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VENTURA COUNTY AGRICULTURAL IRRIGATED LANDS GROUP (VCAILG)

2022 Groundwater Management Practice Evaluation Report

SUBMITTED TO:

LOS ANGELES REGIONAL WATER QUALITY CONTROL BOARD

SUBMITTED BY:

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science | policy | solutions

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INTRODUCTION AND PURPOSE

On April 8, 2021, the Los Angeles Regional Water Quality Control Board adopted the Conditional Waiver (Waiver) of Waste Discharge Requirements for Discharges from Irrigated Lands within the Los Angeles Region (Order No. R4-2021-0045) as a one-year extension of the 2016 Conditional Waiver (Order No. R4-2016-0143). Subsequently, in April 2022, the Waiver was extended through December 31, 2022, via Order No. R4-2021-0045-A01. The terms of the 2016 Conditional Waiver and its extensions include requirements related to tracking and management of nitrate in groundwater. In brief, the requirements consist of the following elements:

- Tracking of groundwater quality beneath irrigated agricultural lands
- Submittal of a "Groundwater Quality Trend Monitoring Plan" (due October 14, 2016)
- Inclusion of the results of the above plan in the discharger's annual monitoring reports (annually, beginning December 15, 2017)
- Assessment of the effectiveness of management practices in protecting groundwater quality
- Submittal of a "Groundwater Management Practice Evaluation Plan" (MPEP; due April 14, 2018)
- Submittal of "Groundwater Management Practice Evaluation Reports" (to be submitted with the discharger's annual monitoring reports beginning December 15, 2020)

As described in Section 1.b.ii of Appendix 3 of the Waiver, the MPEP is intended to focus on nitrate concentrations in groundwater, related to protection of drinking water:

> *"ii. In order to assess the effectiveness of management practices in protecting groundwater quality, Discharger Groups shall submit a work plan to monitor areas where irrigated agricultural lands have the potential to impact groundwater basins, exceedances of nitrate have been confirmed, and groundwater is a significant drinking water source, to determine if management practices implemented on the land surface are protective of underlying groundwater quality. The same monitoring wells in 1.b.i and previous studies can be used where available and appropriate for the monitoring objectives."* (Waiver, Appendix 3 at Section 1.b.ii)

After a series of steps and meetings with Regional Board staff, a revised MPEP was submitted to the Regional Board on May 17, 2019, that entailed a pilot study in the Fillmore Subbasin.[1] The project approach involved a sequence of three steps:

1. Presence of sewage markers (pharmaceutical and personal care products (PPCPs)) and/or other markers as appropriate) and dual stable isotope signatures of nitrate in groundwater samples from existing wells will be used to identify likely sources of the nitrate.

[1] The Fillmore groundwater basin is considered a subbasin of the Santa Clara River Valley Basin.

2. If fertilizer is implicated as a source of nitrate in wells, existing BMP survey data will be utilized to search for associations between agricultural practices (such as crop types, prevalence of general practices and/or adoption rates of pertinent specific BMPs) and presence of fertilizer-related nitrate in wells. If appropriate, survey data may be aggregated and evaluated for subareas of irrigated land overlying the basin.
3. Results of Step b will be used to adjust outreach and education if appropriate, and potentially to add additional questions to future BMP surveys.

The revised MPEP including the three-step project approach above was conditionally accepted by the Regional Board on October 4, 2019.[2] The requirement for annual implementation of the MPEP was carried forward in two extensions of the Waiver that have occurred to date (Order No. R4-2021-0045, Order No. R4-2021-0045-A01).

This report serves as the third Groundwater Management Practice Evaluation Report, due December 15, 2022. Background information about the Fillmore Subbasin and the rationales that supported development of the project approach are available in the MPEP. An excerpt from the MPEP that describes the use of dual stable isotope signatures of nitrate to evaluate nitrate sources in groundwater is provided as Attachment 1. Because the PPCP lab results from the 2020 effort were unreliable and practically unusable, sampling for PPCPs was omitted from the approach starting in 2021.[3]

GROUNDWATER QUALITY SAMPLING

METHODS

VCAILG obtained permission to sample thirteen wells for this project, which were identified for sample labeling and reporting purposes as Wells A-M.[4] In 2022, sampling took place between May 9 and August 8. Well J was not sampled in 2022 because it was non-operational. Two field replicates and one field blank were generated for each well for each of the following two analyses:

- Nitrate-N
- Stable Isotopes of Nitrate ($\partial^{18}O$ and $\partial^{15}N$)

Wells were sampled during irrigation cycles; all pumps had been on for more than one hour before water samples were taken. Samples were chilled (using ice and refrigeration) from time of sampling through delivery to the analytical laboratories.

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[2] The single condition in the acceptance letter was related to obtaining access agreements for wells sampled by VCAILG as opposed those sampled by potential sampling partners. No wells were sampled by VCAILG during the project that were not owned by VCAILG members. Consequently, members' Waiver participation agreements (which allow access for any VCAILG monitoring needs) served as access agreements.
[3] PPCPs were frequently detected in field blanks and laboratory blanks in 2020. In addition, different sets of PPCP compounds were sometimes reported by the lab for both field replicates for a single well, further complicating interpretation of results. VCAILG submitted a letter to the Regional Board on April 9, 2021, indicating their intention to drop PPCPs from the 2021 protocol, with a detailed justification, that provided an opportunity for Regional Board staff to provide feedback before field work preparation needed to proceed in May 2021. No response was received from the Regional Board, and PPCPs were not included in the 2021 and 2022 protocols.
[4] Permission to sample was contingent on anonymity. Consequently, State Well Numbers, parcel numbers, screen depths, and other information from public datasets or VCAILG reports or project planning documents that could be used to determine well ownership or location is not provided in this report.

The laboratory methods used to analyze the stable isotopes of nitrate are described in detail in Attachment 2. In brief, the method involves using ion exchange techniques to convert dissolved nitrate to crystalline silver nitrate, which is then analyzed using an elemental analyzer interfaced with an isotope ratio mass spectrometer. Nitrate-N concentrations were analyzed using EPA Method 4500.

RESULTS

The dual isotope signatures and nitrate-N concentrations for the sampled wells are illustrated in Figure 1. The $\partial^{18}O$ signatures ranged 5.15 – 13.10 ‰. The $\partial^{15}N$ signatures occupied a wider range (6.50 – 24.20 ‰). *None of the wells had dual isotope signatures indicating either nitrate-based or ammonia-based fertilizer as a source of nitrate in groundwater*. The isotope results indicated that animal waste (either manure or septic waste) was potentially the only source of nitrate in seven of the wells. The other five wells had isotope signatures well within the signature space for soil N and/or manure and septic waste. In cases where more than one nitrate source is possible, none of the potential sources can be ruled out.

The isotope data and the locations of the sampled wells supported their continued assignment to one of three "zones" (Zones A, B, C), first identified in the 2020 MPEP report,[5] which are described in Table 1 and illustrated in Figure 2. Together, Zones A and B comprise the Fillmore Subbasin. Zone C is outside the current boundary of the Fillmore Subbasin, and is an area where groundwater rises as it exits the Piru Subbasin, supporting a gaining reach in the Santa Clara River. The dual isotope signatures of individual wells are illustrated by zones in Figure 3. Specific isotope signatures and nitrate-N concentrations for individual wells are listed in Table 2.

[5] Larry Walker Associates. 2020. Ventura County Agricultural Irrigated Lands Group (VCAILG) Groundwater Management Practice Evaluation Report. Submitted to Los Angeles Regional Water Quality Control Board. December 15, 2020.

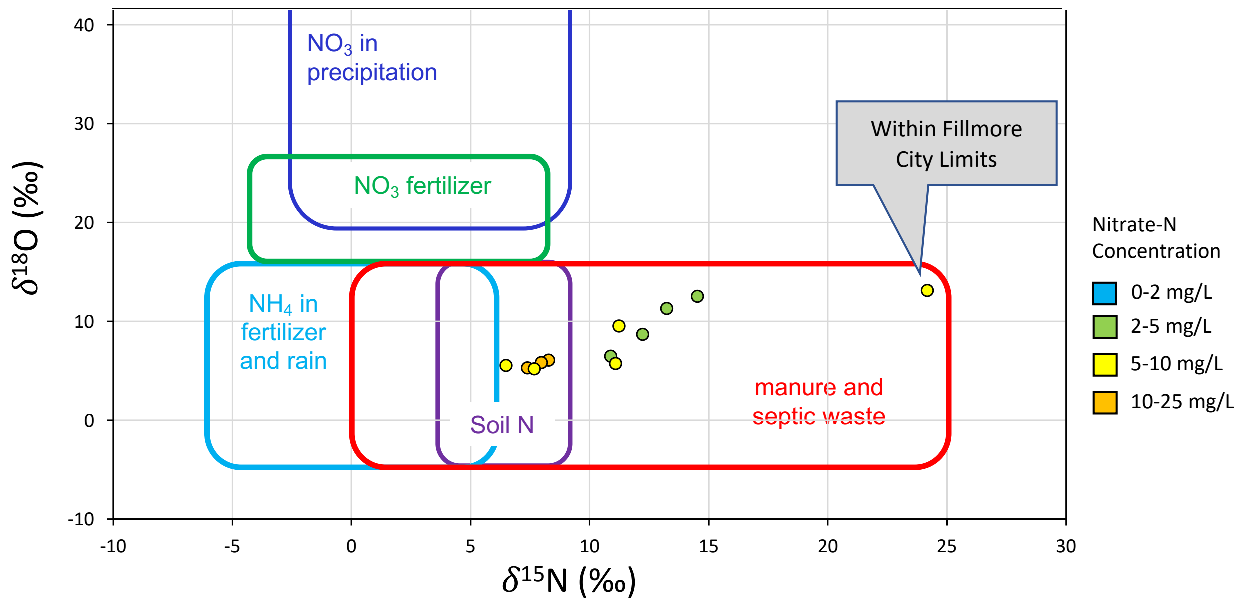

Figure 1. Dual Isotope Signatures and Nitrate-N Concentrations of Sampled Wells

Table 1. Description of Zones and Potential Nitrate Sources Based on Dual Isotope Signatures

Zone and Description		Potential Nitrate Sources Indicated by Dual Isotope Signatures		Number of Wells Sampled in the Zone
		Soil N	Animal Waste (Manure or Septic Waste)	
A	Within the Fillmore Subbasin boundary, area North of Hwy 126 and West of the Sespe Creek Channel	✖	✖	5
B	Within the Fillmore Subbasin boundary, East of the Sespe Creek Channel and/or South of 126. Includes the Pole Creek Fan underlying the City of Fillmore		✖	4
C	Area excluded from the Fillmore Subbasin after the 2018 DWR Basin Boundary Modification, characterized by rising groundwater exiting the Piru Subbasin		✖	3

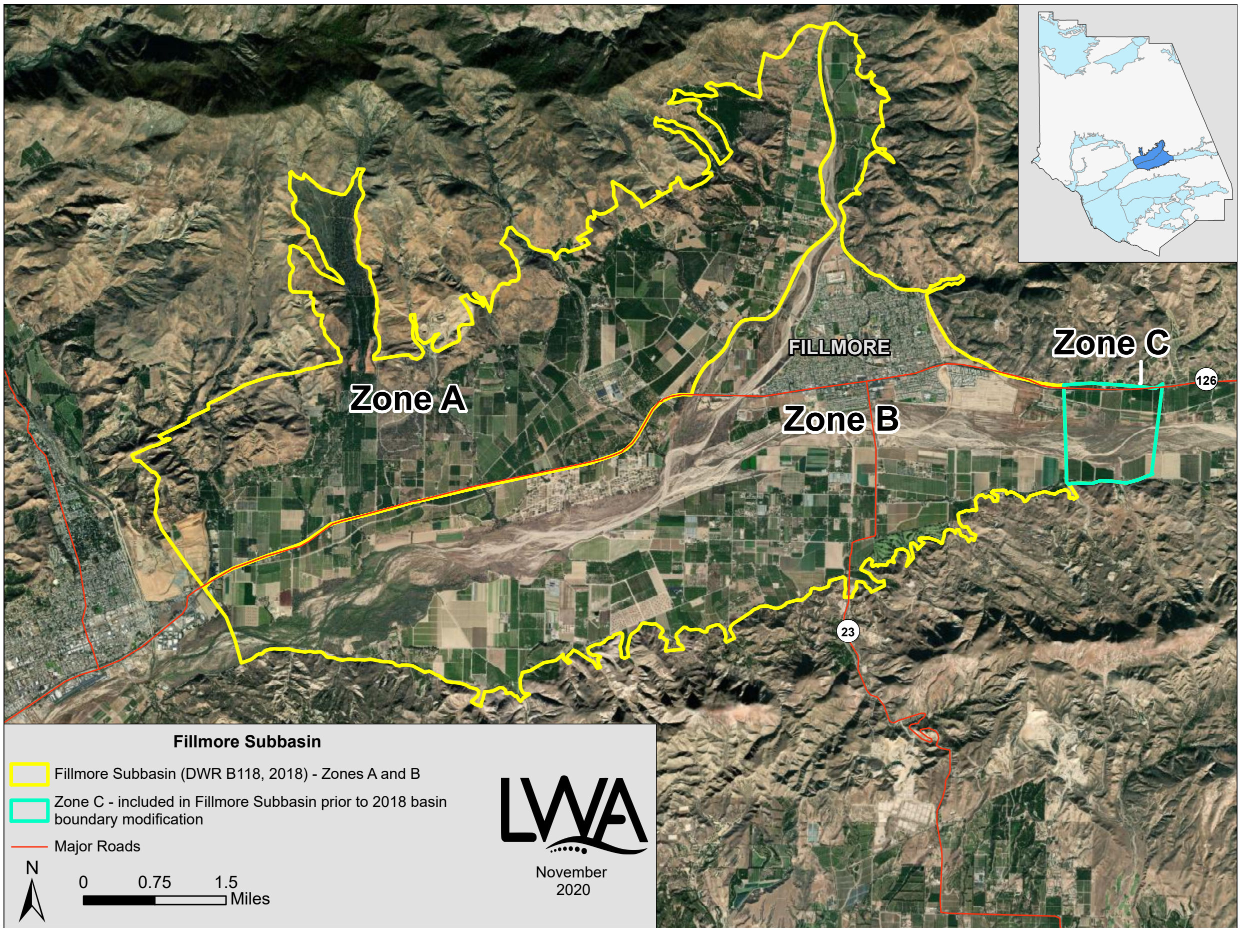

Figure 2. Zones Identified Based on Dual Isotope Signatures of Groundwater Nitrate. Zone C is outside the current DWR boundaries of the Fillmore Subbasin.

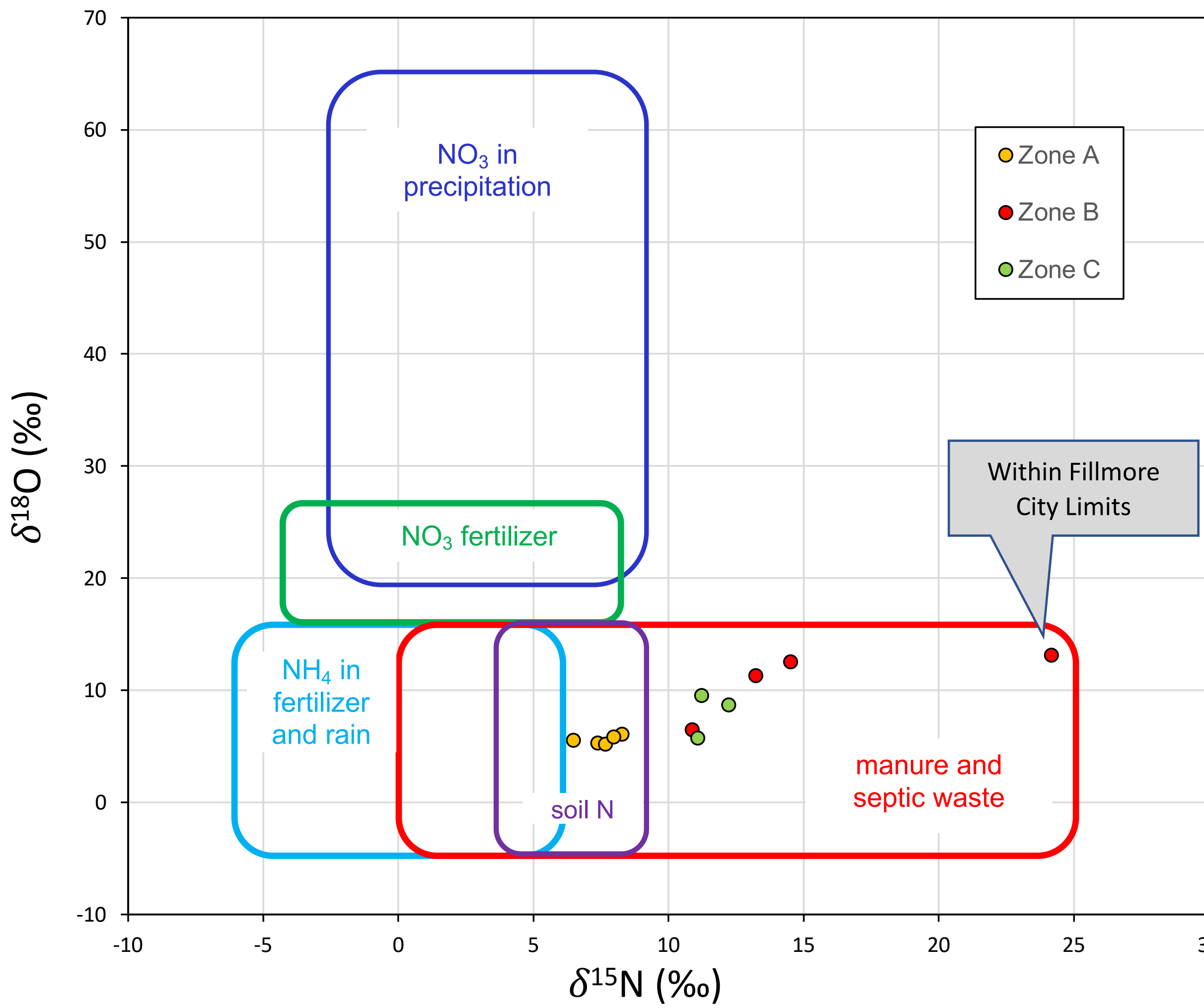

Figure 3. Dual Isotope Signatures for Individual Wells by Zone

Table 2. Results of Stable Isotope and Nitrate Analyses

Zone	Well ID	Sample Date	Stable Isotope Signature of Nitrate (‰) [a]		Isotope Based Source Categories	Nitrate-N (mg/L)
			$\partial^{15}N$	$\partial^{18}O$		
A	Well F	5/9/22	8.30	6.05	Soil N or Manure and Septic Waste	12.00
	Well H	8/2/22	6.50	5.50	Soil N or Manure and Septic Waste	8.75
	Well I	8/2/22	7.40	5.25	Soil N or Manure and Septic Waste	16.20
	Well K	8/4/22	7.70	5.15	Soil N or Manure and Septic Waste	9.55
	Well L	8/2/22	8.00	5.80	Soil N or Manure and Septic Waste	16.80
B	Well A	5/9/22	10.90	6.45	Manure and Septic Waste	2.35
	Well B	5/9/22	14.55	12.50	Manure and Septic Waste	2.64
	Well C	5/17/22	13.25	11.25	Manure and Septic Waste	2.48
	Well D	5/9/22	24.20	13.10	Manure and Septic Waste	6.95
C	Well E	5/11/22	12.25	8.65	Manure and Septic Waste	2.35
	Well G	5/10/21	11.25	9.50	Manure and Septic Waste	6.77
	Well M	8/8/22	11.10	5.70	Manure and Septic Waste	5.50

[a] Values are averages for two field replicates.

GROUNDWATER NITRATE TRENDS

Nitrate concentrations (rolling 3-year averages) and temporal nitrate trends are reported annually for 22 wells in the Fillmore Subbasin in the annual VCAILG Groundwater Quality Trend Monitoring Reports (hereinafter, "Nitrate Trends Reports") due in December each year. Many wells from the Fillmore Subbasin (with variable chronologies of nitrate data) were excluded from the annual trends reports after application of screening criteria developed at the request of the Regional Board staff, a process completed in October 2018. After the 2018 screening step, twenty-one wells from the Fillmore Subbasin were omitted from subsequent Nitrate Trends Reports because their nitrate time series did not pass the "climatic criterion" requiring data from each of three periods within the most recent complete climatic cycle.[6] Using a process described in the 2020 MPEP report, 14 of these 21 wells were deemed appropriate for inclusion in MPEP report trend analysis, resulting in a total of 36 wells for which time series plots and trend determinations are included in MPEP reports.

Average nitrate-N concentrations for the 36 wells were computed using publicly available data from July 2019-June 2022. Statistical trend outcomes ("increasing," "decreasing," or "no trend") and nitrate concentration bins were assigned to wells using the same procedures used for the Nitrate Trends Reports. Trends for wells in Zone C, which are outside of the Fillmore Subbasin, were not evaluated for this report.[7] Nitrate trends and concentrations for the 36 wells are illustrated in Figure 4. Bar charts breaking down the trend results for Zones A and B are provided in Figure 5. Time series plots of nitrate-N concentrations are provided for the 36 wells in Attachment 3.

Statistically significant temporal trends in nitrate concentrations were lacking for most of the wells in the Fillmore Subbasin. An increasing trend was only observed for 4 wells in the basin but the 2019-2022 nitrate averages for these wells were below the MCL for nitrate-N. Four wells in Zone A have 2019-2022 average nitrate-N concentrations above the MCL of 10 mg/L. Most of the wells in Zone B have 2019-2022 average nitrate-N concentrations below 5 mg/L, and none have concentrations that exceed the MCL.

