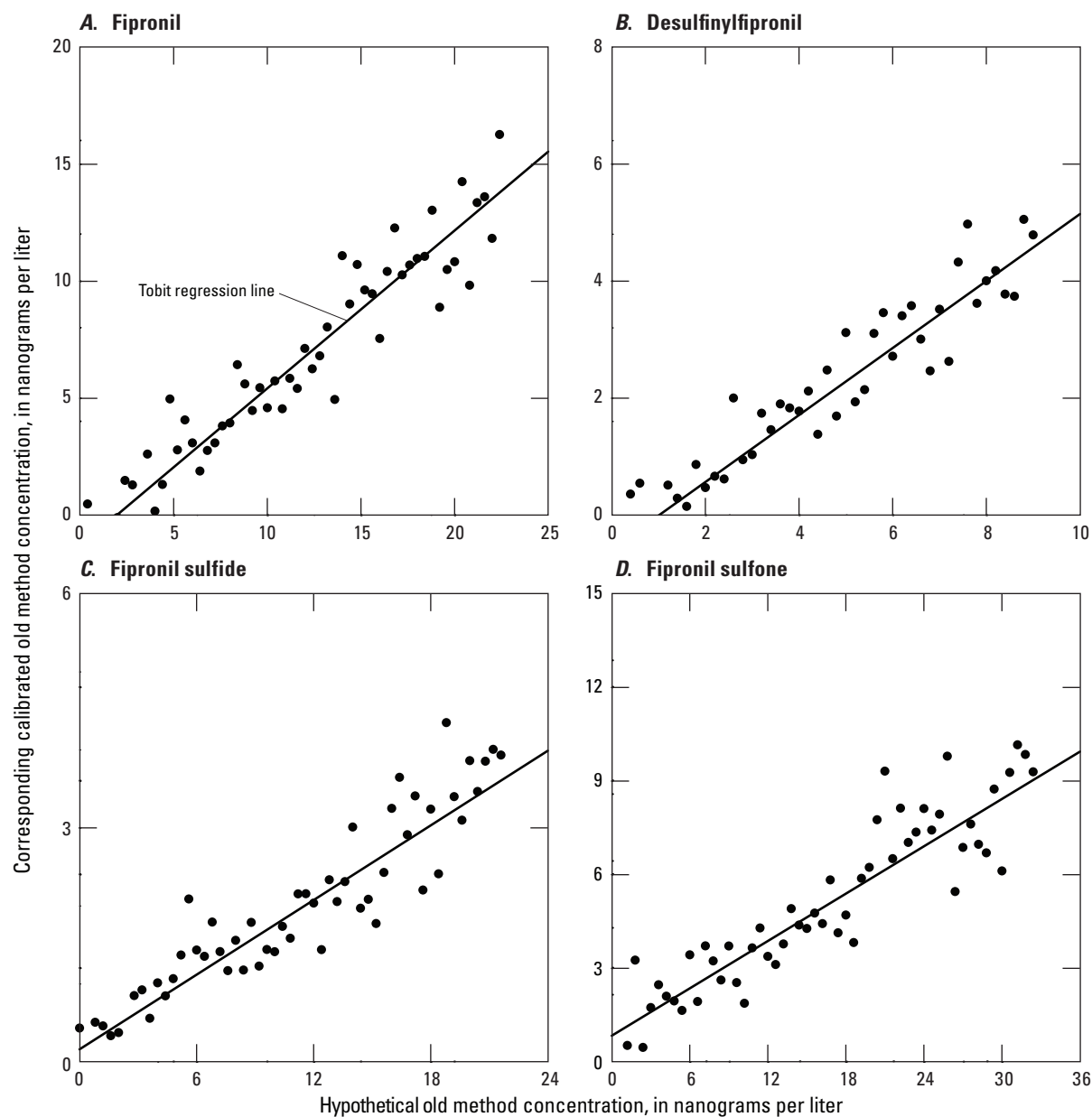


**Figure 9.** Cumulative probability density function plots for concentrations from the old method calibrated to the new method using coefficients obtained via the five regression methods for A, fipronil; B, desulfinylfipronil; C, fipronil sulfide; and D, fipronil sulfone.