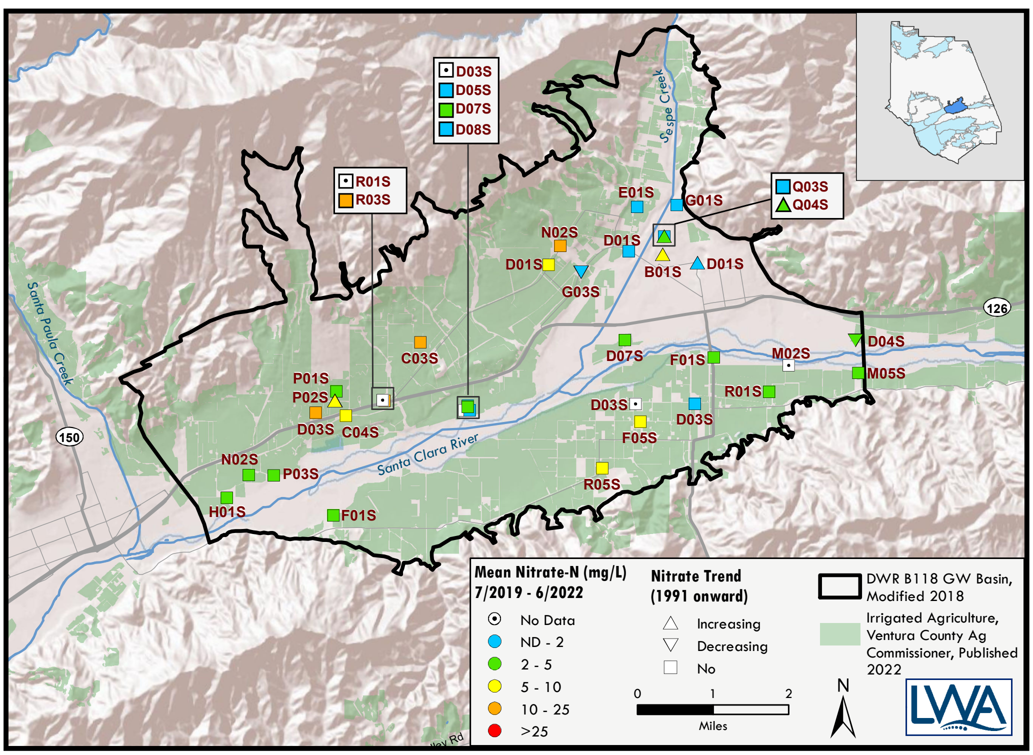

Figure 4. Nitrate Concentration Trends for Wells in the Fillmore Subbasin

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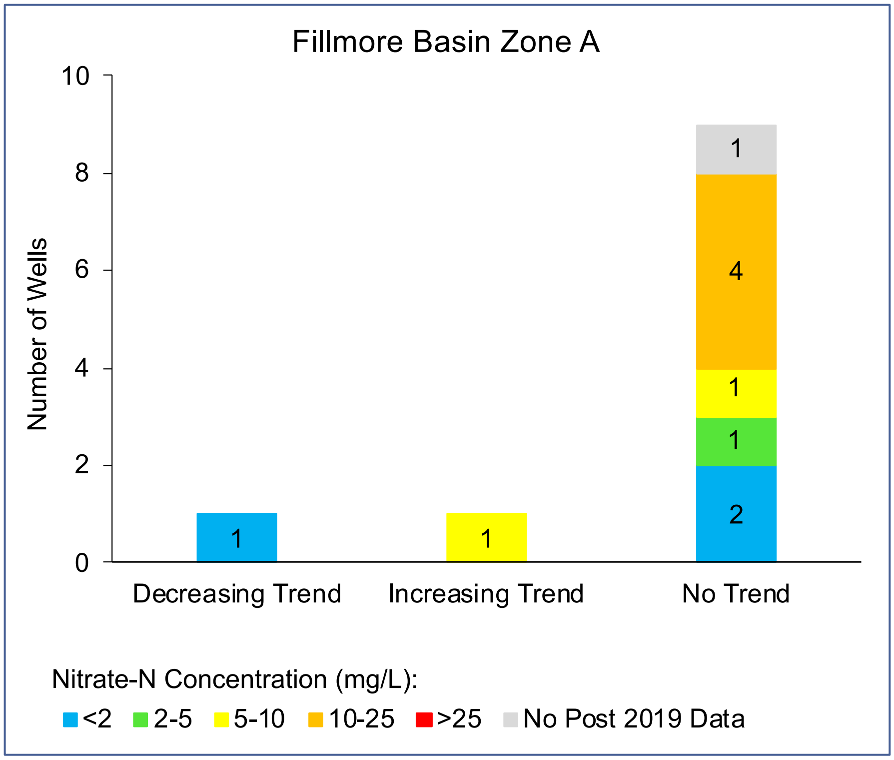
[6] Wet period (1991-1997), Interim period (1998-2006), Dry period (2007-2016)

[7] No wells from the western portion of the Piru Subbasin meet criteria for inclusion in VCAILG's annual Groundwater Quality Trends Reports.



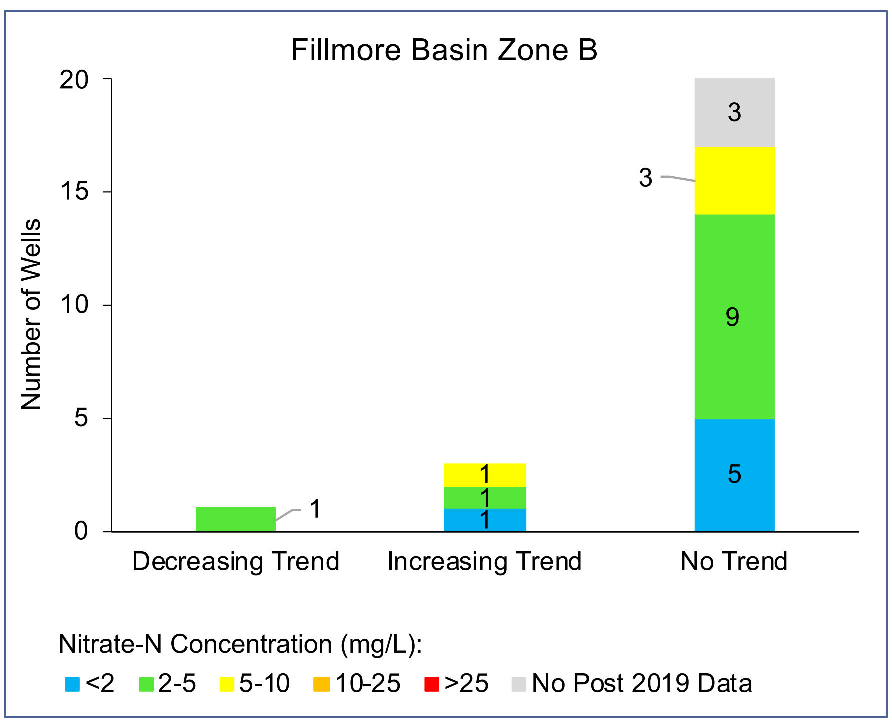


Figure 5. Breakdown of Nitrate Concentration Trends for Wells in the Fillmore Subbasin

CROP TYPES AND AGRICULTURAL PRACTICES

CROP TYPES

Crop types grown in Zones A and B are illustrated in Figure 6, and summarized in Table 3.[8] Orchards (avocado and citrus) dominate the agricultural acreage in both zones, although avocado acreage is more prevalent in Zone A. Nursery acreage is similar in the two zones. The main difference in crop types between the two zones is the higher proportion of non-orchard crops (e.g., rotational and row crops) in Zone B.

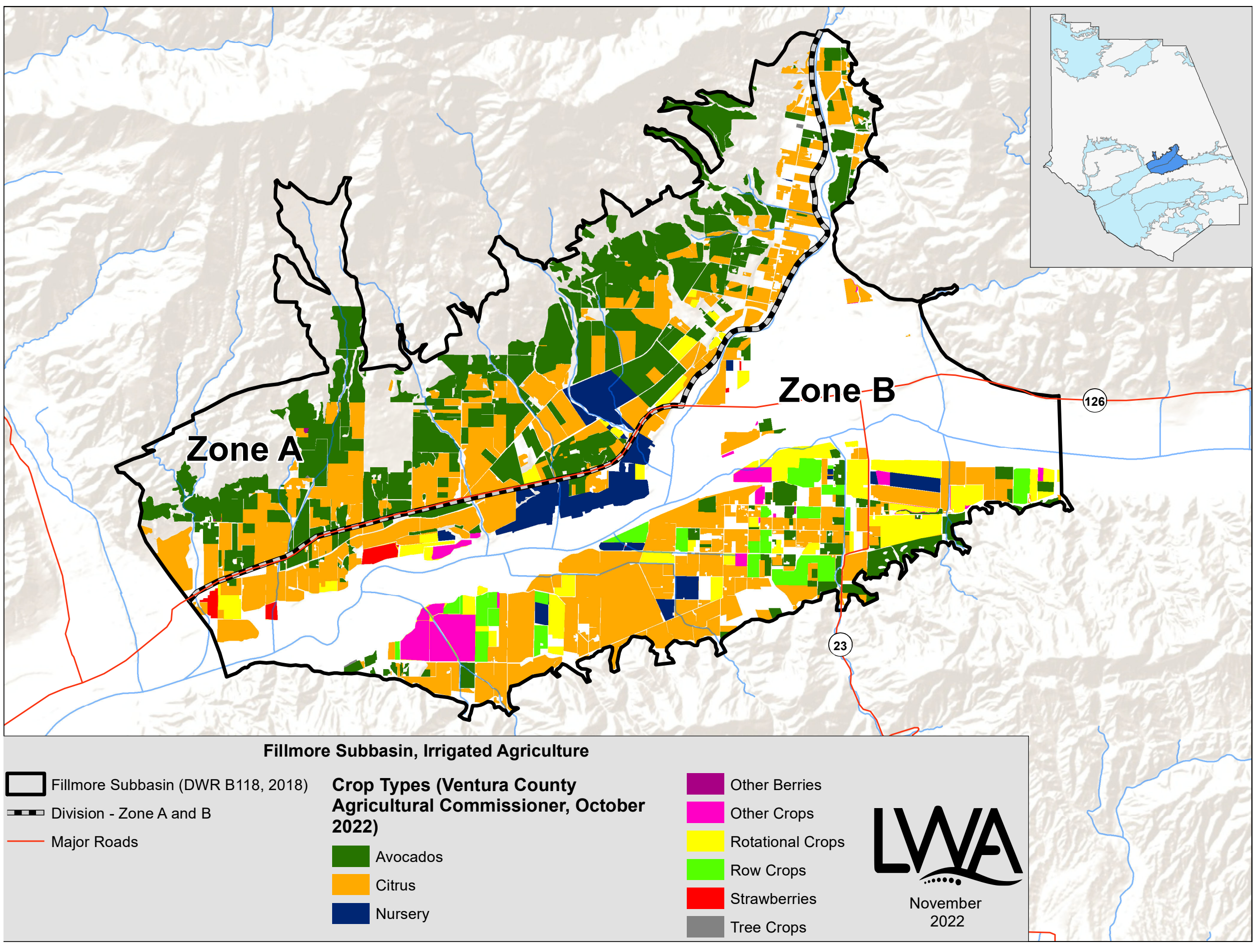


Figure 6. Crop Types by Zone in the Fillmore Subbasin

[8] Agricultural practices and crop types in Zone C, which is outside of the Fillmore Subbasin, were not evaluated for this report.

Table 3. Crop Type Coverage in the Fillmore Subbasin by Zone

Crop Type	Zone A		Zone B	
	Acreage	Percent	Acreage	Percent
Avocados	4,431	57.7%	1,140	11.3%
Citrus	2,851	37.1%	4,426	43.7%
Nursery	180	2.3%	547	5.4%
Other Berries	1	0.0%	2	0.0%
Other Crops			775	7.6%
Rotational Crops [a]	210	2.7%	2,620	25.9%
Row Crops [b]			519	5.1%
Sod				
Strawberries			99	1.0%
Tree Crops	3	0.0%	6	0.1%

[a] Rotational crops included pastureland, pumpkin, and other undefined rotational crops in the Agricultural Commissioner database.
[b] Row crops included cilantro, tomato, kale, green onion, mint, corn, and squash; the primary row crop was cilantro.

VCAILG ENROLLMENT STATUS

The VCAILG enrollment status of agricultural parcels in Zones A and B as of October 2022 is illustrated in Figure 7 and summarized in Table 4. A higher percentage of agricultural parcels is enrolled in VCAILG in Zone A (97%) compared to Zone B (83%).

Table 4. Summary of VCAILG Enrollment of Agricultural parcels in Zones A and B in the Fillmore Subbasin in October 2022

Parcel Enrollment Status	Zone A		Zone B	
	Acreage[a]	Percent	Acreage[b]	Percent
Enrolled	6,940	93.8%	5,967	83.2%
Not Enrolled	455	6.2%	1,205	16.8%

[a] 45 acres are Exempt from enrollment in Zone A.
[b] 372 acres are Exempt from enrollment in Zone B.

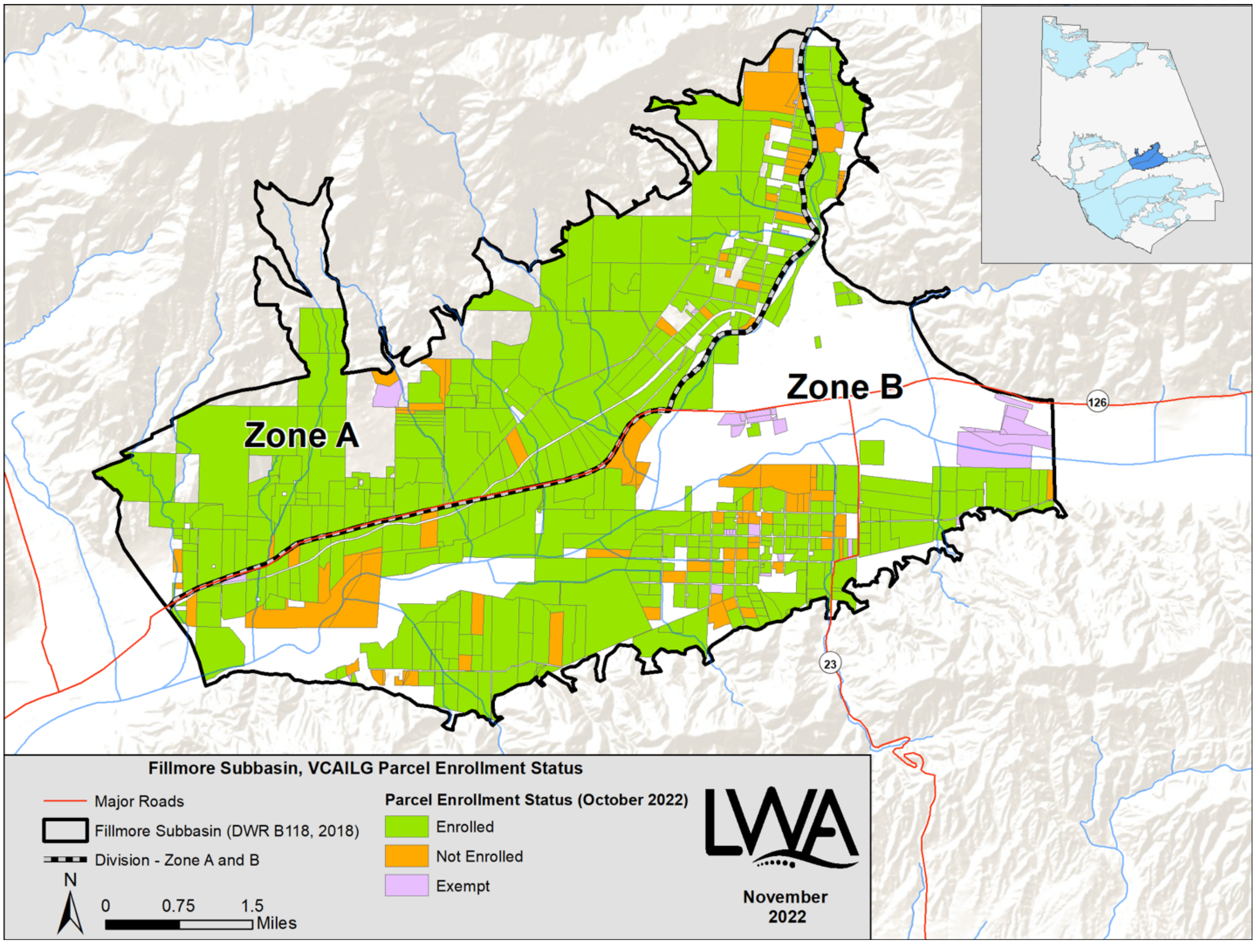


Figure 7. VCAILG Enrollment Status of Agricultural Parcels in the Fillmore Subbasin

AGRICULTURAL PRACTICES

Survey results from VCAILG's agricultural practices surveys are customarily binned using "Responsibility Areas" and monitoring site drainages. For the 2020 MPEP report, 2020 survey data was re-evaluated after assigning surveyed parcels within the Fillmore Subbasin boundary to either Zone A or Zone B. The 2020 survey remains the most recent survey available; results of the 2020 analysis are provided below with no change from that presented in the 2020 and 2021 MPEP reports. Crop data and general production practices for surveyed parcels in Zones A and B are contrasted in Table 5. Adoption rates for pertinent best managements practices (BMPs) in surveyed parcels in Zones A and B are presented in Table 6.[9]

[9] Responses to survey questions #15-16, regarding pest control methods, were not included.

Table 5. 2020 Survey Results for Crop Types and General Production Practices in Zones A and B in the Fillmore Subbasin

Crop or Practice	Zone A		Zone B	
	Acres with Crop or Practice	% of Surveyed Acres	Acres with Crop or Practice	% of Surveyed Acres
Crop Type				
Strawberries	0.5	< 0.1%	2	< 0.1%
Blueberries	0	-	1	< 0.1%
Raspberries	1	< 0.1%	0	-
Row Crop	62	2%	735	23%
Orchard	3,445	93%	2,065	66%
Nursery	180	5%	272	9%
Flower	0	-	54	2%
Sod	1	< 0.1%	0	-
Other	7	0.2%	0	-
Overhead Cover in Production Areas [a]				
Hoop House	9	0.3%	11	0.4%
No Cover	227	6%	1,047	33%
Greenhouse	10	0.3%	3	0.1%
Shade	5	0.1%	3	0.1%
Other	0	-	0	-
Surface Treatments in Production Areas				
Bare Soil	1,065	29%	1,810	58%
Cover Crop	245	7%	572	18%
Plastic	8	0.2%	199	6%
Weed Cloth	8	0.2%	20	1%
Mulch	2,229	60%	626	20%
Gravel	95	3%	238	8%
Other	159	4%	74	2%
Irrigation Systems in Production Areas				
Drip Only	347	9%	493	16%
Microsprinkler/Drip	0	-	12	0.4%
Microsprinkler	3,312	90%	2,050	66%
Overhead Sprinkler	11	0.3%	109	4%
Overhead/Drip	17	0.5%	330	11%
Furrow Flood	0	-	136	4%
Hand Watering	10	0.3%	0	-
Other	1	< 0.1%	0	-

[a] Owing to its irrelevance, overhead cover information is not generated for orchard acreage through the on-line survey.

Table 6. Adoption Rates for Best Management Practices in Zones A and B of the Fillmore Subbasin from the 2020 Survey

Survey Question	Units	Zone A		Zone B	
		Surveyed Units Meeting Criterion	% of Total Applicable Surveyed Units	Surveyed Units Meeting Criterion	% of Total Applicable Surveyed Units
Irrigation and Salinity Management					
Q1: Is the irrigation system tested for distribution uniformity at least once every 3 years?	Acres	2,682	73%	1,771	62%
Q2: Is soil moisture used as determinant of irrigation practices?	Acres	2,822	76%	2549	81%
Q3: Is soil EC used to determine when salt leaching is necessary?	Acres	784	22%	795	29%
Nutrient Management					
Q4a: Is there a Nutrient Management Plan for the parcel?	Acres	2,113	57%	1,846	59%
Q4b: Is it a Certified Nutrient Management Plan?	Acres	1,439	39%	1171	37%
Q5a: Are soil residual nitrate tests done?	Acres	2,251	61%	2,168	69%
Q5b: Is fertilizer adjusted using residual soil nitrate?	Acres	2,249	61%	2,168	69%
Q6: Are leaf/petiole tests conducted?	Acres	3,086	85%	2533	86%
Q7a: Is nitrate measured in fertigation water?	Acres	2,439	66%	1,909	61%
Q7b: Is fertilizer adjusted using fertigation water nitrate levels?	Acres	2,439	66%	1907	61%
Q8: Is fertilizer adjusted based on nutrients provided by cover crops?	Acres	657	36%	872	40%
Sediment Management					
Q9: How many cropped acres have a slope greater than 2%?	Acres	1,468	40%	276	9%
Q10: Erosion control is used on how many of the sloped cropped acres?	Acres	942	64%	146	53%
Q11. How much non-cropped area is bare soil?	Acres	196	12%	303	28%
Q12a: How many feet of ditches exist?	Feet	110,528	N/A	171,031	N/A
Q12b: How many feet of ditches are protected from erosion?	Feet	90,995	82%	33,952	20%
Q13a: Are grassed waterways present?	Acres	127	3%	279	9%
Q13b: How many acres drain to grassed waterways?	Acres	32	1%	162	5%
Q14: How many acres are treated by vegetated filter strips?	Acres	17	0.5%	229	7%
Pest Management					
Q17a: How many acres are organically farmed?	Acres	103	3%	325	10%
Q17b: How many acres are conventionally farmed?	Acres	3,594	97%	2804	90%
Runoff Management/Treatment					
Q18: How many acres produce irrigation runoff?	Acres	74	2%	560	18%
Q19: Runoff from how many acres is treated or detained?	Acres	165	4%	444	14%

DISCUSSION OF RESULTS

As was true in 2020 and 2021, no clear evidence was obtained in the study that use of fertilizer is causing nitrate contamination of groundwater in the Fillmore Subbasin. *None of the wells sampled in 2022 had dual isotope signatures indicating nitrate-based or ammonia-based fertilizer as a source of nitrate in groundwater*. As was also true in 2020 and 2021, the dual isotope signatures obtained in 2022 support septic waste as a potential source of nitrate in all the wells sampled – especially in Zones B and C where, in 2022, septic waste and/or manure was the only potential source of nitrate indicated by isotopic signatures. Per the 2020 survey results, ten percent of surveyed agricultural acreage is farmed organically in Zone B; however, the survey does not collect data on use of manure, so it is not possible to speculate about the potential role of manure application on groundwater quality.

The 2020/2021 water year (WY 21) was the driest on record in Ventura County for the period 1927-2021; the Fillmore area received only ~3 inches of rain during the water year, compared to the long term average of ~17 inches.[10] Despite the extreme paucity of natural groundwater recharge in the year separating the 2020 and 2021 rounds of well sampling, the isotopic signatures in the more permeable Zones B and C (see below) moved further away from the signature space for nitrate from ammonia fertilizer (see 2021 report). Instead, the isotopic evidence for septic waste as a source of nitrate in Zones B and C was stronger after the exceptionally dry winter of WY 21, compared to WY 20. Although rainfall in WY 22 (14.62 in.) was closer to the long-term average, the isotopic signatures from wells in the basin continued to show increasing evidence for septic or animal waste as a source of groundwater nitrate. In fact, the isotopic signatures for wells in Zone A moved completely out of the signature space for nitrate derived from ammonia fertilizer, eliminating ammonia fertilizer as a potential source of nitrate in the well samples from Zone A in 2022.

Results of VCAILG's 2020 agricultural practices survey do not explain why nitrate concentrations remain somewhat lower in Zone B than Zone A. First, the lack of isotopic evidence for fertilizer influence across the basin in 2022 renders the evaluation of agricultural practices somewhat moot. Second, the 2020 survey did not indicate that practices that would limit nitrate migration to groundwater are more prevalent in Zone B than in Zone A. <u>Adoption rates for irrigation and nutrient management BMPs were very similar in Zones A and B</u>. Short-lived crops (such as rotational and row crops), which involve more soil disturbance, frequent plant establishment periods, and typically have shallower rooting depths compared to tree crops, are practically absent in Zone A. Less efficient irrigation practices (overhead sprinklers, furrow flood) are in use in 20% of the production area in Zone B, but are rare in Zone A. This difference in irrigation practices likely contributes to the higher percentage of acreage in Zone B that produces irrigation runoff (18% vs. 2%). Irrigation runoff is less prevalent in Zone A despite more sloped terrain; 40% of cropped area in Zone A has a slope greater >2%, compared to 9% in Zone B.

Other differences between zones in production practices that could potentially influence nitrate leaching were as follows:

[10] http://www.vcwatershed.net/fws/reports/wettest-driest-report

- A higher percentage of production area in Zone B is bare soil (58% vs 29%).
- A lower percentage of production area in Zone B is treated with mulch (20% vs 60%)
- A higher percentage of production area in Zone B is treated with cover crops (18% vs 7%)
- Runoff from more of the acres in Zone B is treated or detained (14% vs 4%), however the incidence of runoff in Zone B is much higher than in Zone A (see above).

Of the differences listed above, the greater use of cover crops in Zone B is the only one that would support lower nitrate migration from agricultural acreage to groundwater in Zone B, compared to Zone A - but the use of cover crops is low in Zone B in any case (18% of production area).

Hydrogeologic factors limit the usefulness of attempts to relate contemporary surface practices with groundwater quality.[11] Zone A is in the upland portion of the basin, is characterized by a greater occurrence of lower permeability soils than Zone B and has a considerably thicker vadose zone (generally several hundred feet in Zone A versus approximately 20-50 feet in Zone B). Thus, the groundwater samples collected in Zone A are impacted by a significantly greater lag time between water infiltration at land surface and arrival at the water table, perhaps many years to a decade or more. The significantly longer residence time of water in the Zone A vadose zone also provides greater opportunity for geochemical and microbiological processes to affect the fate of nitrate as it is transported to the water table, as compared to Zone B. These factors further complicate the interpretation of BMP adoption rates, irrigation practices, etc. Another key difference is that Zone B receives direct recharge from the Santa Clara River and Sespe Creek, which mixes with percolating applied water, whereas Zone A does not. This may be a reason why Zone B nitrate concentrations are generally lower than Zone A; however, this observation alone does not shed light on potential nitrate sources.

As was true in 2020 and 2021, VCAILG is not proposing specific outreach guided by the findings of this study, for the following reasons:

- Well monitoring data in 2022 did not show any evidence that nitrate- or ammonium-based fertilizer is the source of nitrate in groundwater.
- BMP survey results in each zone were well aligned and differences are more representative of the variations in crop types rather than a demonstration of greater implementation of specific BMPs that are protective of groundwater quality.

Furthermore, growers in the eastern portion of the Fillmore Subbasin were required to begin implementing certified nitrogen management plans beginning in April 2021 per the 2020 VCAILG Water Quality Management Plan. Growers in the remainder of the Fillmore Subbasin will follow suit when irrigation and nitrogen management planning requirements of the State Water Resources Control Board Order WQ 2018-00002 become in effect (i.e., the statewide precedential components of the East San Joaquin WDR for irrigated agricultural lands).

[11] Description of hydrogeologic factors provided as personal communication from Bryan Bondy, PG, CHG, December 6, 2020, supported by evaluation of geologic cross sections provided by United Water Conservation District.

Attachment 1. Use of Dual Stable Isotope Signatures for Nitrate Source Analysis

Both nitrogen and oxygen have naturally occurring stable isotopes. The stable isotopes of nitrogen are ^{14}N (called "N-fourteen", with 7 protons and neutrons) and ^{15}N (called "N-fifteen," with 7 protons and 8 neutrons). ^{14}N is the most common isotope, accounting for over 99% of nitrogen atoms. The stable isotopes of oxygen are ^{16}O, ^{17}O, and ^{18}O, each with 8 protons and with 8, 9, and 10 neutrons, respectively. ^{16}O is the most common isotope; the isotopic composition of oxygen atoms in the Earth's atmosphere is 99.759% ^{16}O, 0.037% ^{17}O and 0.204% ^{18}O. Stable oxygen isotope analysis in geophysical, meteorological, or biogeochemical investigations usually involves ^{16}O and ^{18}O. The ratio of stable isotopes in a given mass of either nitrogen or oxygen are used to generate "delta" values, with units of "per mil" (‰, parts per thousand), as follows:

$$\partial^{18}\mathrm{O} = \left(\left(\frac{\frac{^{18}\mathrm{O}}{^{16}\mathrm{O}}\, sample}{\frac{^{18}\mathrm{O}}{^{16}\mathrm{O}}\, standard} \right) - 1 \right) x\ 1000\ ‰$$

$$\partial^{15}\mathrm{N} = \left(\left(\frac{\frac{^{15}\mathrm{N}}{^{14}\mathrm{N}}\, sample}{\frac{^{15}\mathrm{N}}{^{14}\mathrm{N}}\, standard} \right) - 1 \right) x\ 1000\ ‰$$

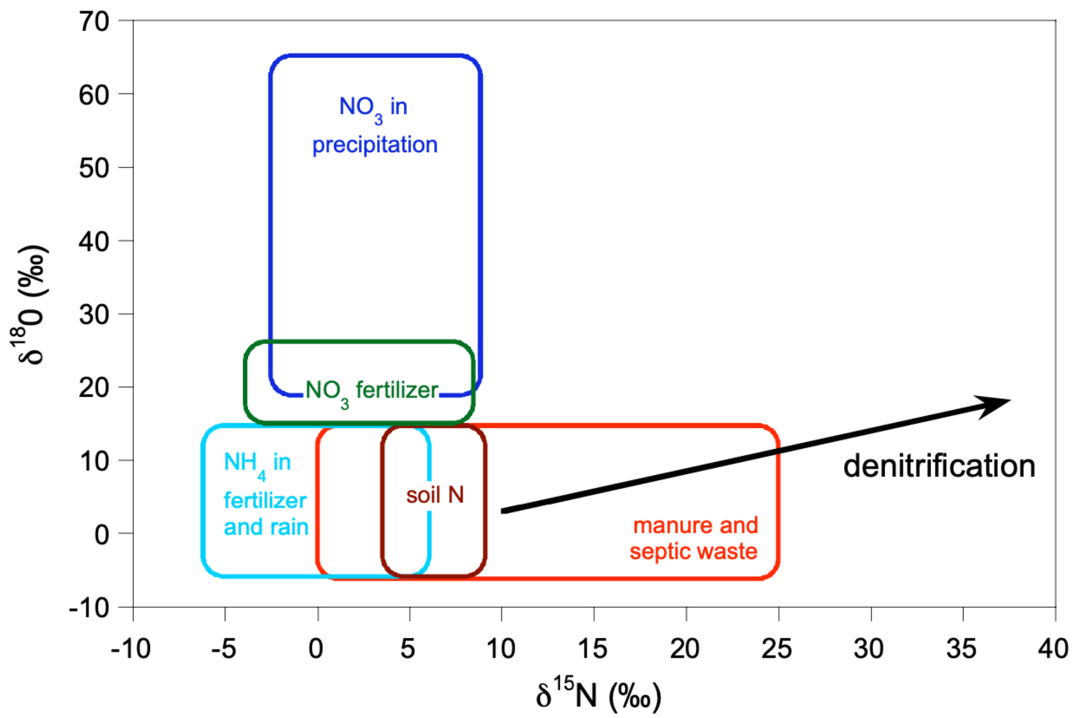
where the standards have a known consensus isotopic composition (such as, for oxygen, the Vienna Standard Mean Ocean Water).

The isotopic composition of N and O in nitrate molecules varies depending on the isotopic composition of the starting materials and the processes that led to the formation of the nitrate. For example, organisms preferentially use the lighter isotope of nitrogen (^{14}N) over the heavy isotope (^{15}N) so that almost anything created by an organism (the product) is isotopically "lighter" than the material not used (the reactant or substrate). For example, when microbes convert ammonium to nitrate (nitrification), the nitrate being formed is lighter (has a lower $\delta^{15}N$ value) than the ammonium being left behind. And as organisms use up the reactant, the $\delta^{15}N$ values of the product and left-over reactant change in predictable manner.

Artificial (inorganic) fertilizers produced by the fixation of atmospheric N_2 include the commonly applied urea, ammonium nitrate, and potassium nitrate. These *anthropogenic* fertilizers have $\partial^{15}N$ values that are uniformly low reflecting their atmospheric source. Animal waste contains a wide variety of N-bearing compounds, both aqueous and solid, but most of the N is in the form of urea. The urea may be hydrolyzed to ammonia, and later oxidized (nitrified) to nitrate. Animals (microbes to invertebrates) are slightly enriched in ^{15}N relative to their diet; the increases in $\partial^{15}N$ in animal tissue and solid waste relative to diet are due mainly to the excretion of isotopically light N in urine or its equivalent. Animal waste products may be further enriched in ^{15}N because of volatilization of ^{15}N-depleted ammonia, and subsequent oxidation of much of the residual waste material may result in nitrate with a high $\partial^{15}N$. By this process, animal waste with a typical $\partial^{15}N$ value of about +5‰ is converted to nitrate with $\partial^{15}N$ values generally in the range of +10 to +20‰, and human and other animal waste become isotopically indistinguishable under most circumstances.

There have been several investigations of the $\partial^{15}N$ values for soil nitrate from different environments (i.e., "natural" soils (tilled and untilled), soils fertilized with synthetic fertilizers or manure, soils contaminated with septic waste, etc.). In general, the soil nitrate produced from fertilizer (average $\partial^{15}N$ value = +4.7 ±5.4‰) and animal waste (average $\partial^{15}N$ = +14.0 ± 8.8‰) are isotopically distinguishable but they both overlap with the compositions of nitrate in precipitation and natural soils. Post-depositional increases in $\partial^{15}NO_3$-N can be caused by denitrification. Increases in $\partial^{15}N$ of nitrate caused by denitrification are less likely in coarse-grained soils where waters percolate rapidly (and have higher concentrations of dissolved oxygen) than in finer-grained soils.

Mixing of nitrate sources in water samples can often be resolved by analysis of both the $\delta^{18}O$ and the $\delta^{15}N$ of nitrate (or other semi-conservative chemical tracers). The generalized relationship between sources of nitrate and the dual isotopic signatures of nitrate are illustrated by the Venn diagram in the figure below. The dual-isotope approach has three main potential benefits: (1) oxygen isotopic *separation* of some sources is greater than for nitrogen isotopes, allowing better source resolution by having two tracers, (2) some nitrate sources that are presently indistinguishable with $\delta^{15}N$ alone (e.g., nitrate fertilizer vs. soil nitrate, atmospheric vs. soil nitrate, synthetic nitrate fertilizer vs. nitrified fertilizer ammonium) may be identified only when the $\delta^{18}O$ of nitrate is analyzed, and (3) oxygen isotopic compositions of nitrate vary systematically with nitrogen isotopic compositions during denitrification. Thus, in systems where the dominant sources of nitrate are isotopically distinctive, source contributions can -- in theory -- be determined despite significant denitrification.



Juxtaposition of dual isotope signatures for nitrate from different sources (recreated from Kendall & McDonnell 1998)

Attachment 2. Method of Analysis of Stable Nitrogen and Oxygen Isotopes of Dissolved Nitrate

Equipment and Supplies

- 0.45 nylon filter paper
- Glass filtration apparatus
- 1N HCl
- $BaCl_2$
- Cation exchange resin
- Anion exchange resin 1N HBr
- Ag_2O
- Flasks
- Stir bars
- Freezer
- Oven
- Freeze-dryer
- Teflon beakers
- Thermo Delta V Plus
- Mettler Toledo MX5 Ultra-Microbalance Thermo TC/EA
- Thermo ConFlo II

Method/Procedure

Nitrate is extracted from groundwater samples and converted into $AgNO_3$ using ion-exchange techniques. The nitrate concentration is determined using an Orion AquaFAST TM colorimeter. The appropriate sample size is filtered and placed on a hot plate to boil. The pH is adjusted to 1-3 using 1N HCl. $BaCl_2$ is added to remove dissolved sulfates, and the sample volume is decreased to 250mL. Precipitated $BaSO_4$ is filtered from the sample and placed into separatory funnels. The sample is allowed to flow through a cation column and then through the anion column, where nitrate is held within the column. 1N HBr is added to the column to strip the nitrate. The eluent is collected, and silver oxide is added to create $AgNO_3$. The sample is filtered, frozen in a Teflon beaker, and placed in a freeze-drying vacuum oven until only the $AgNO_3$ crystals remain. The crystals are then analyzed using for $\delta^{15}N$ using an EA-IRMS and analyzed for $\delta^{18}O$ using a TC/EA-IRMS system.

Analysis of $\delta^{15}N$ is performed using a Carlo Erba Elemental Analyzer. 1.2 milligrams of $AgNO_3$ are weighed into tin boats and placed in an Autosampler with helium purge. The sample is flash combusted inside the combustion reactor, as shown in this reaction $N + O_2 \rightarrow N_xO_y + N_2$. The products of combustion reaction are then carried to the reduction reactor where excess oxygen is removed, and nitrogen oxides (N_xO_y) are reduced to elemental nitrogen (N_2). The N_2 gas is introduced to the IRMS through a ConFlo II interface. Sample values are referenced against international standards.

Analysis of $\delta^{18}O$ is performed using a Thermo TC/EA. 300 micrograms of $AgNO_3$ is weighed into silver boats and placed in a zero blank autosampler. The sample is thermally converted to CO gas in the EA furnace. The CO gas is introduced into the IRMS through a ConFlo II interface. Sample values are referenced against international standards.

Maintenance

Glassware is washed and rinsed with deionized water to remove residual sample and residual $AgNO_3$.

QA/QC

At a minimum, every tenth sample preparation is a duplicate. Approximately every tenth EA/TCEA analysis a set of standards is analyzed after every ten samples, along with at least one check standard per analysis run.

Calculation

Calculations are performed by the software on the IRMS (Isotope Ratio Mass Spectrometer) at the time of analysis. Data normalization against primary international standards is performed using Microsoft Excel.

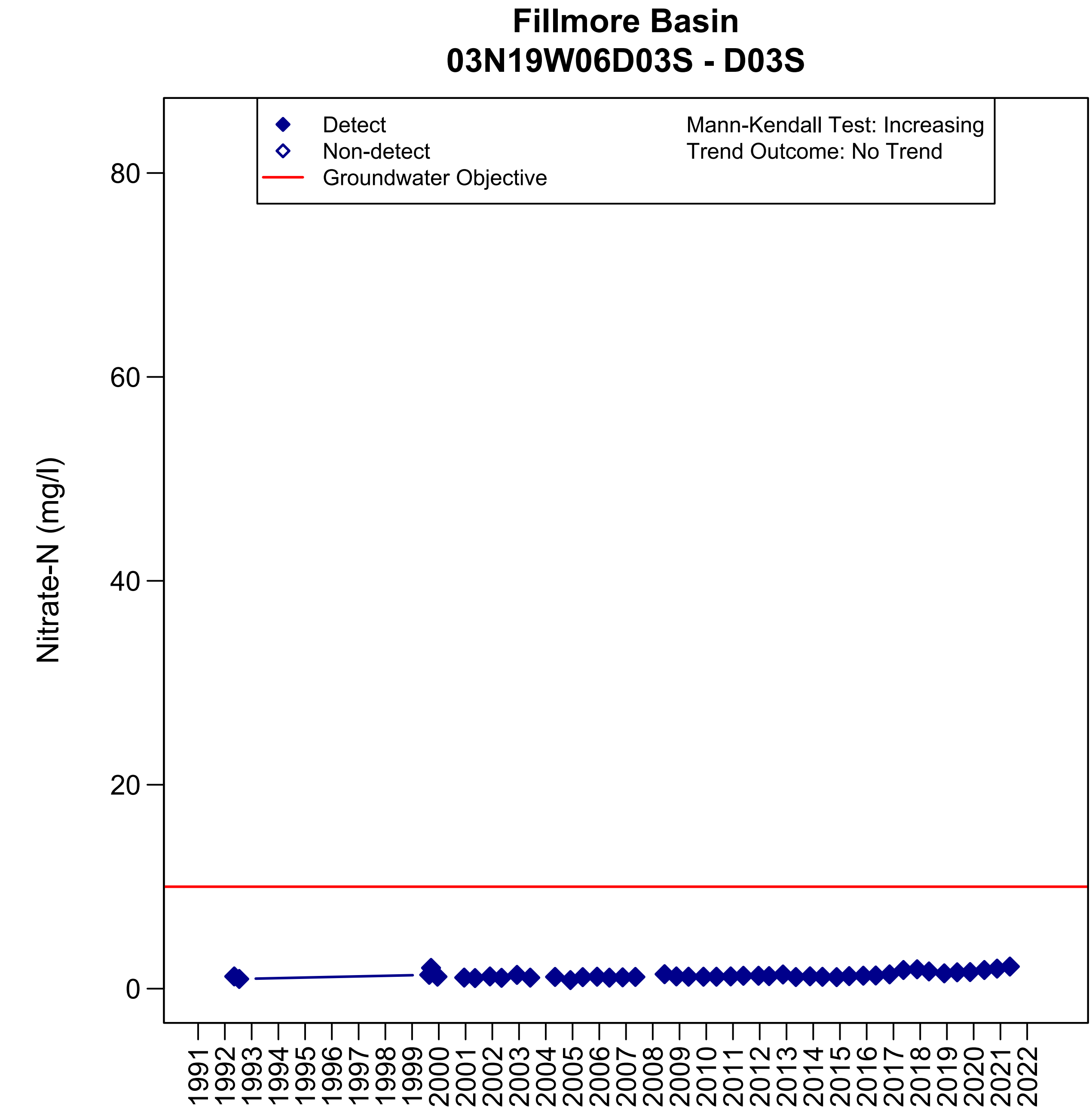
Documentation

All records of sample preparation and notes are handwritten in bound logbooks. All sample data including the date prepared are stored electronically and in print.

Sample Handling

Samples should be collected and frozen until analyzed. Samples should be shipped overnight in a cooler on ice. Filtering prior to shipment is preferred but is not required.