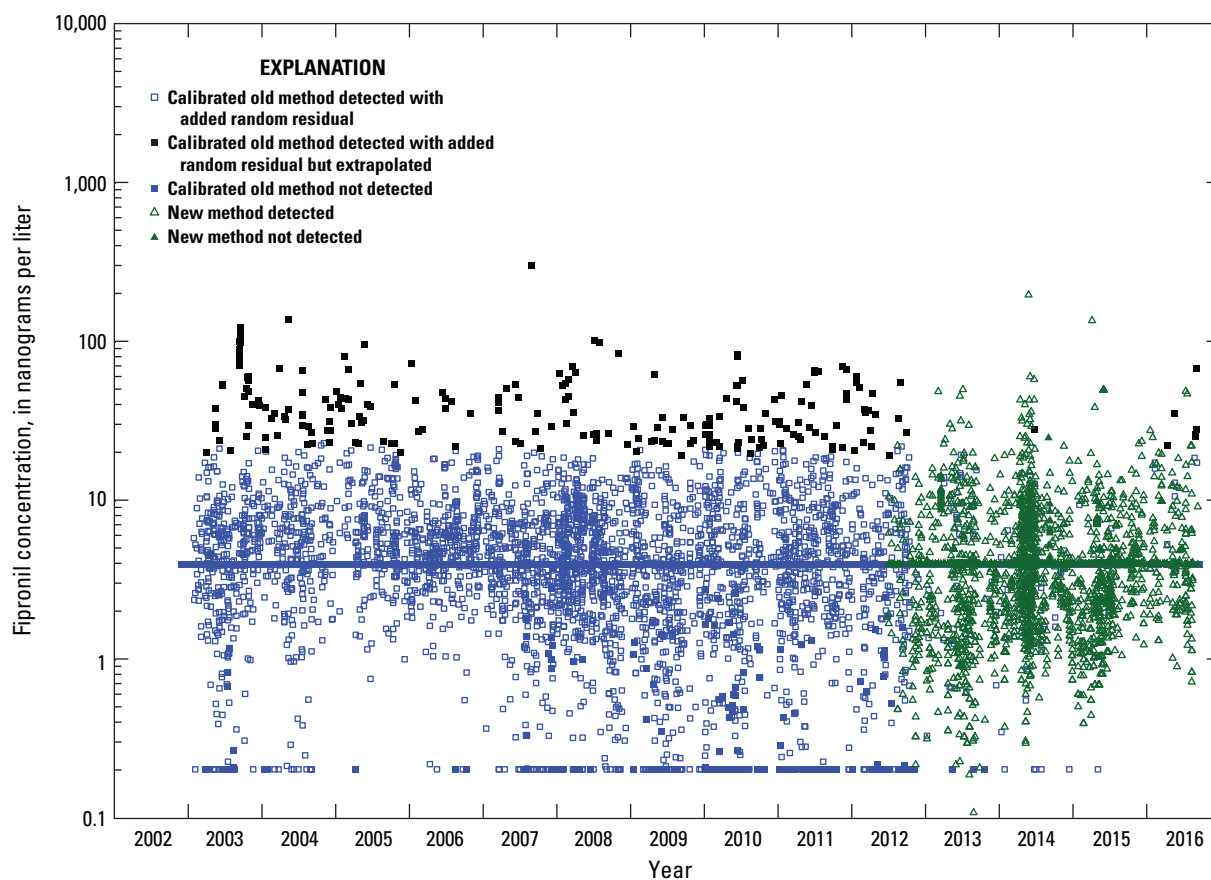




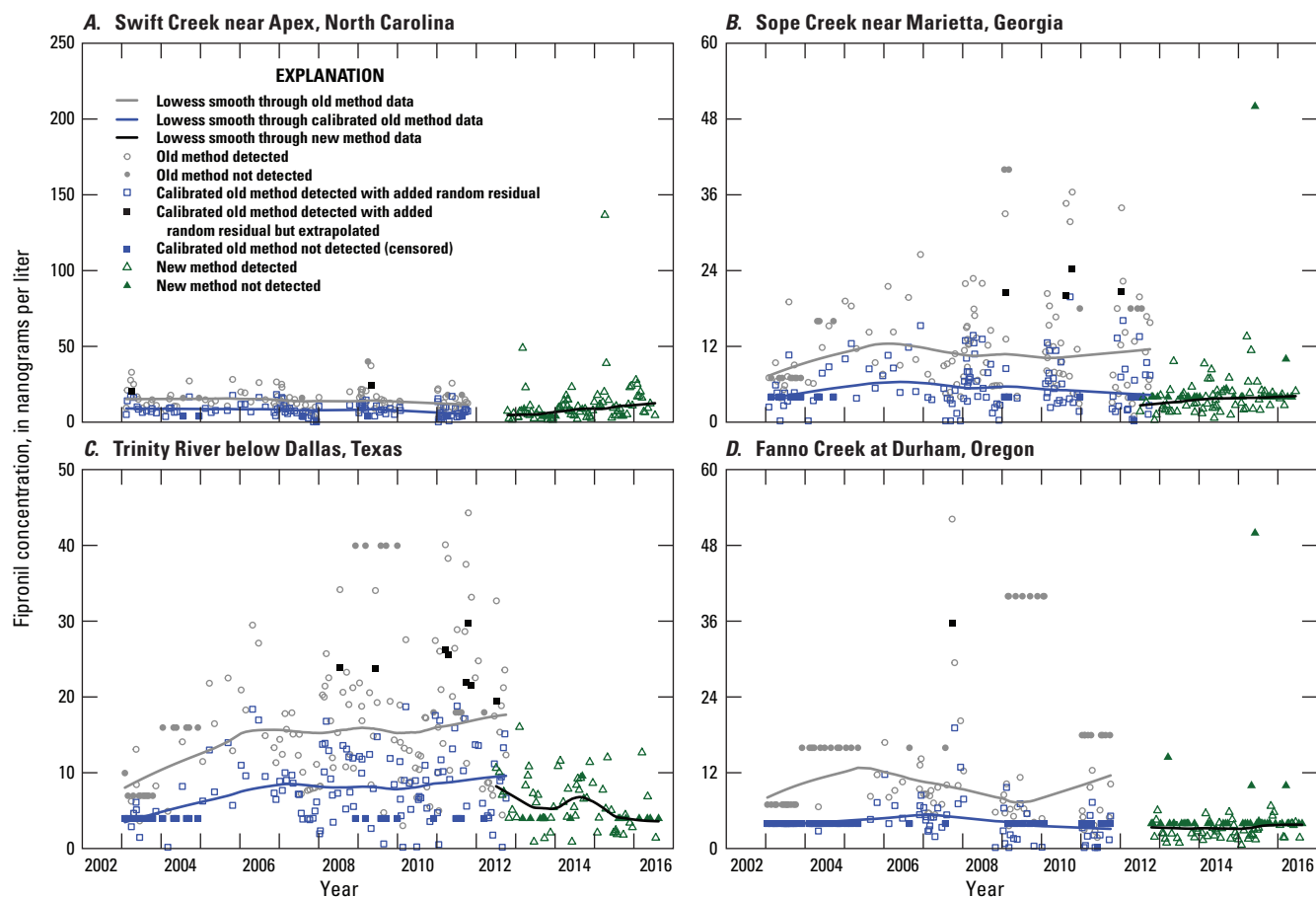
**Figure 10.** Relation of fipronil concentrations from the National Water Information System, as determined by the old method but calibrated to the new method using coefficients obtained via tobit regression and those determined by the new method, to time.