Attachment 3. Nitrate-N Concentration Time Series Plots for Wells in the Fillmore Subbasin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03N19W06D03S - D03S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: Increasing
Trend Outcome: No Trend
Nitrate-N (mg/l)
0
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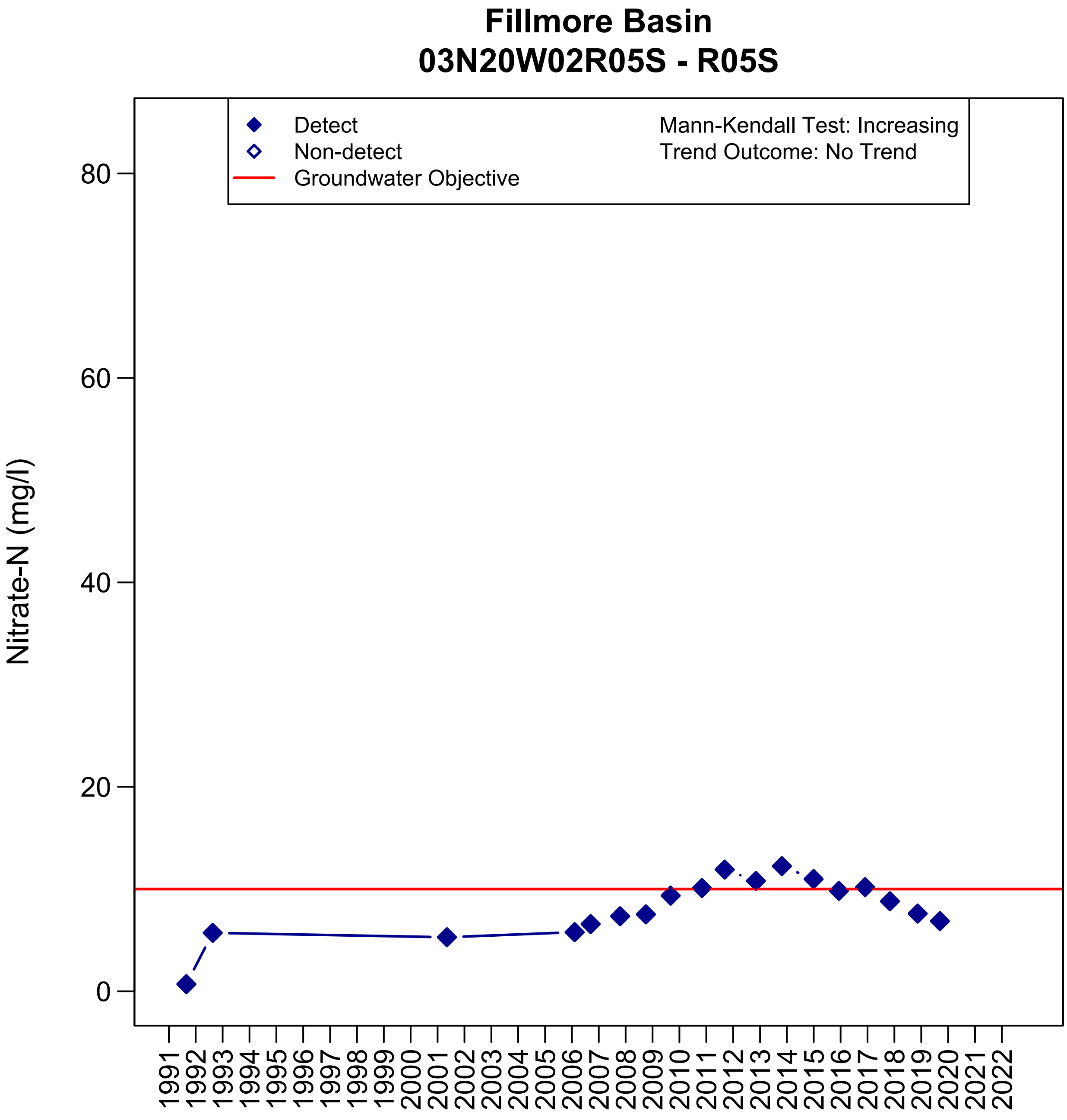
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Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: Increasing
Trend Outcome: No Trend
Nitrate-N (mg/l)
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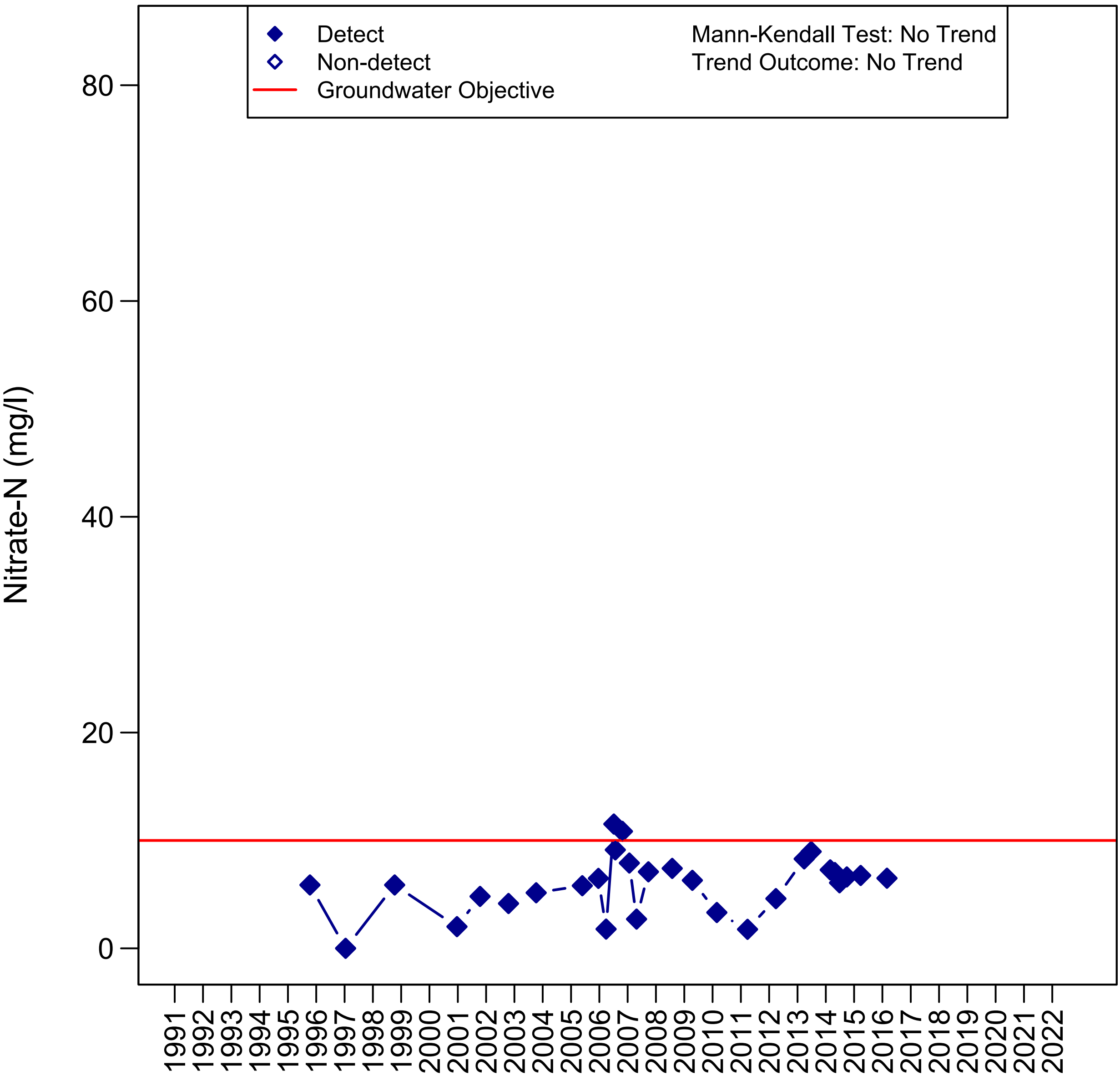
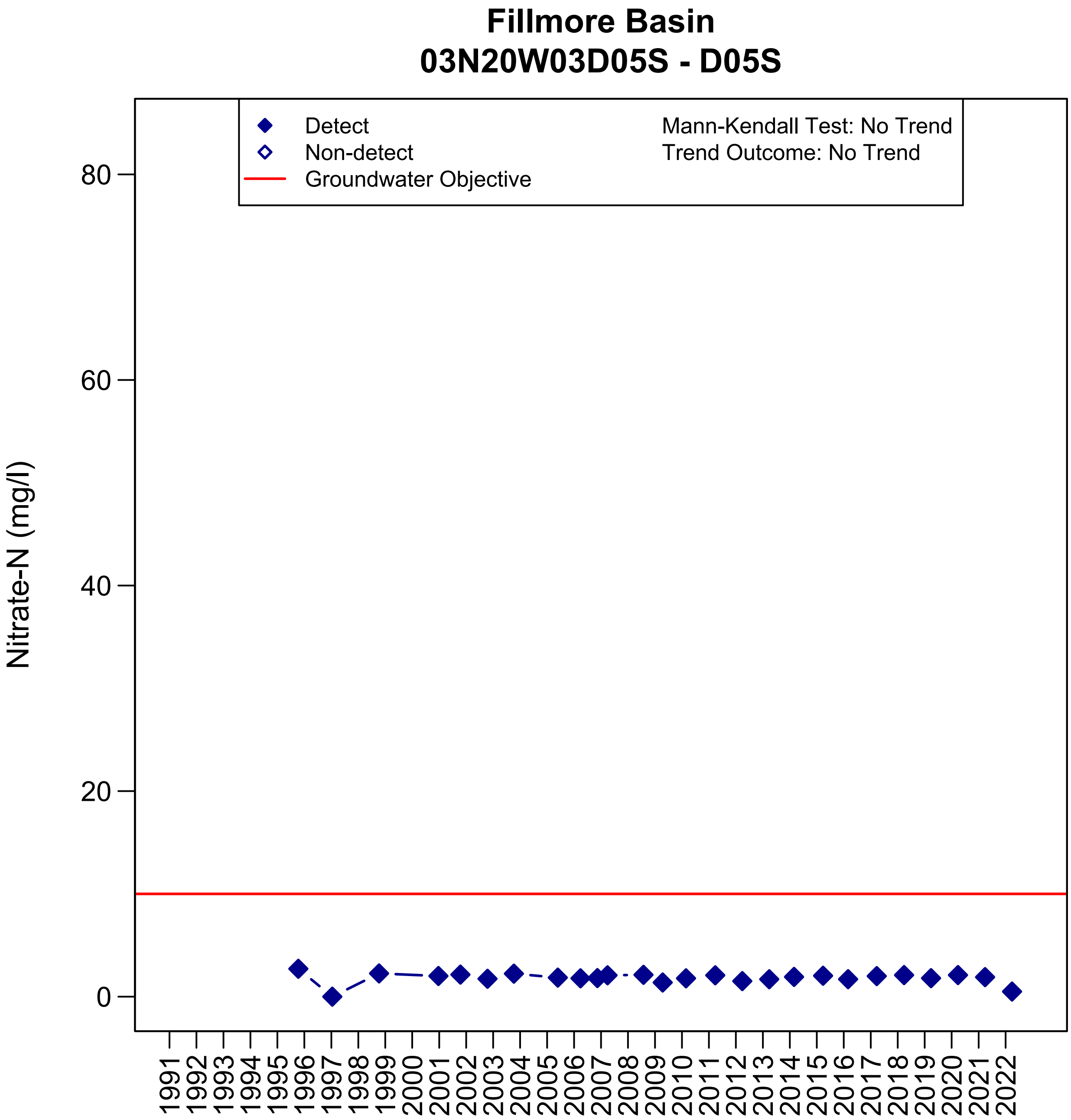
Fillmore Basin
03N20W03D03S - D03S

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Detect
Non-detect
Groundwater Objective
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Trend Outcome: No Trend
Nitrate-N (mg/l)
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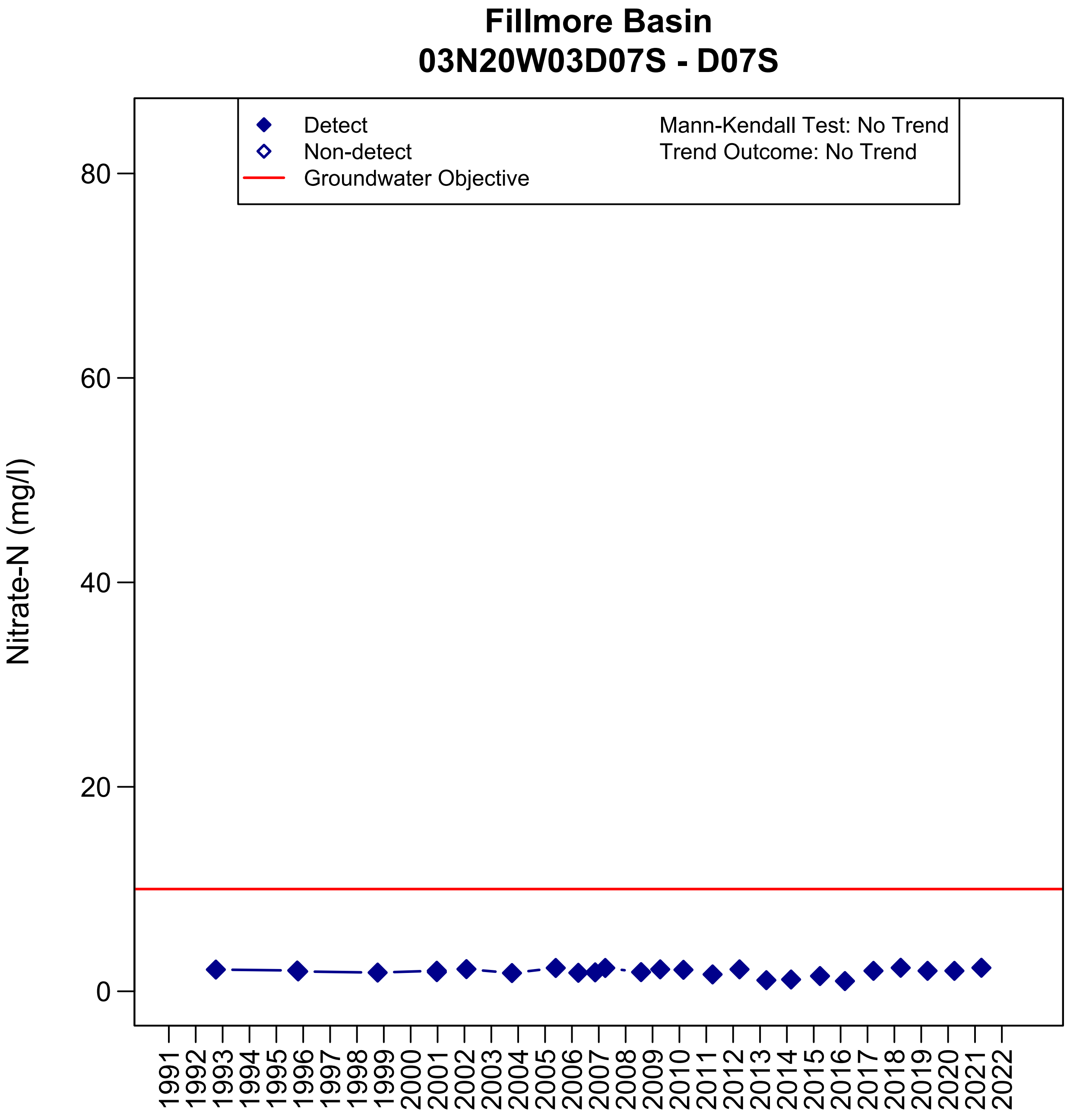
Fillmore Basin
03N20W03D07S - D07S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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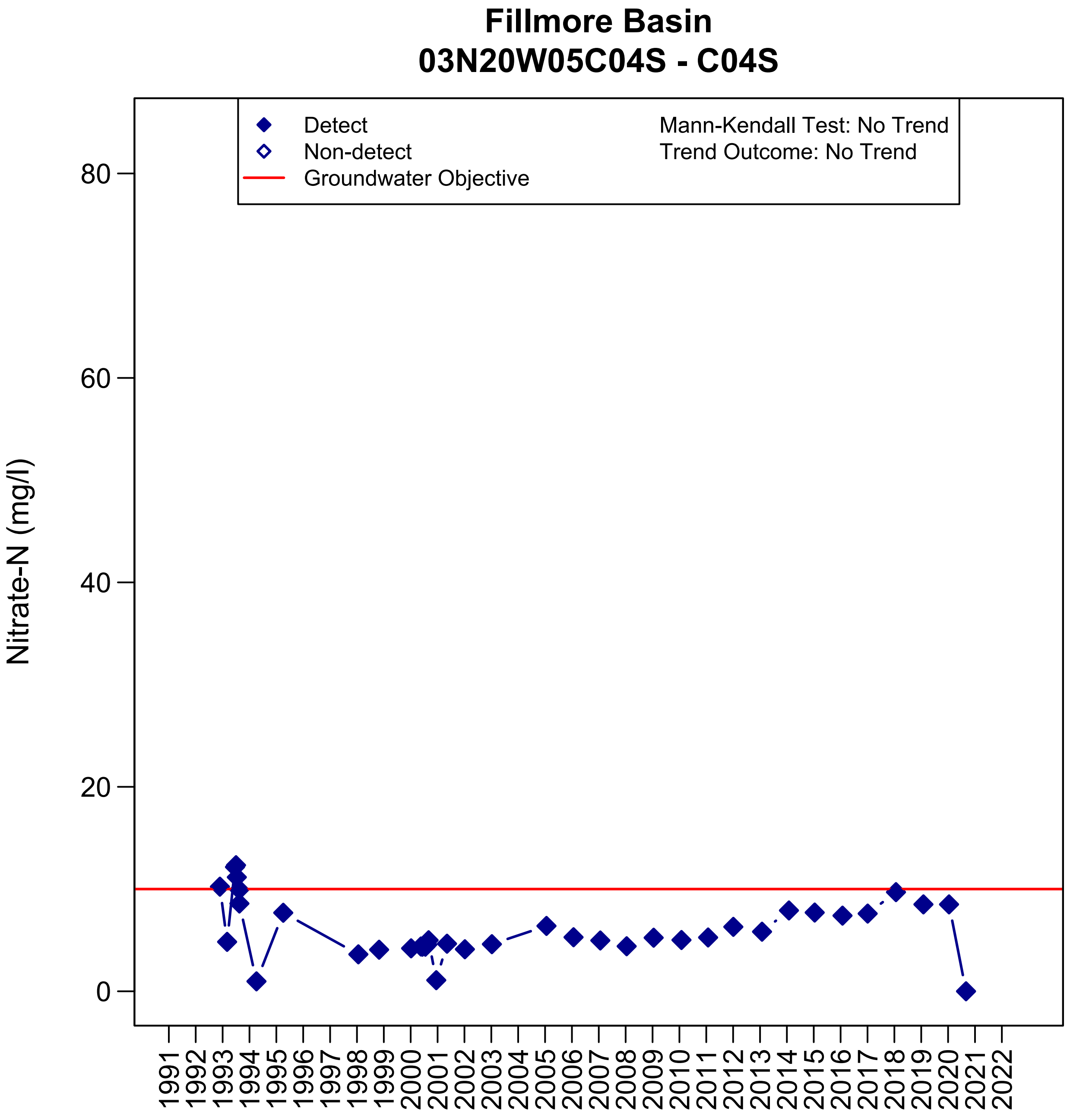
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03N20W05C04S - C04S
Detect
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Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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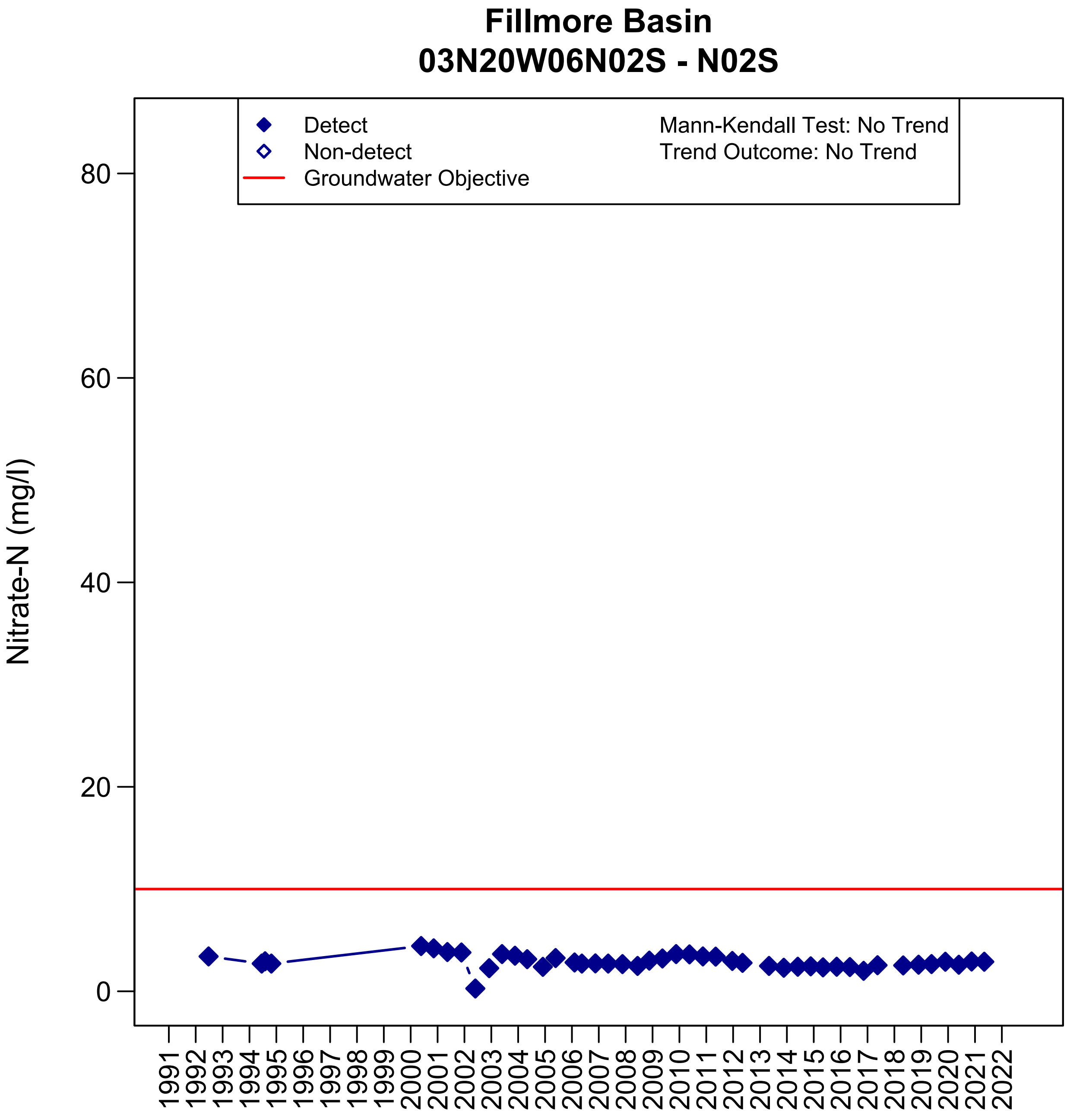
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Detect
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Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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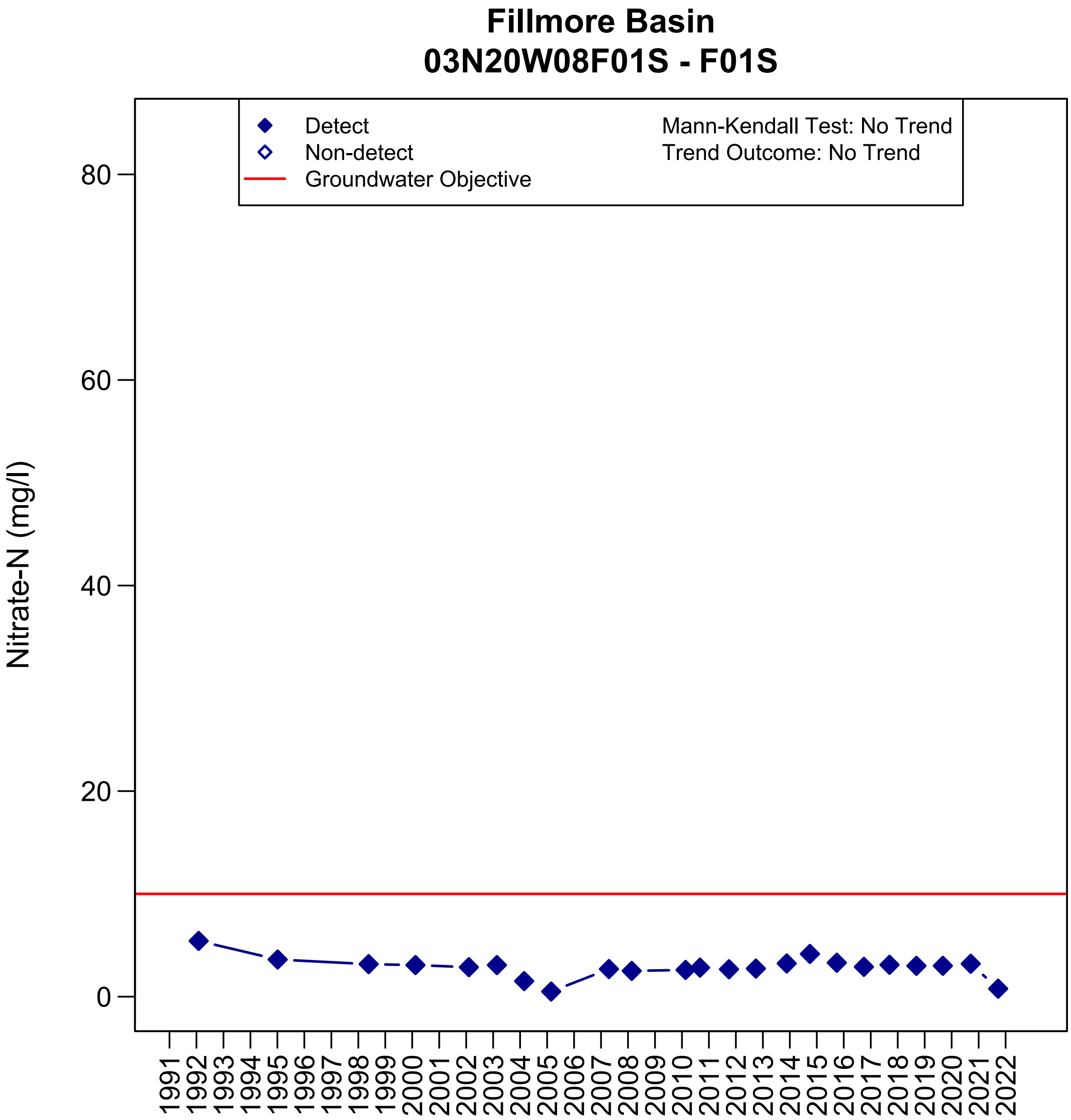

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Detect
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Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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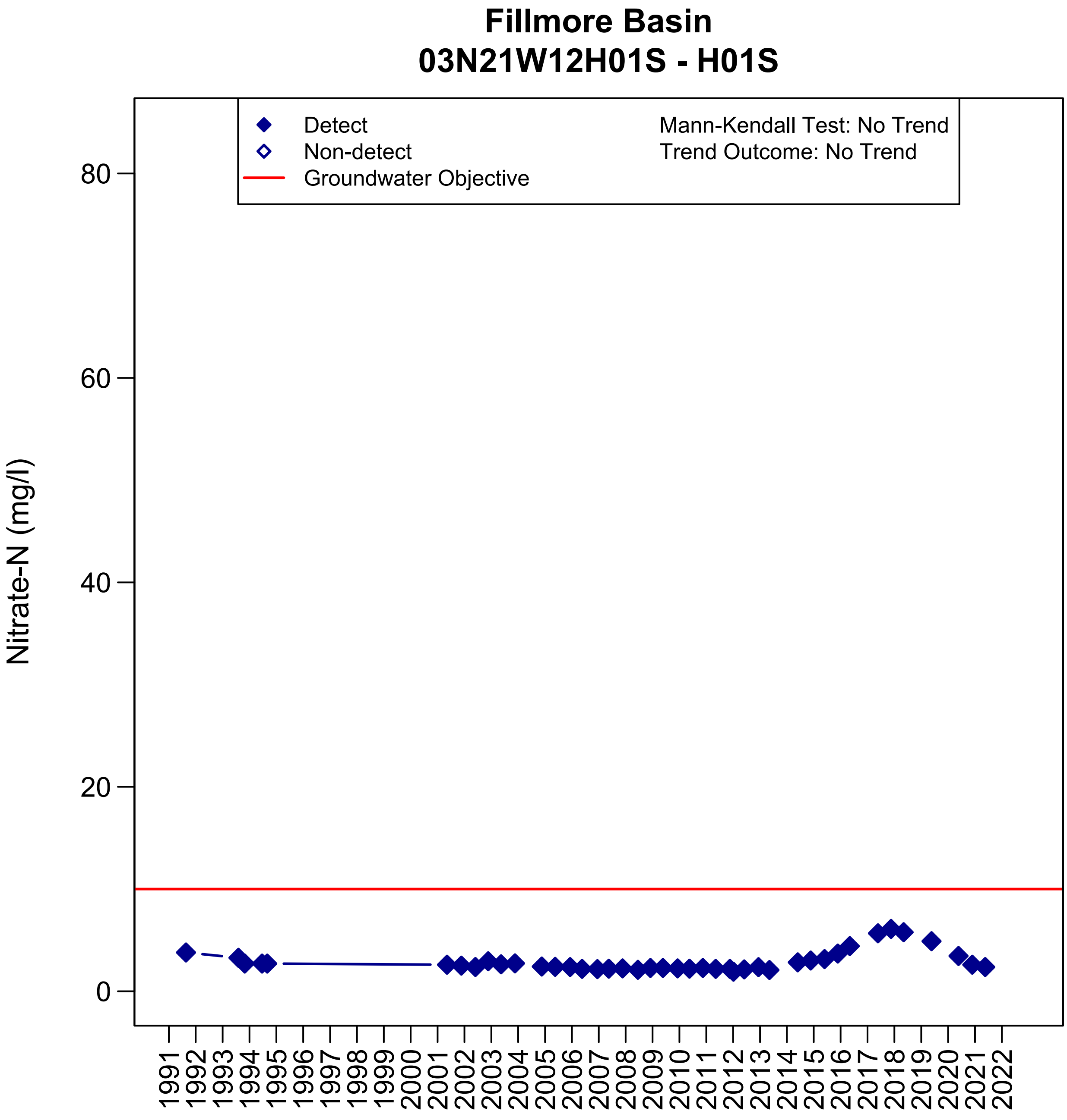

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03N21W12H01S - H01S
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Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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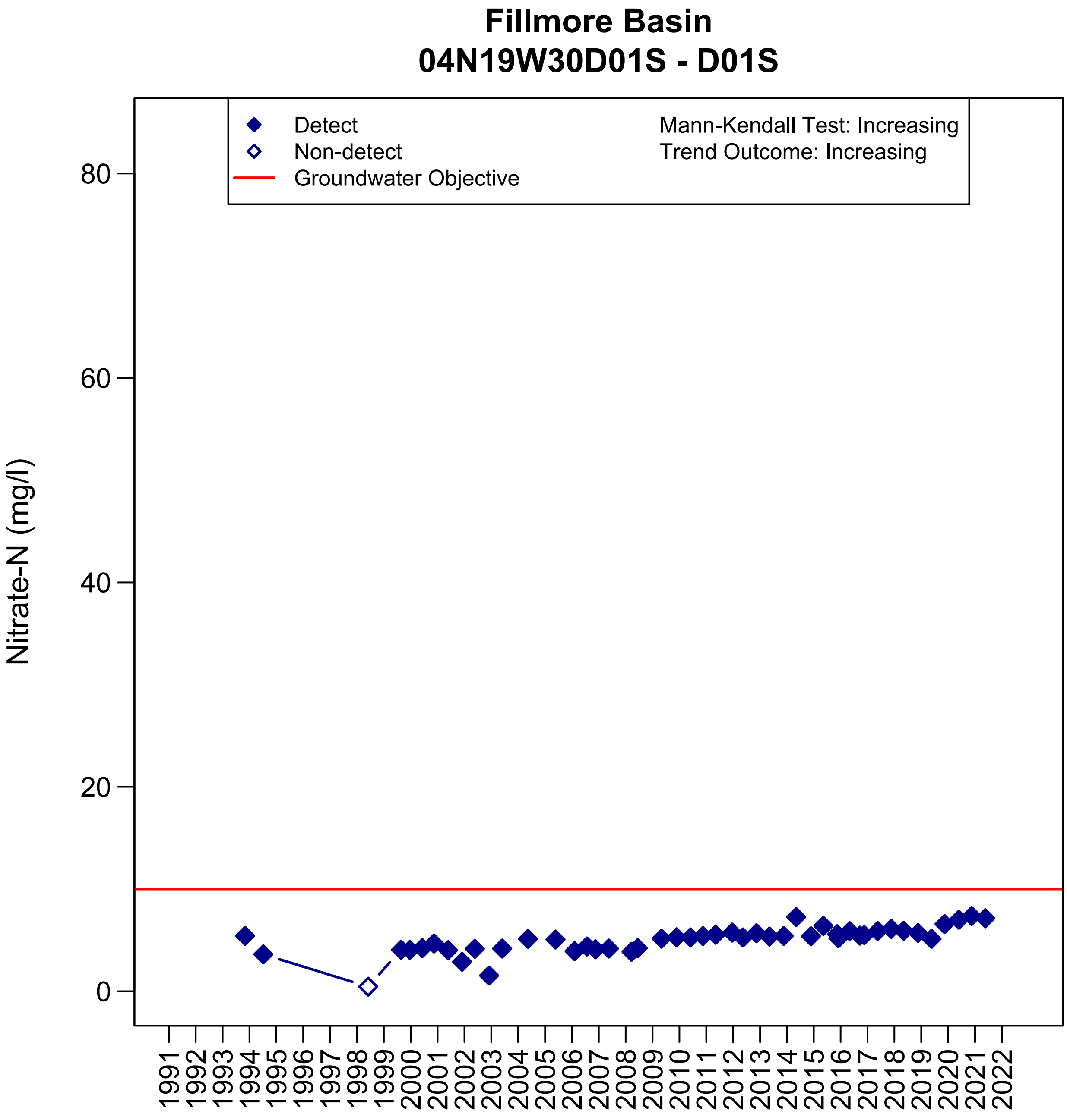
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04N19W30D01S - D01S
Detect
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Groundwater Objective
Mann-Kendall Test: Increasing
Trend Outcome: Increasing
Nitrate-N (mg/l)
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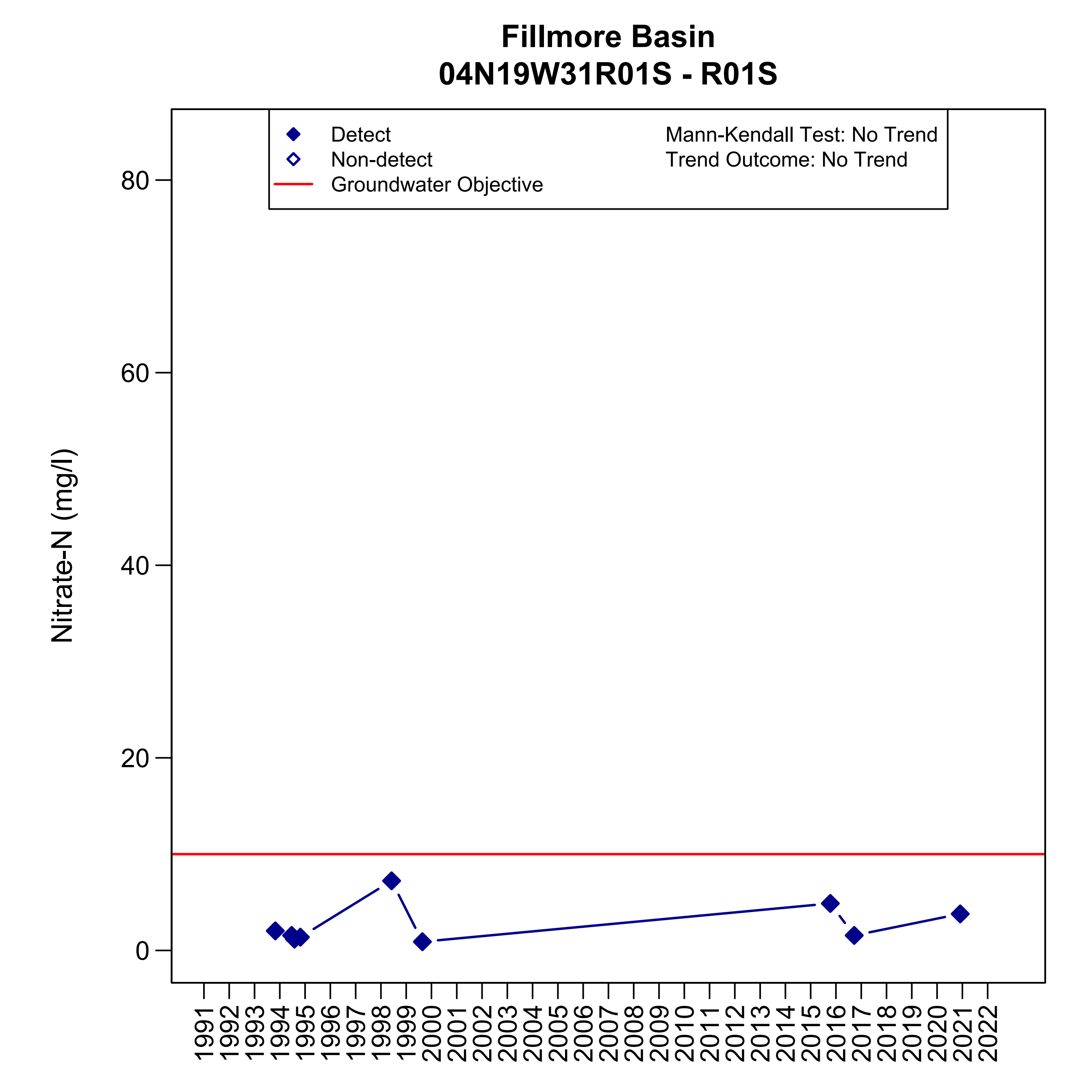

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Detect
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Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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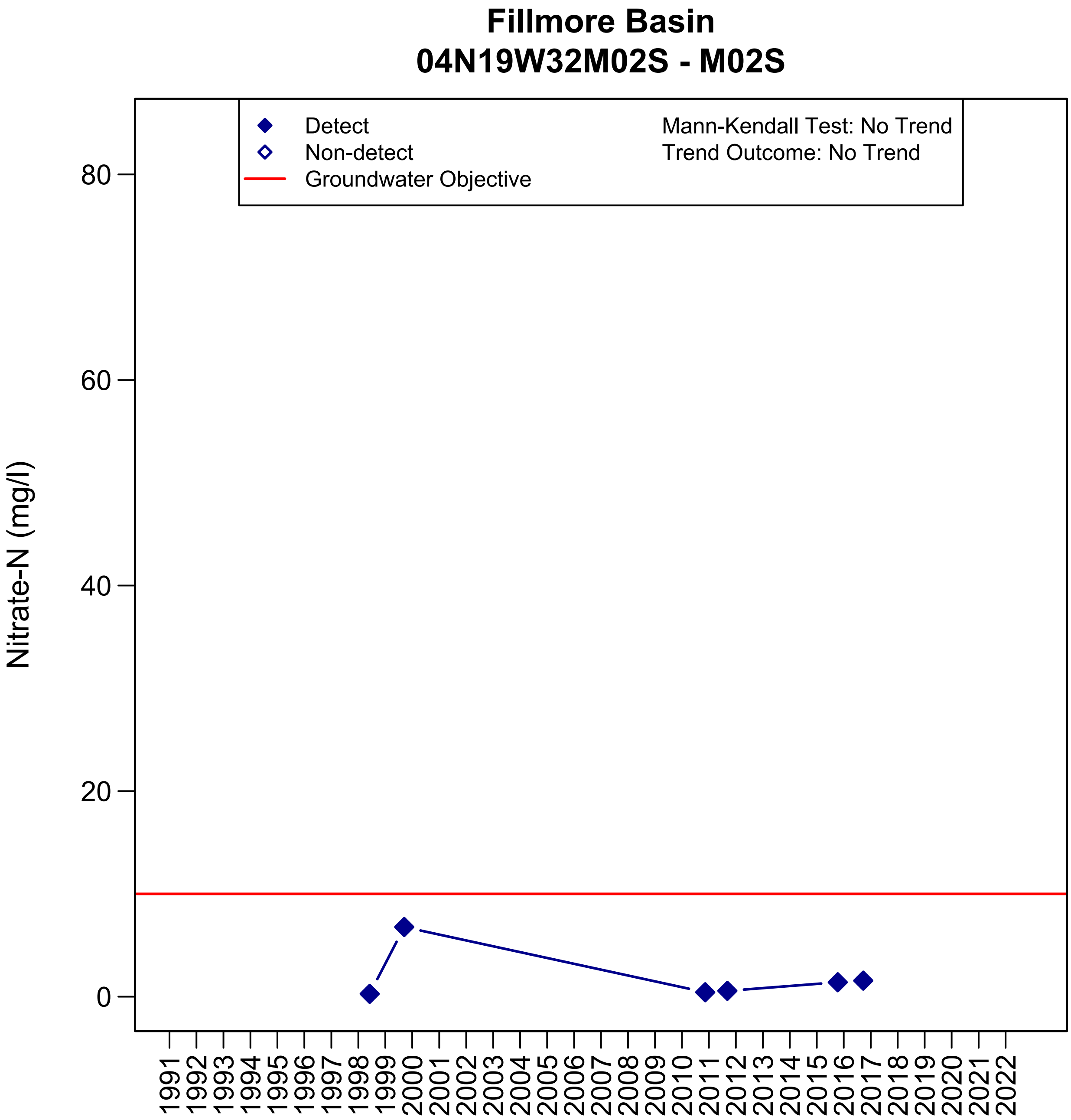

Fillmore Basin
04N19W32M02S - M02S
Detect
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Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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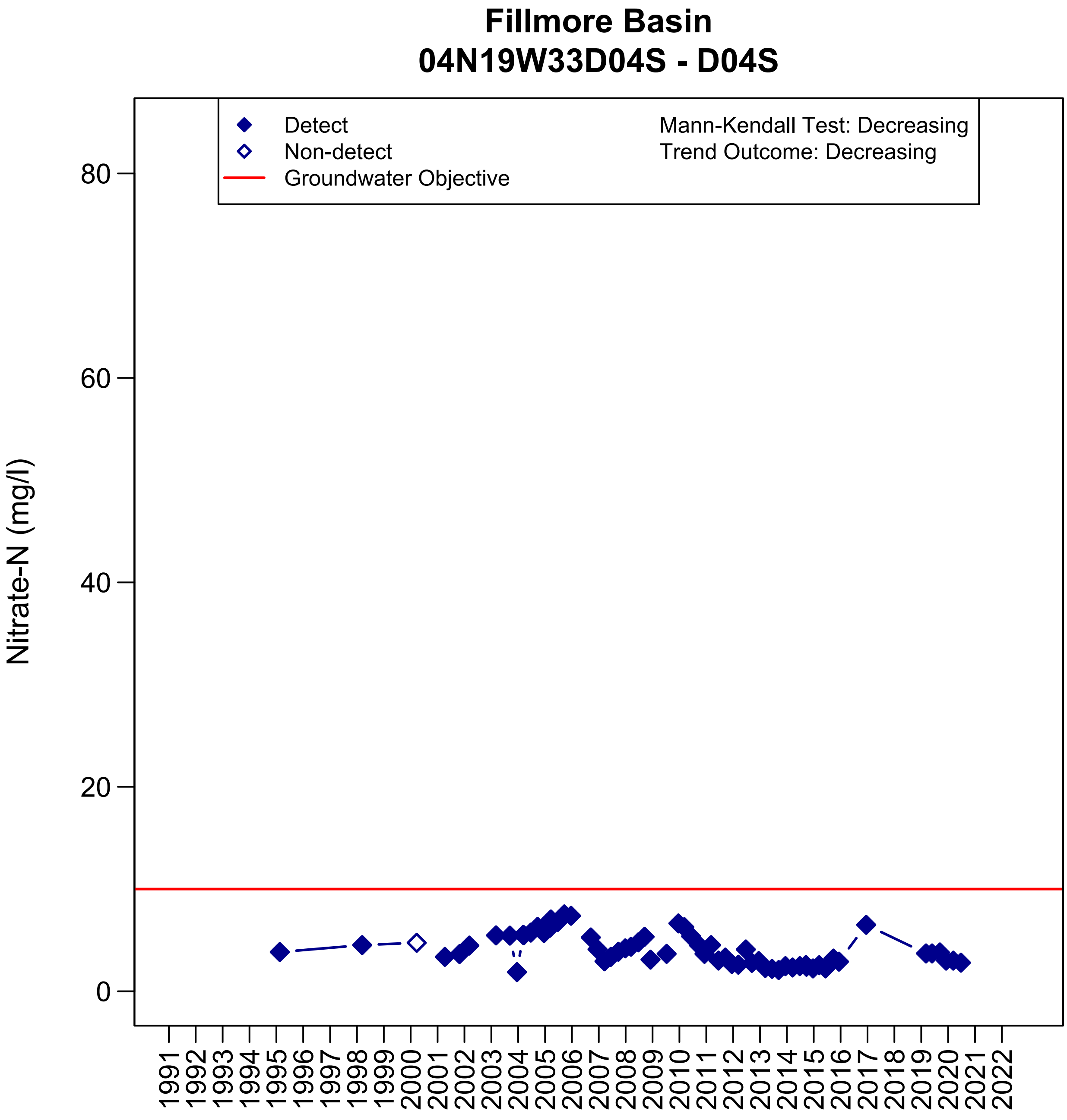

Fillmore Basin
04N19W33D04S - D04S
Detect
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Groundwater Objective
Mann-Kendall Test: Decreasing
Trend Outcome: Decreasing
Nitrate-N (mg/l)
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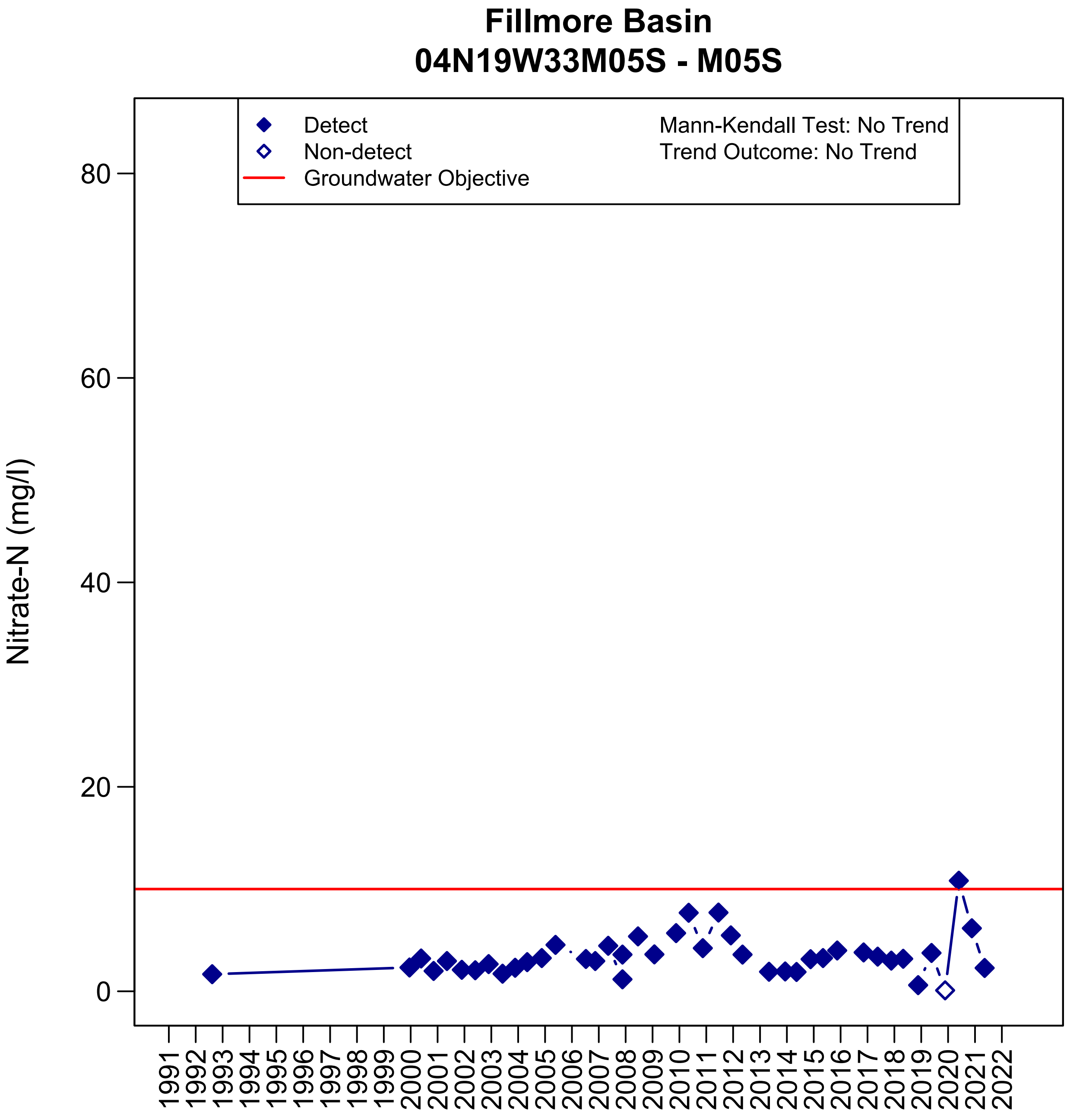