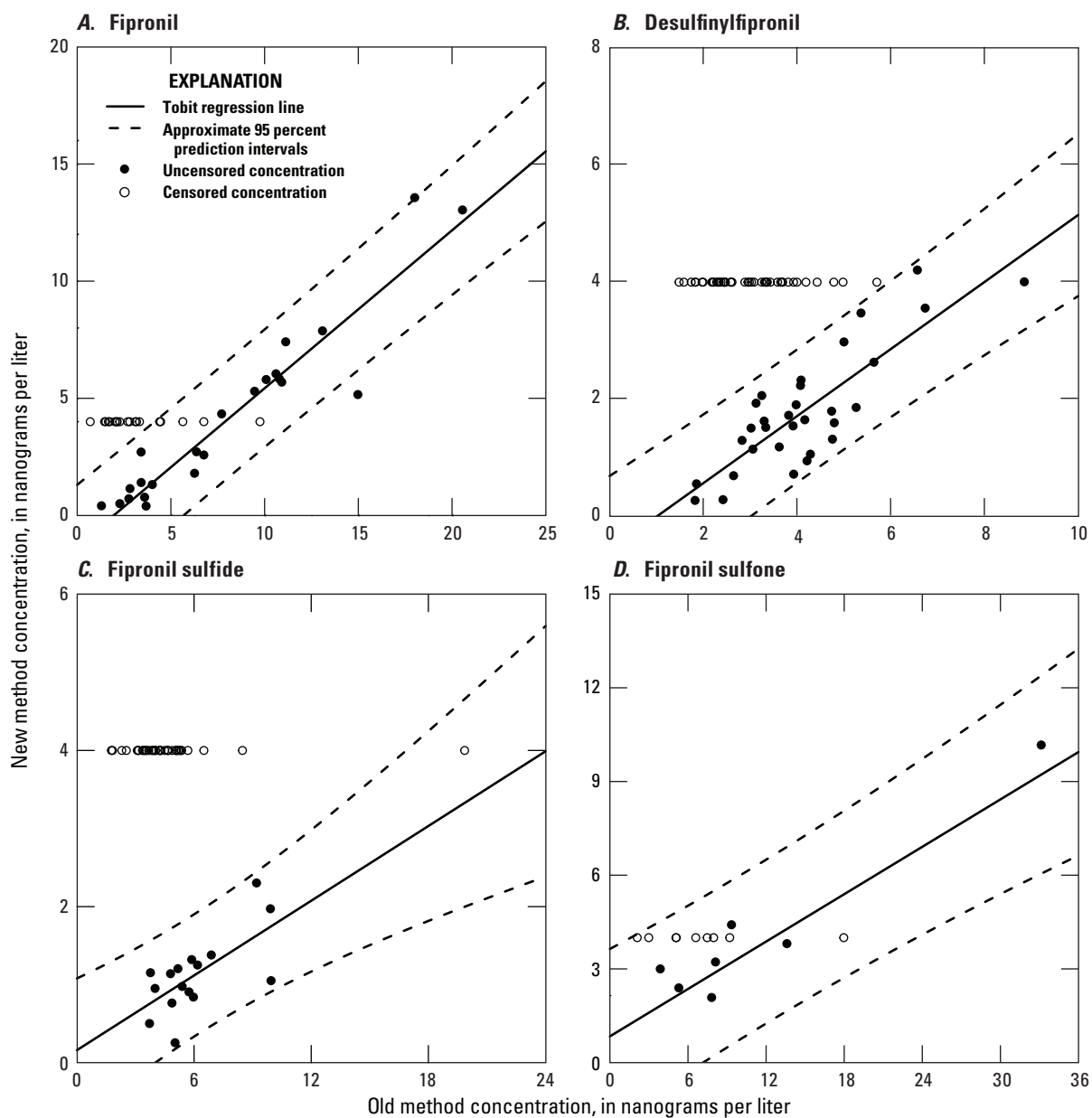
**Figure 11.** Example relation of fipronil concentrations, as determined by the old method but calibrated to the new method using coefficients obtained via tobit regression with random residuals added.



**Figure 12.** Relation of fipronil concentrations from the National Water Information System, as determined by the old method but calibrated to the new method using coefficients obtained via tobit regression with random residuals added and those determined by the new method, to time.