Fillmore Basin
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Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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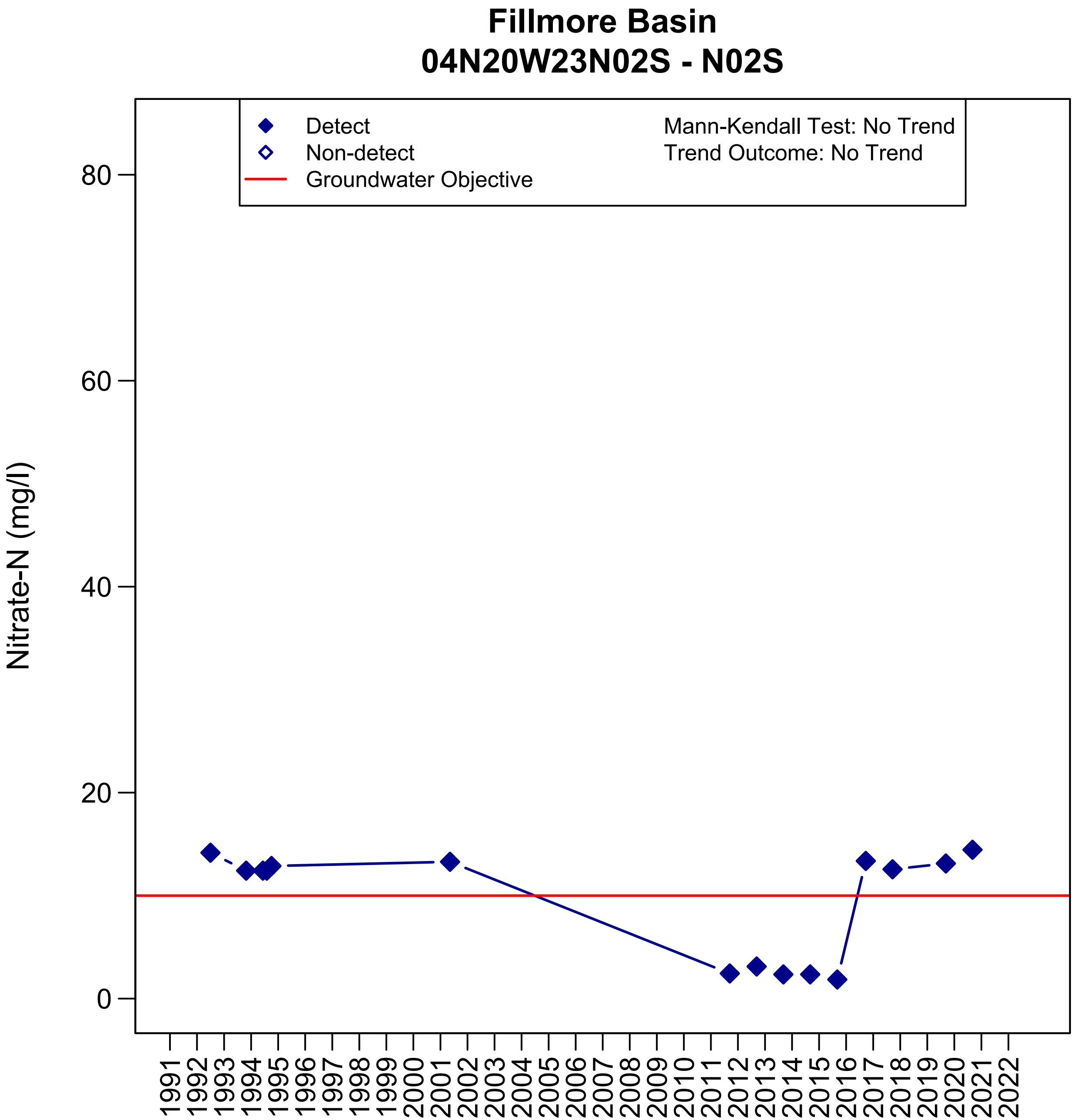

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Detect
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Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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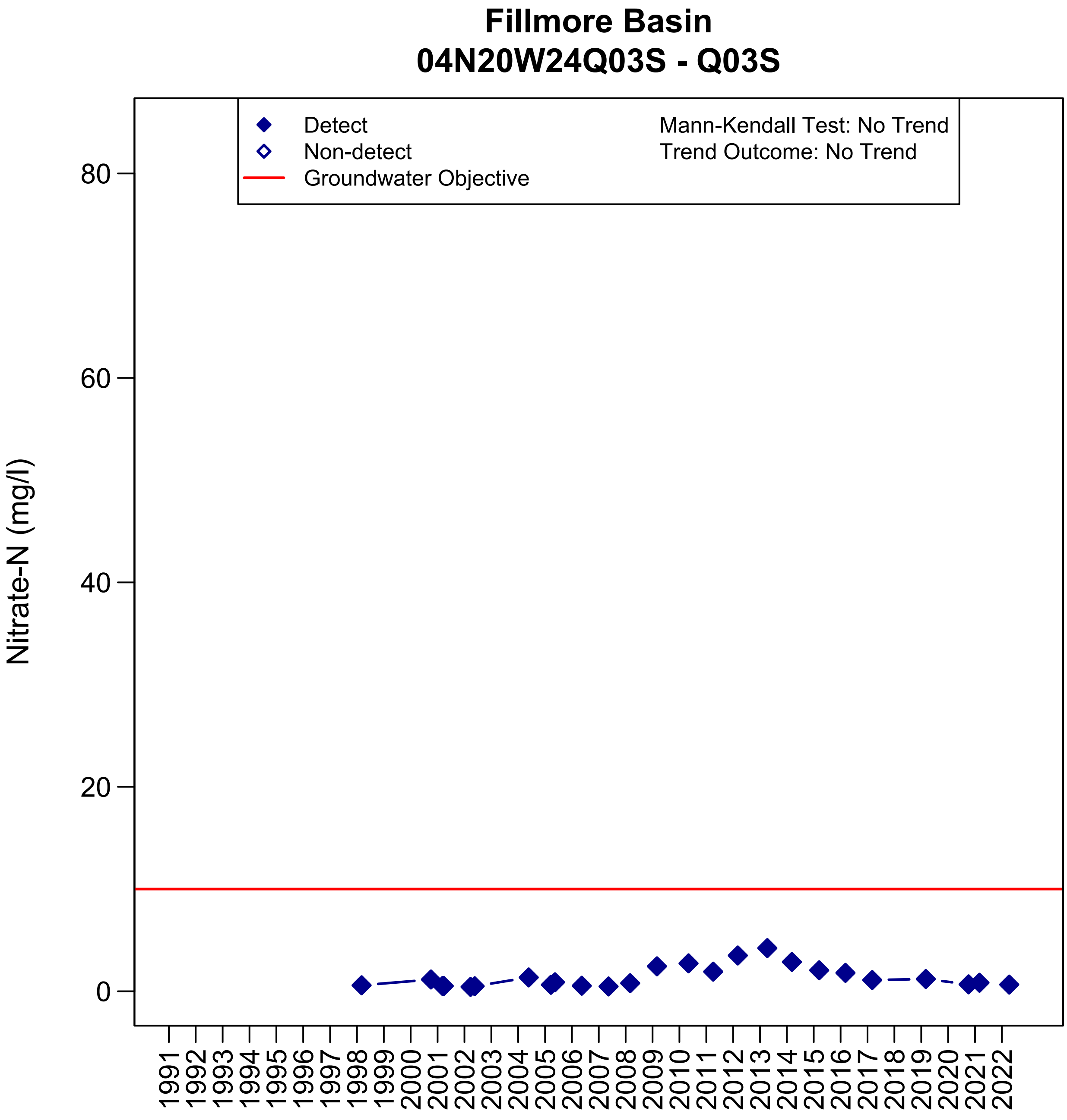
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Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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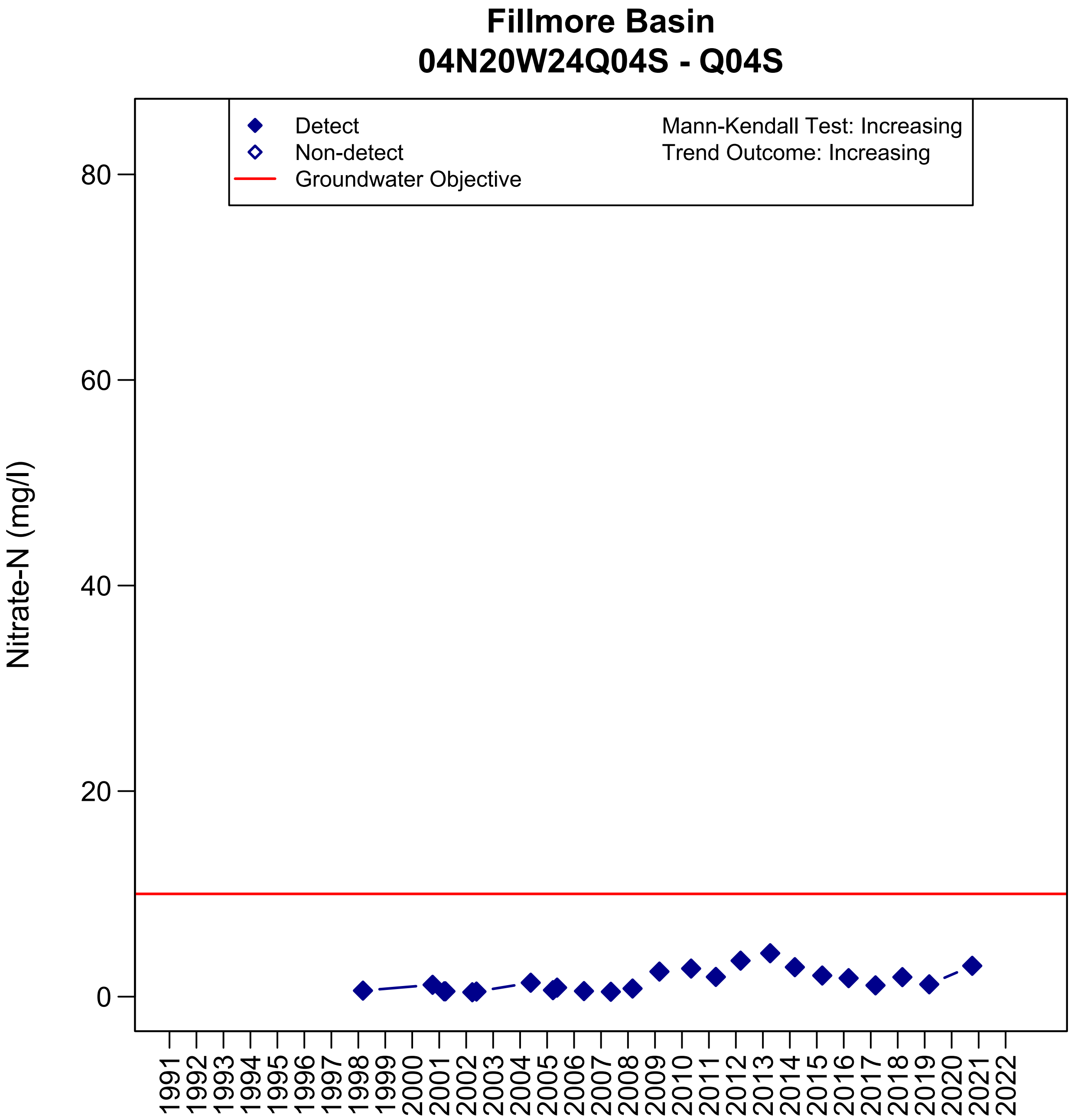
Fillmore Basin
04N20W24Q04S - Q04S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: Increasing
Trend Outcome: Increasing
Nitrate-N (mg/l)
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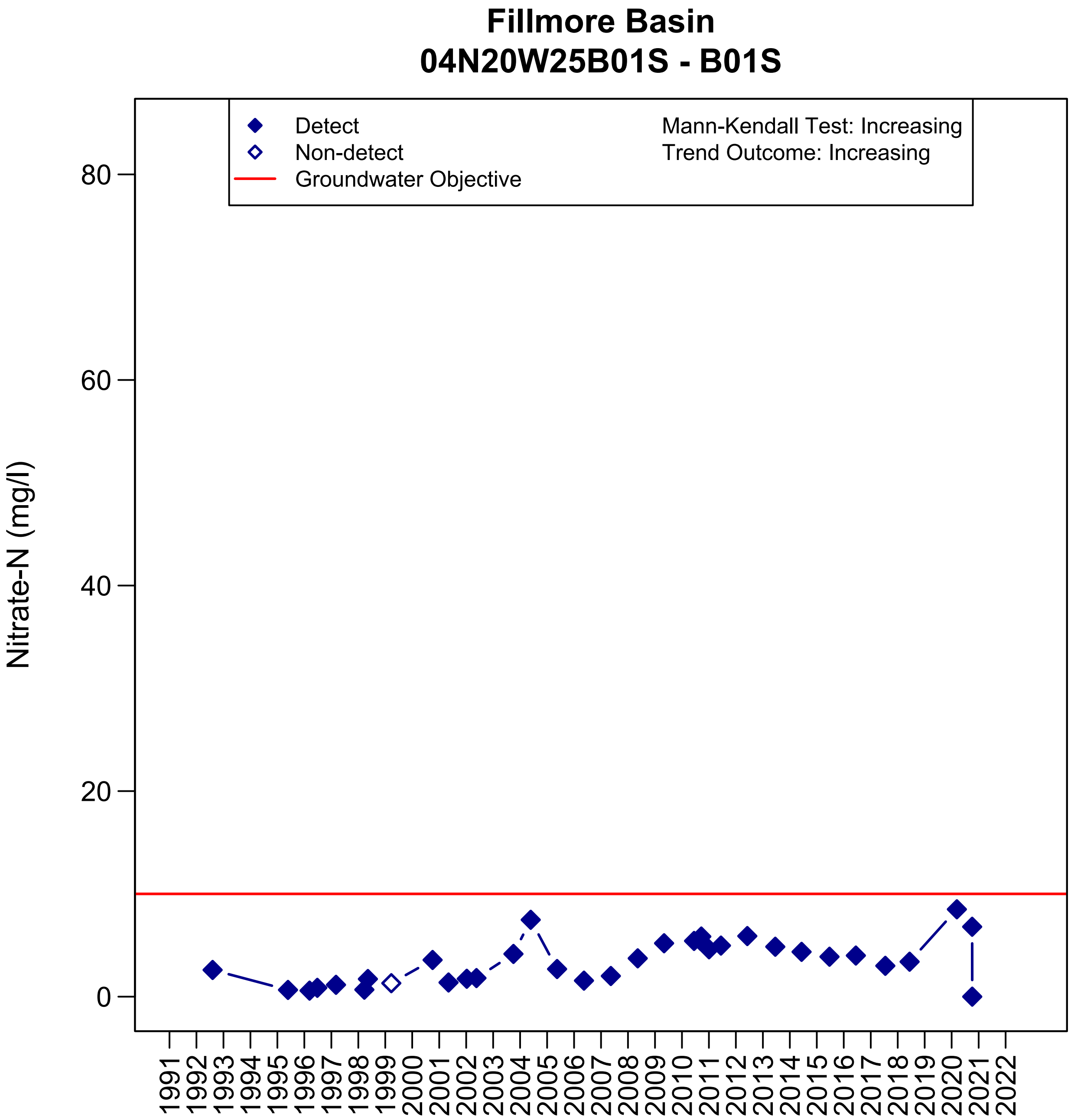
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Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: Increasing
Trend Outcome: Increasing
Nitrate-N (mg/l)
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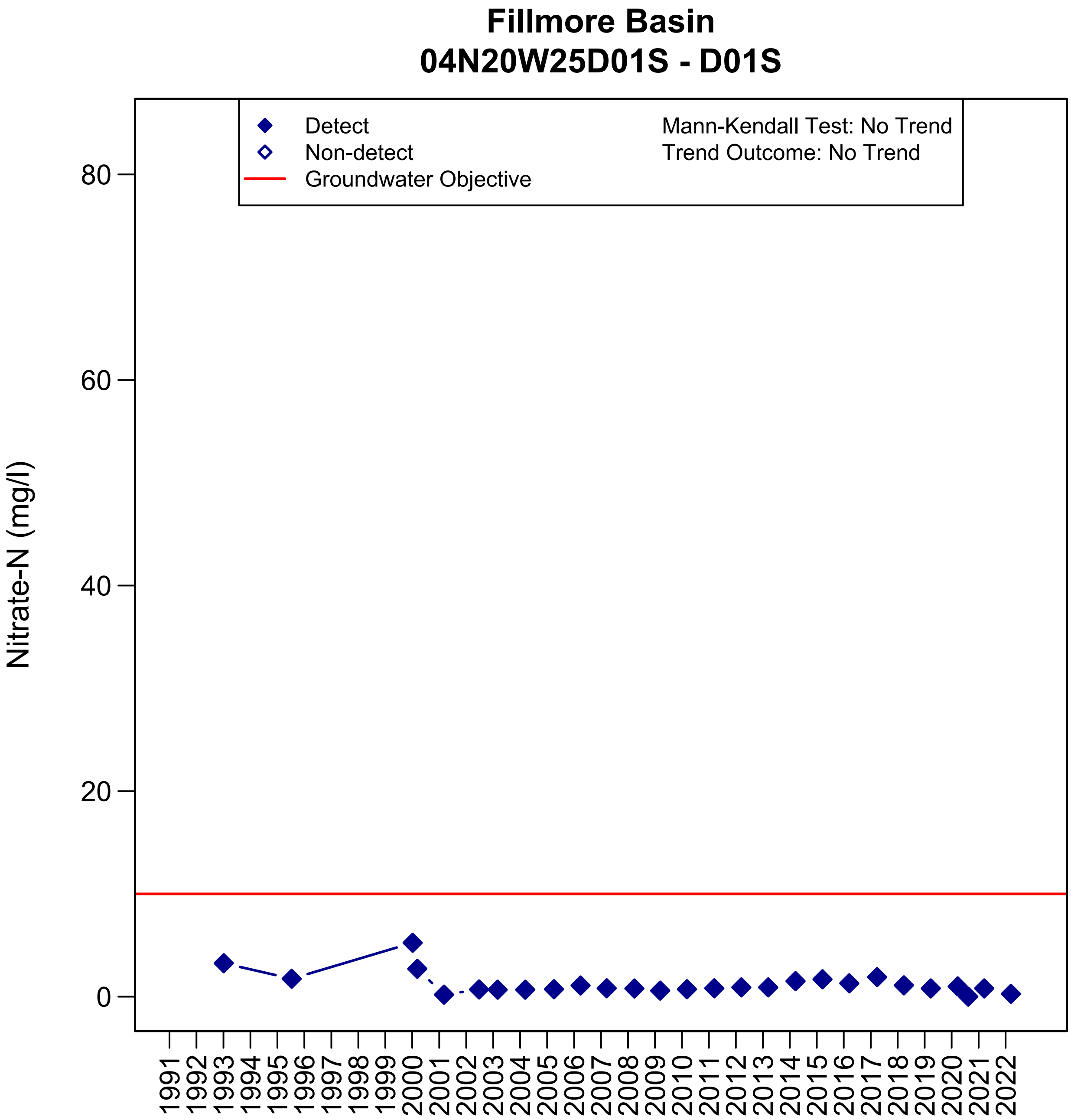

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Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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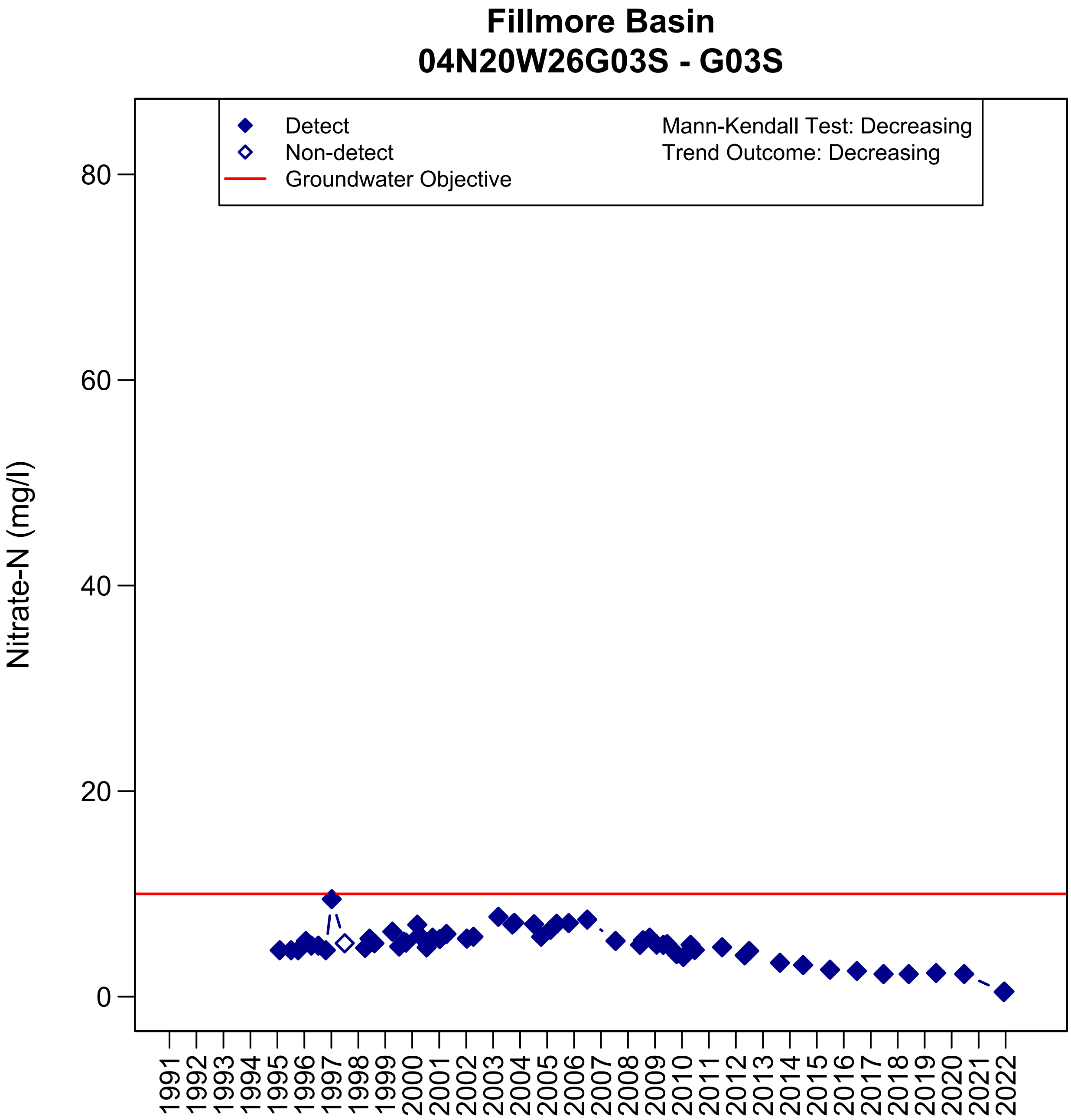
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Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: Decreasing
Trend Outcome: Decreasing
Nitrate-N (mg/l)
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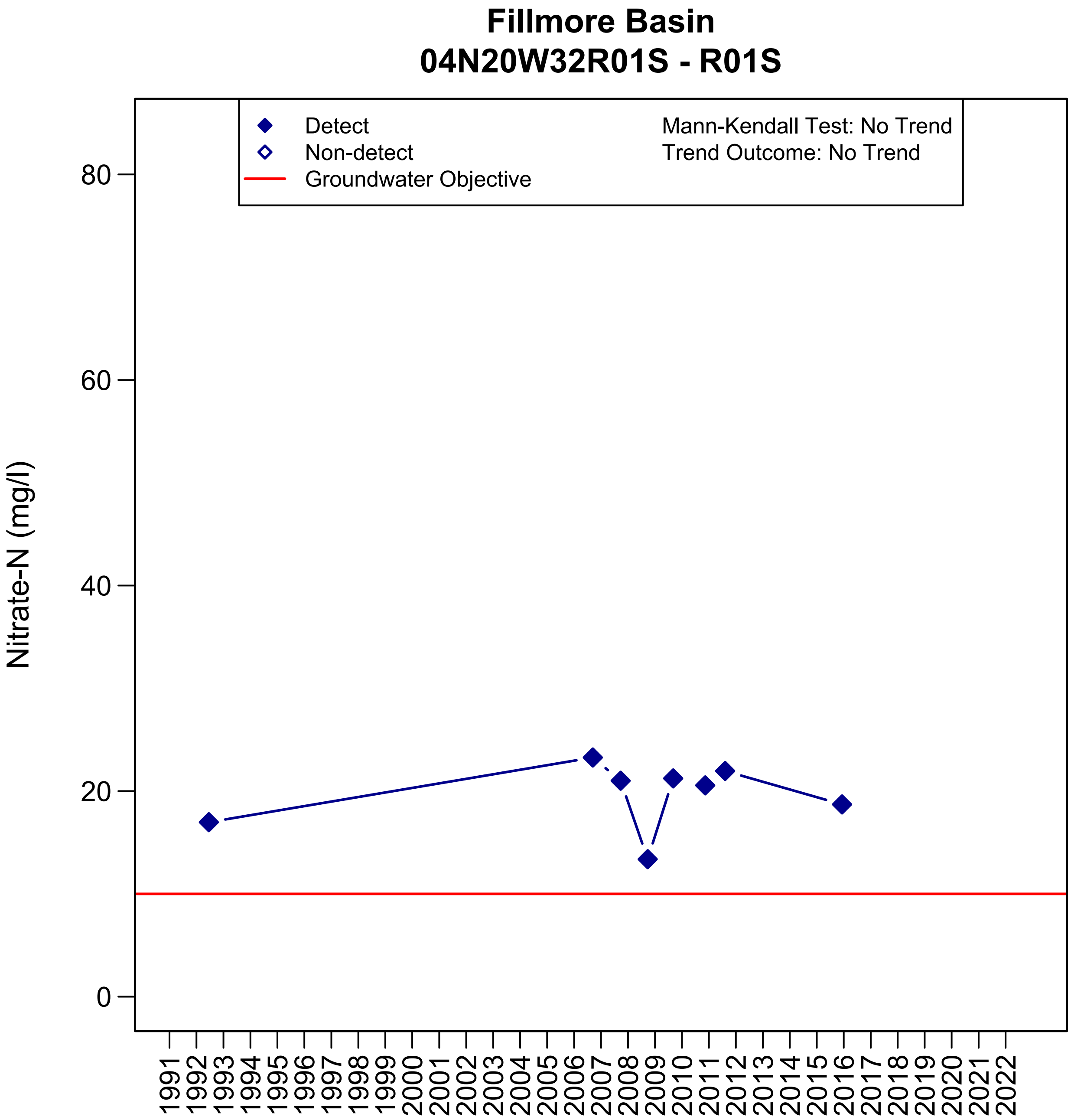
Fillmore Basin
04N20W32R01S - R01S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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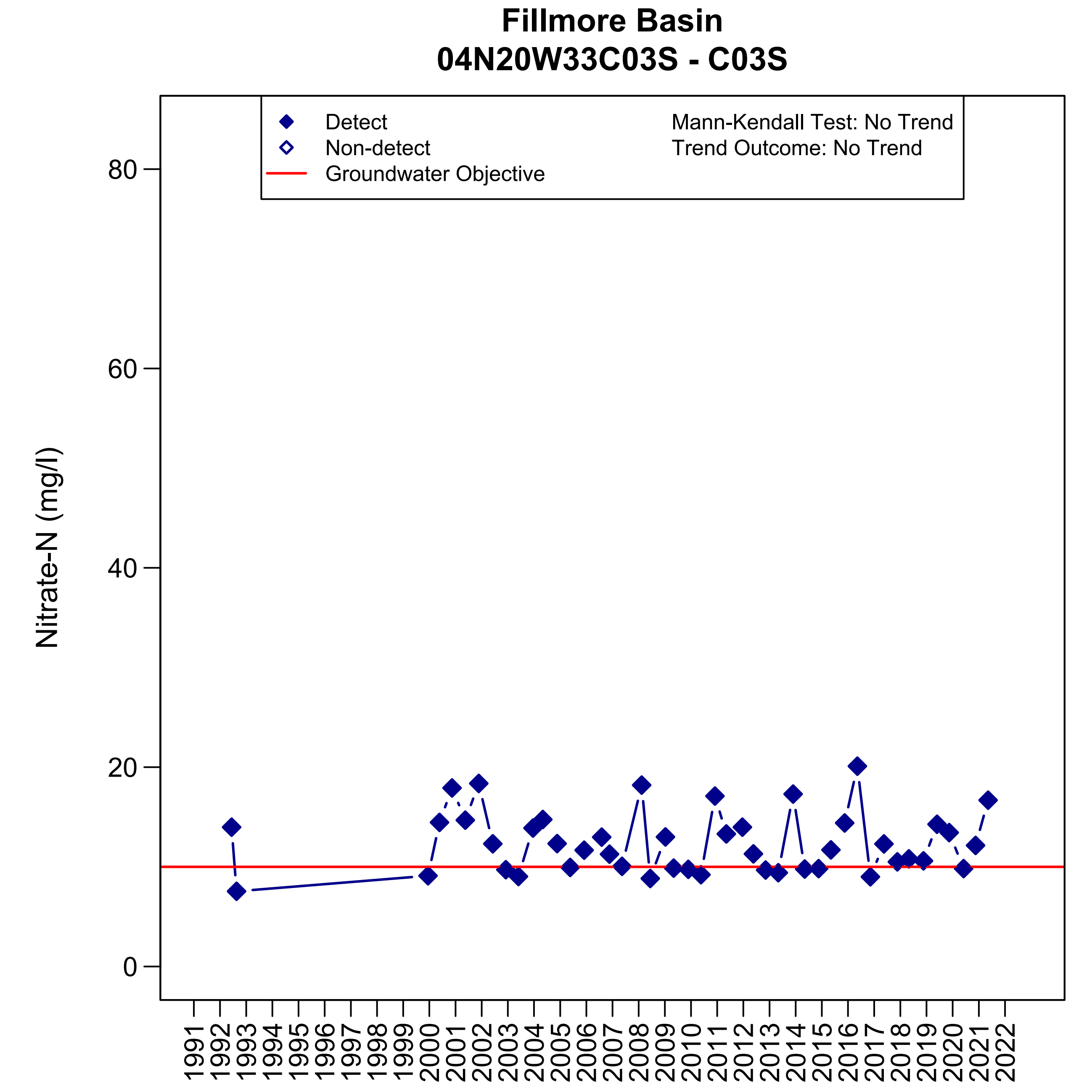
Fillmore Basin
04N20W33C03S - C03S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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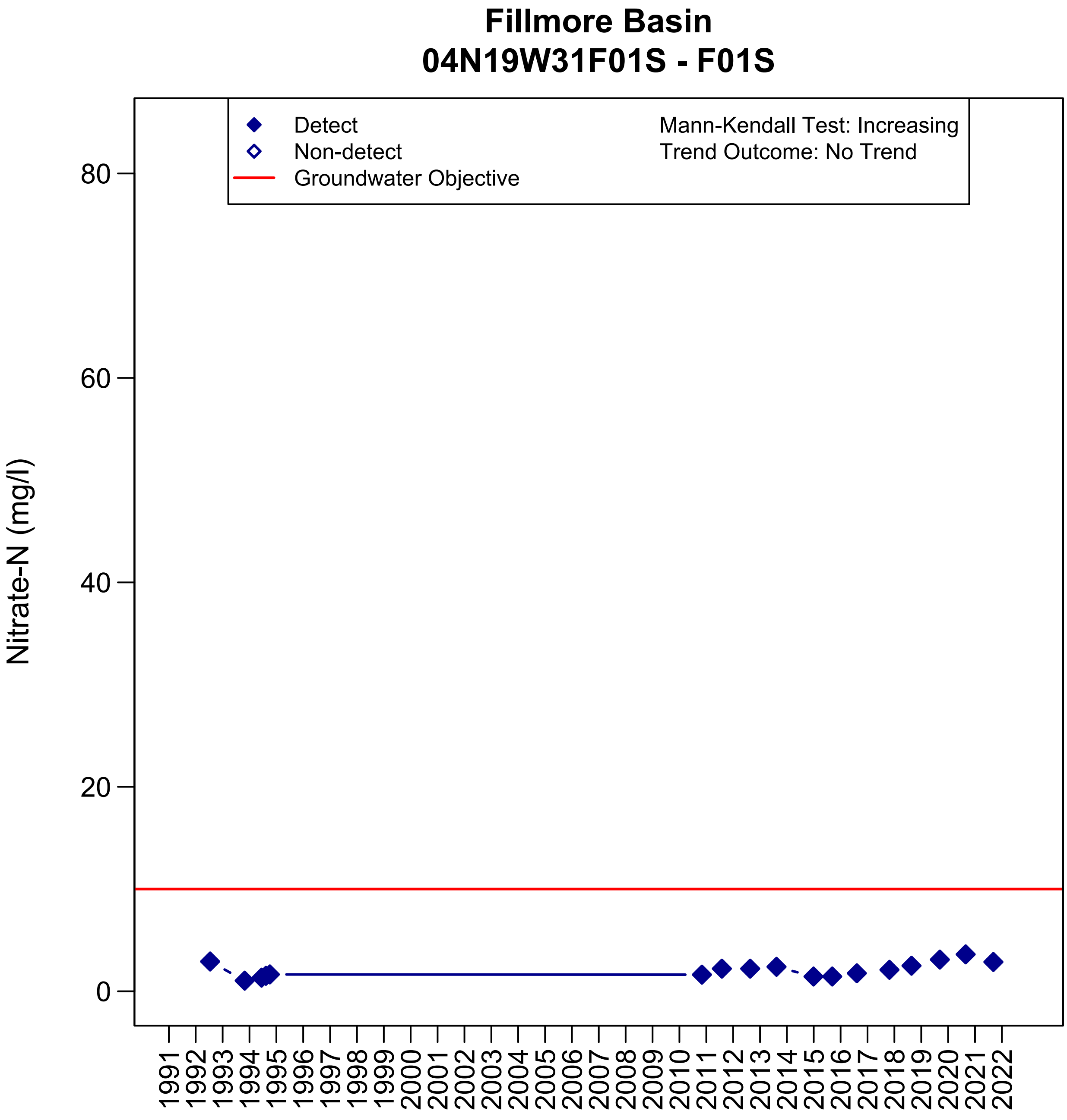
Fillmore Basin
04N19W31F01S - F01S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: Increasing
Trend Outcome: No Trend
Nitrate-N (mg/l)
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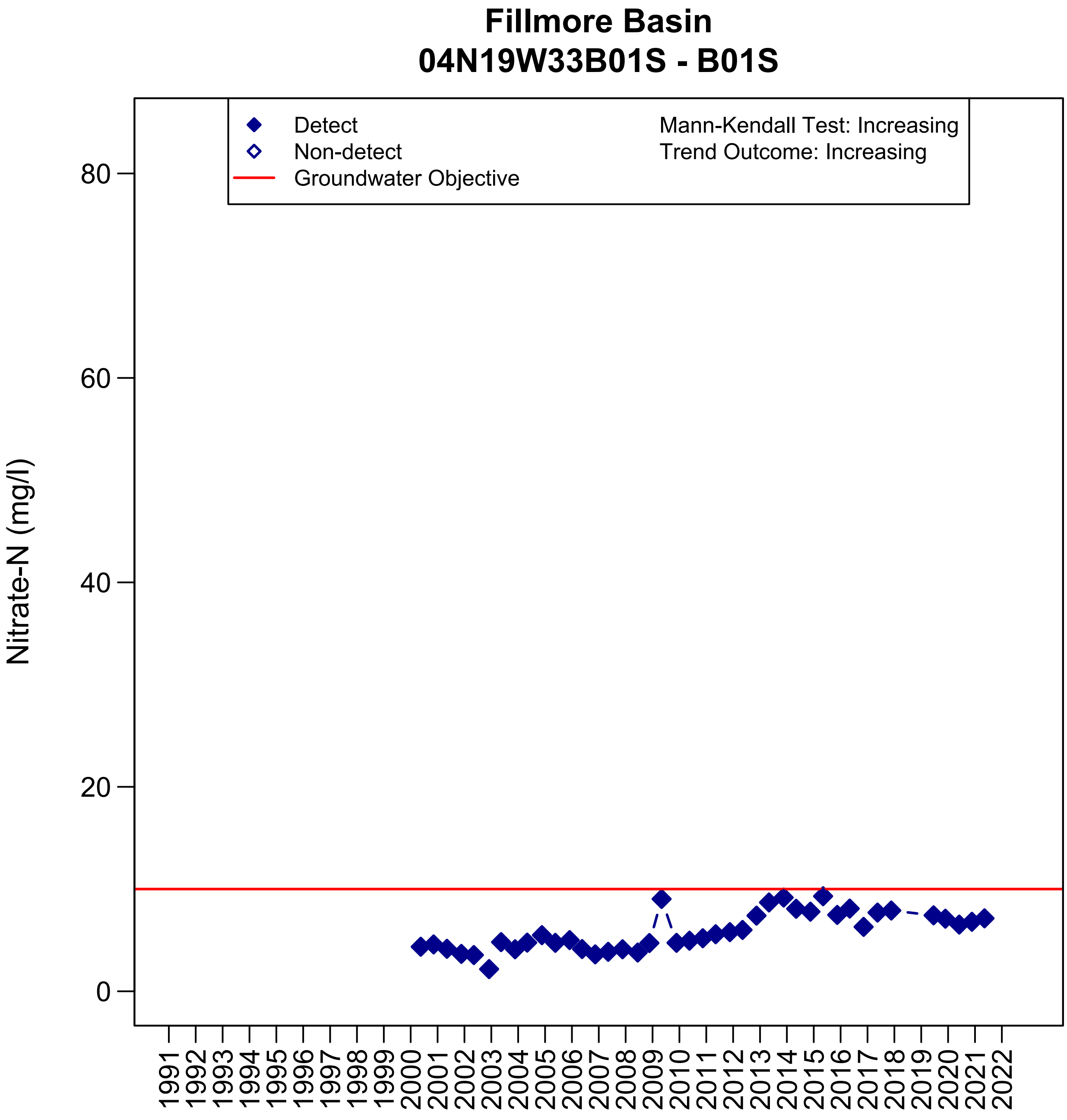

Fillmore Basin
04N19W33B01S - B01S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: Increasing
Trend Outcome: Increasing
Nitrate-N (mg/l)
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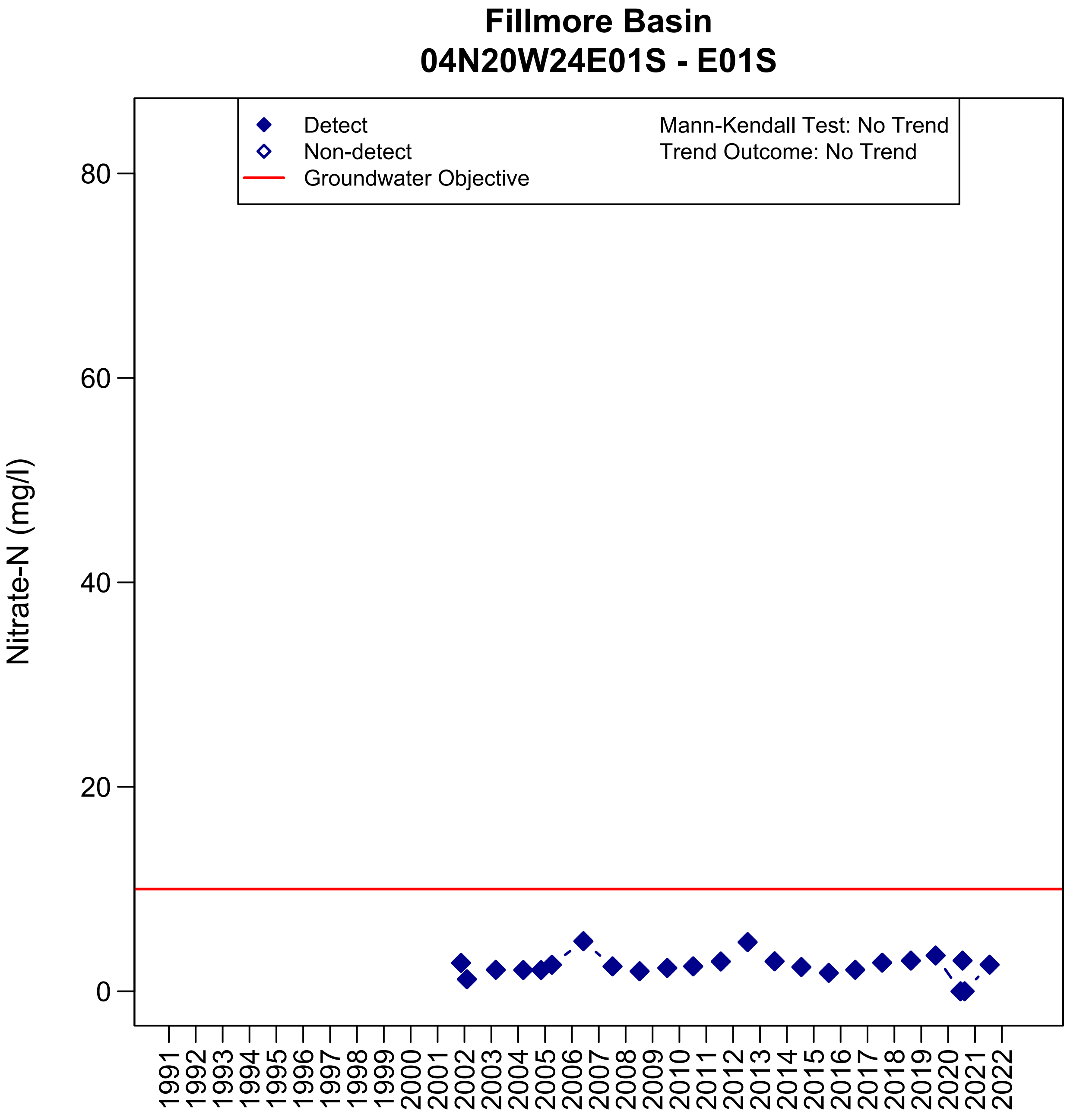