**Figure 13.** Relation of fipronil concentrations from the National Water Information System, as determined by the old method but calibrated to the new method using coefficients obtained via tobit regression with random noise added and those determined by the new method, to time for *A*, Swift Creek near Apex, N.C.; *B*, Sope Creek near Marietta, Ga.; *C*, Trinity River below Dallas, Tex.; and *D*, Fanno Creek at Durham, Oreg.



**Figure 14.** Relation of concentrations analyzed by the old and new methods, the line fit by tobit regression, and the approximate 95-percent prediction interval around the regression line for *A*, fipronil; *B*, desulfinylfipronil; *C*, fipronil sulfide; and *D*, fipronil sulfone.

## Limitations

The calibration approach used in this study has a number of important limitations. Several of these are related specifically to aspects of regression analysis. One major limitation is the previously described problem of the suitability of the available data with the alternative regression methods applicable to methods comparison. Another limitation is that the sample sizes available for doing regression analysis to develop the relation between the old and new methods were small, especially for fipronil sulfone. Linnet (1999) states that the 40–100 samples typically used for method comparison studies may be inadequate. The number of samples available for this investigation is at or below the low end of the range Linnet questions as being sufficient. There is also the limitation that the data available from the method comparison field study did not cover the entire range of concentrations observed in the data retrieved from NWIS, necessitating extrapolation of some values. Further, the data used to develop the regression equations were from samples collected at a number of different streams across the country. The single regression equation used to calibrate the old method to the new method for each of the four compounds may not adequately reflect conditions in individual streams.

As previously described, two outlier values were excluded from the regression analysis. This was done because those values would have severely biased the regression coefficients to an unknown degree. Observations that appear to be outliers may, in fact, be providing important information about the relation. The two excluded outliers contained the highest concentrations of fipronil and fipronil sulfone measured during the method comparison study. If those measurements were correct and not outliers due to measurement or some other error, they would provide evidence that the relation between the old and new methods for those two compounds was not linear. If the relations are not linear, extrapolation error for fipronil and fipronil sulfone could be substantial.

Reporting levels for the NWIS data determined by the old method varied through time and were sometimes different from the reporting levels in effect during the field study. For fipronil, 12 percent of the reporting limits in the NWIS data used were greater than the one in effect during the field study (18 ng/L), although only 7 percent of these were greater than 20 ng/L. For desulfinylfipronil, the percentage of reporting limits in NWIS was even greater as 67 percent were greater than the 12 ng/L reporting limit during the field study. However, only 4 percent of these were above a reporting limit of 13 ng/L. Only a few reporting limits in NWIS exceeded that in effect during the field study for fipronil sulfide (12 ng/L) and fipronil sulfone (24 ng/L). Calibrated values for nondetected concentrations of these four compounds were set equal to the reporting limit of the new method during the field study for that compound. As previously described in the section “Application of the Regression Equations to NWIS Data,” when a compound was not detected by the old method during the field study, in almost all cases it was either not detected by

the new method or detected by the new method at a concentration less than the reporting limit. It is not known what effect the raised reporting limits have on the pattern of compounds not being detected in the new method when not detected by the old method seen during the field study or how that affects the substitution approach used for this circumstance in this investigation.

There are also several limitations associated with the data available for correcting concentrations for recovery used for this investigation. Only laboratory reagent spike data were available for correcting the data retrieved from NWIS for recovery. Martin and others (2009) have documented differences in recovery of laboratory reagent and field matrix-spike data. For the period 2002–2005, they found that for three of the four compounds (all but desulfinylfipronil), recoveries in the laboratory reagent spikes tended to be lower than in field matrix spikes (the median difference in recovery ranged from 6 to 9 percent). Recoveries of desulfinylfipronil in laboratory reagent spikes tended to be higher than in the field matrix spikes (the median difference in recovery was 4 percent). As was seen in this investigation, variability in recovery for both laboratory reagent and field matrix spikes was quite high. It is thus not known if the differences in recovery seen by Martin and others (2009) were pronounced enough to affect the results of this investigation. Further, while the environmental samples from the field study had associated field matrix spikes so that environmental samples could be individually corrected for recovery, the data from NWIS could only be corrected for recovery using a smoothing approach. This procedure does not account for all the variability seen in recovery and thus likely adds additional uncertainty to the calibrated concentrations. Finally, it is not known how the anomalous schedule 2033 recovery during the time of the field study (fig. 2) affects the relation between the two methods and what effect it may have on how well the relation holds through time.

One final limitation pertains to the use and interpretation of the calibrated values. Calibrated values, both with and without random residual error added, are provided in the data release (Crawford and Baker, 2017). The calibrated values with the added random residual error maintain the variance seen in the measured data. However, these values should be used in aggregate rather than individually. For example, the calibrated values with the added random residual error should be used for examining the data for temporal or spatial patterns. The best estimate of an individual concentration determined by the old method adjusted to reflect differences in the laboratory methods is the calibrated value without the added random residual. These latter values should be used for comparing individual samples to water-quality or aquatic health benchmark values; however, they should also be interpreted within the context of the prediction interval.

## Summary

In October 2012, the U.S. Geological Survey (USGS) began measuring the concentration of the pesticide fipronil and three of its degradates (desulfinylfipronil, fipronil sulfide, and fipronil sulfone) by a new laboratory method using direct aqueous-injection liquid chromatography tandem mass spectrometry (DAI LC–MS/MS). This method replaced the previous method in use since 2002 that used gas chromatography/mass spectrometry (GC/MS). Both of these methods provide results for multiple pesticides. However, the performance of the two methods is not comparable for all chemical compounds. For fipronil and the three degradates, concentrations produced by the DAI LC–MS/MS method are substantially lower than the GC/MS method.

A methods comparison field study was done in 2012 to document differences in the performance of the methods. Stream-water samples were collected at 48 sites across the United States representing agricultural and urban streams as well as major rivers. Most sites were sampled on three dates. For each site visit an environmental sample and a field matrix spike were collected and analyzed by each method. Spiking typically increased the concentration of fipronil and its degradates by approximately 0.1 µg/L for the GC/MS method and by 250 ng/L (0.25 µg/L) for the DAI LC–MS/MS method.

The field matrix spikes were used to correct the environmental concentrations for recovery. Recoveries for samples analyzed by the GC/MS method were generally greater than 100 percent, with median recoveries ranging from 110 to 144 percent for the four compounds. Fipronil had the highest recovery for the old method, which was typically about 20 percent higher than the three degradates. In contrast, recoveries in samples analyzed by the DAI LC–MS/MS method were similar and generally less than 100 percent, with median recoveries ranging 85 to 91 percent for the four compounds.

A method was developed to correct for differences in concentrations obtained by the two laboratory methods. The method develops a relation between paired water samples obtained by one laboratory method to those obtained by another. This relation is then used to calibrate data obtained by the older method in order to remove any biases attributable to differences in the methods. Regression analysis was used for developing the relation between the methods. Because of complicating factors in the available data (samples with nondetected concentrations, measurement uncertainty in both laboratory methods, and outlier values), several alternative regression approaches were evaluated for developing the relations. No single regression method was available that addressed all the complications in the available data previously described. Ordinary least squares regression, reverse ordinary least squares regression, Deming regression, Passing-Bablok regression, and tobit regression were evaluated. Results obtained from the various methods were generally similar. Tobit regression was chosen to calibrate concentrations determined by the GC/MS method to those determined by the DAI LC–MS/MS method, as it allowed for the use of more of the available data than any

of the other methods and it provided an estimate of variance of the residual error about the regression line.

The coefficients of the equations obtained from the tobit regressions were used to calibrate over 16,600 observations of fipronil and the three degradates determined by the GC/MS method retrieved from the USGS National Water Information System (NWIS). The calibrated values were then compared to over 7,800 observations of fipronil, and the three degradates were determined by the DAI LC–MS/MS method also retrieved from NWIS. The original and calibrated values from the GC/MS method, along with measures of uncertainty in the calibrated values and the original values from the DAI LC–MS/MS method, are provided in an accompanying data release (Crawford and Baker, 2017).

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