Fillmore Basin
04N20W24E01S - E01S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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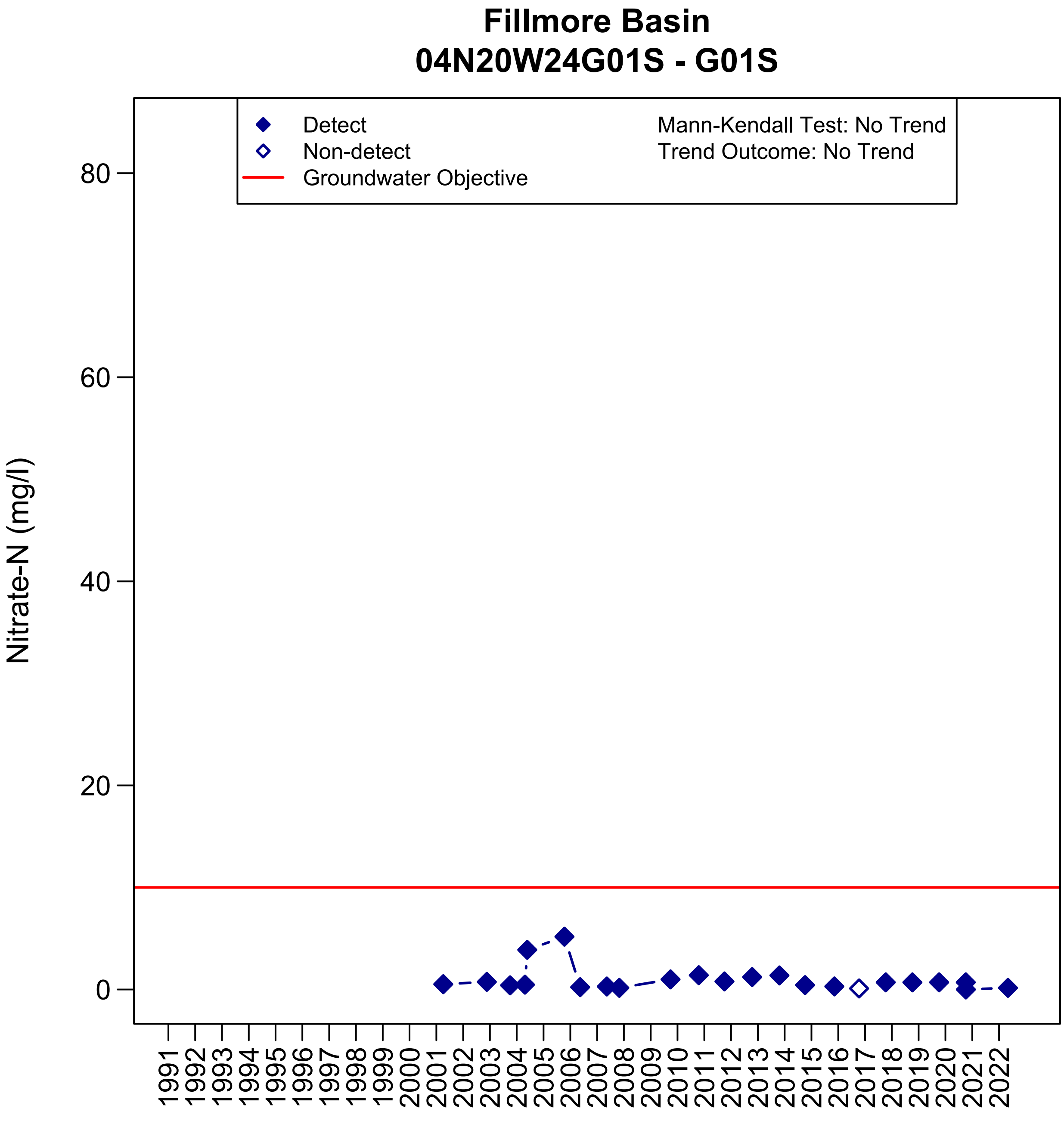
Fillmore Basin
04N20W24G01S - G01S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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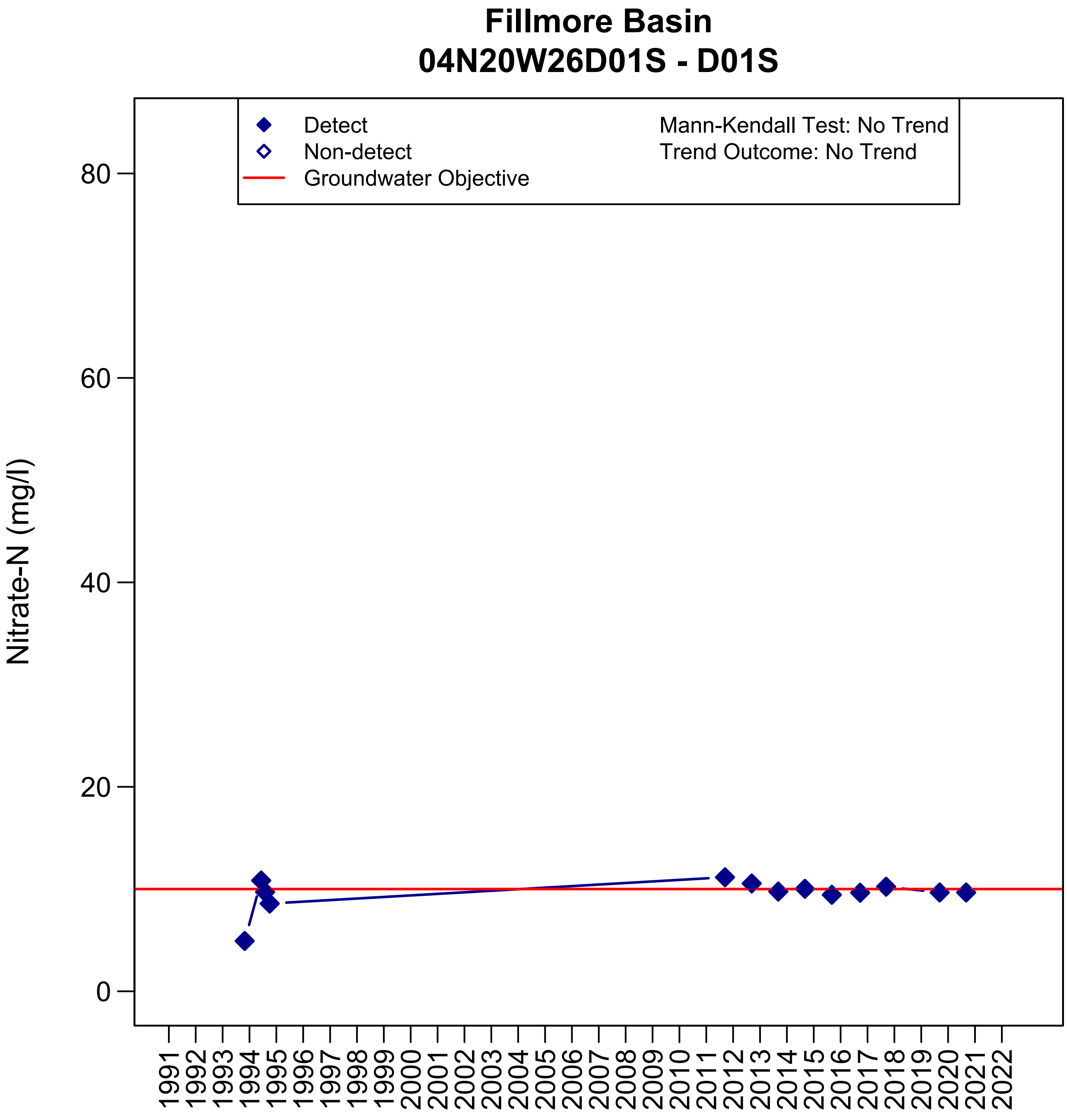
Fillmore Basin
04N20W26D01S - D01S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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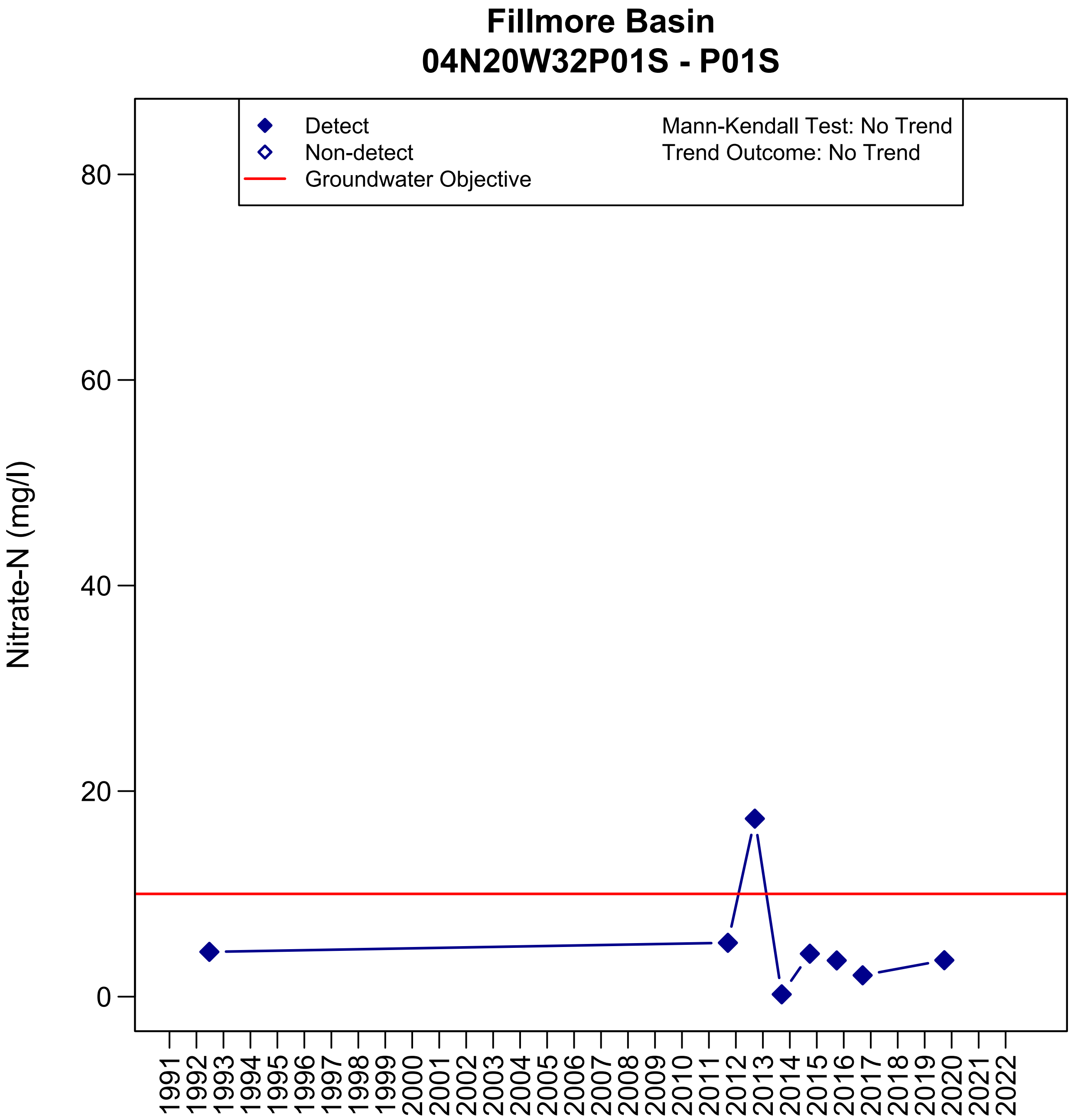

Fillmore Basin
04N20W32P01S - P01S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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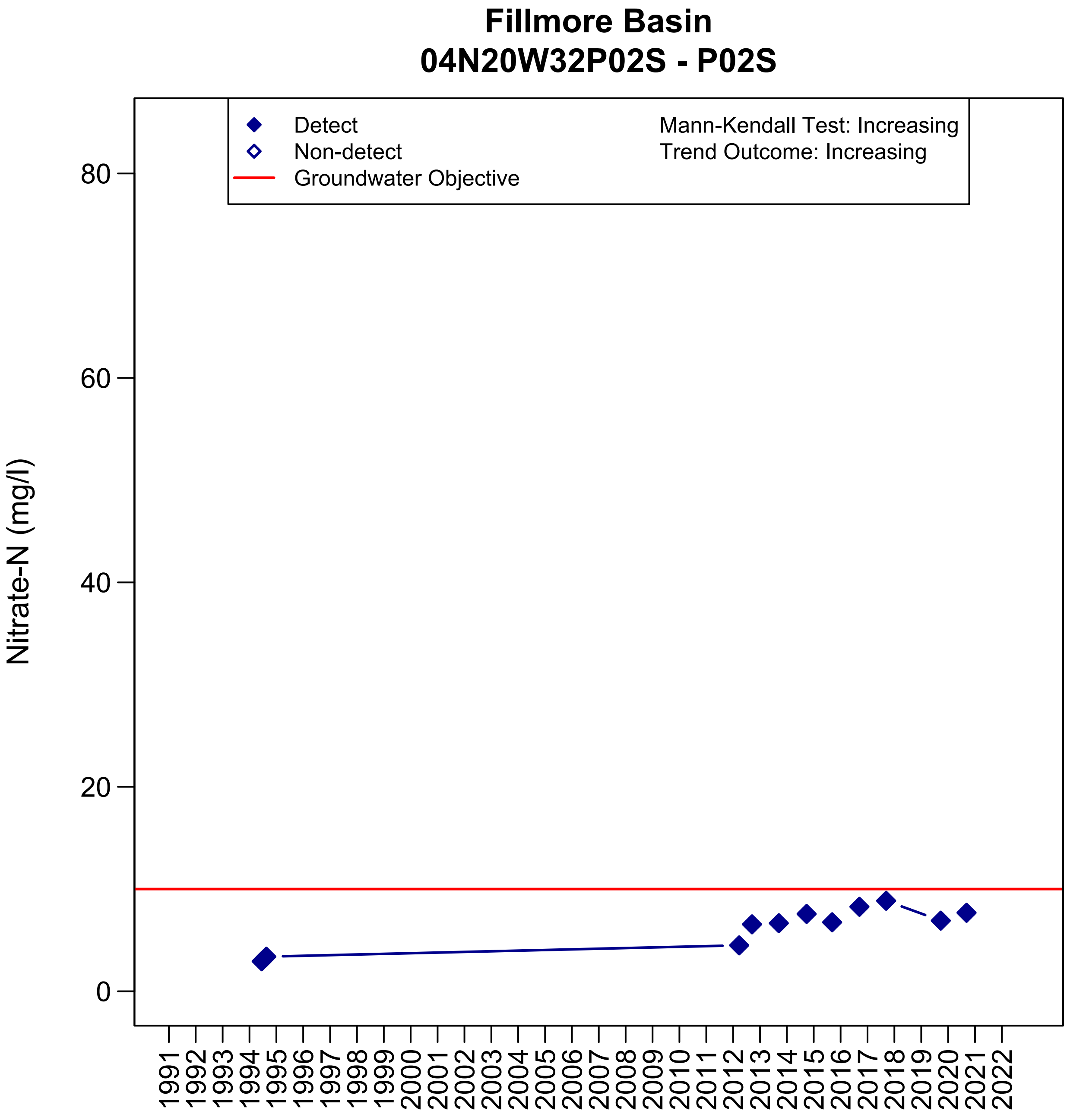

Fillmore Basin
04N20W32P02S - P02S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: Increasing
Trend Outcome: Increasing
Nitrate-N (mg/l)
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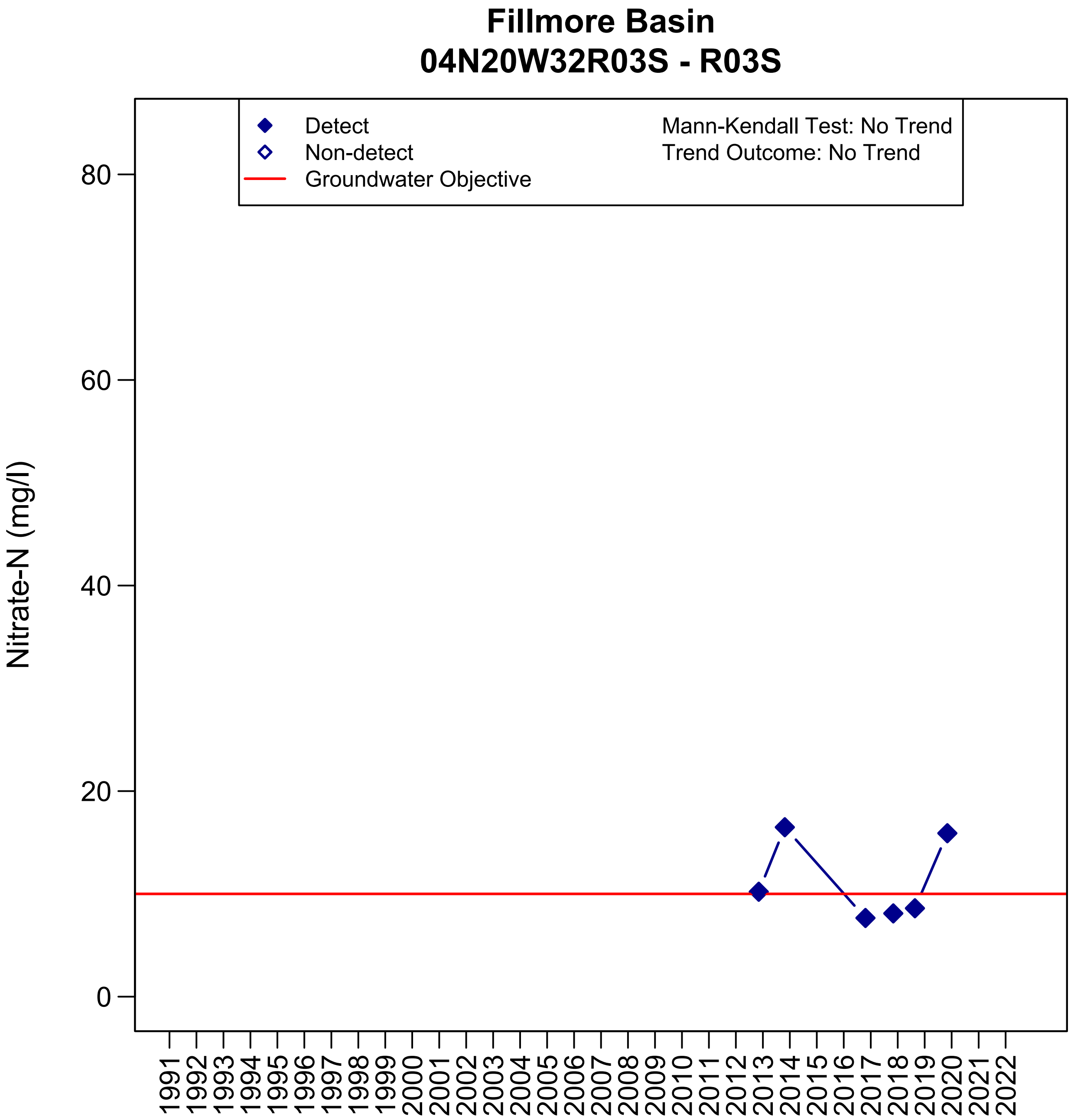
Fillmore Basin
04N20W32R03S - R03S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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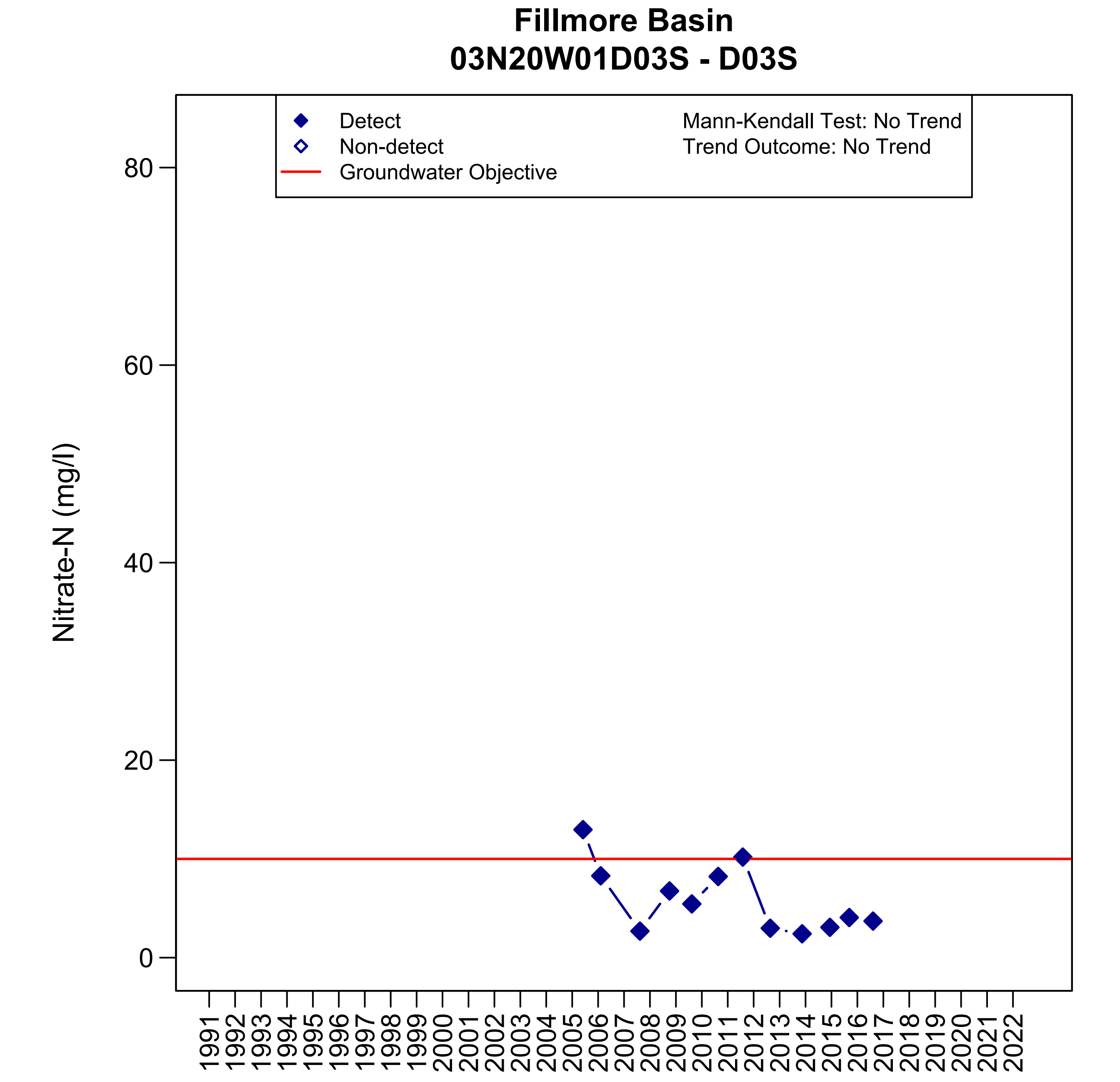

Fillmore Basin
03N20W01D03S - D03S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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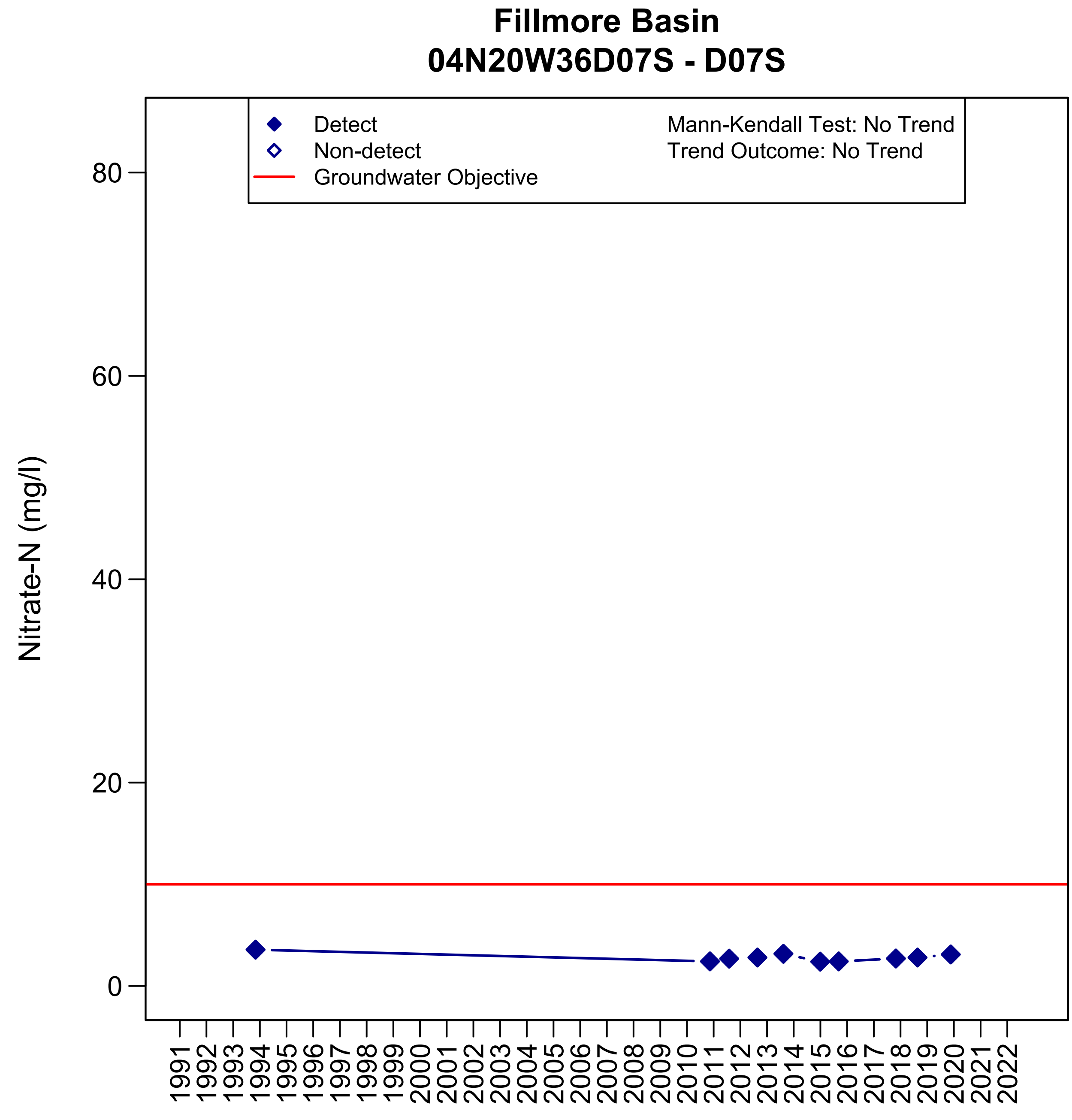

Fillmore Basin
04N20W36D07S - D07S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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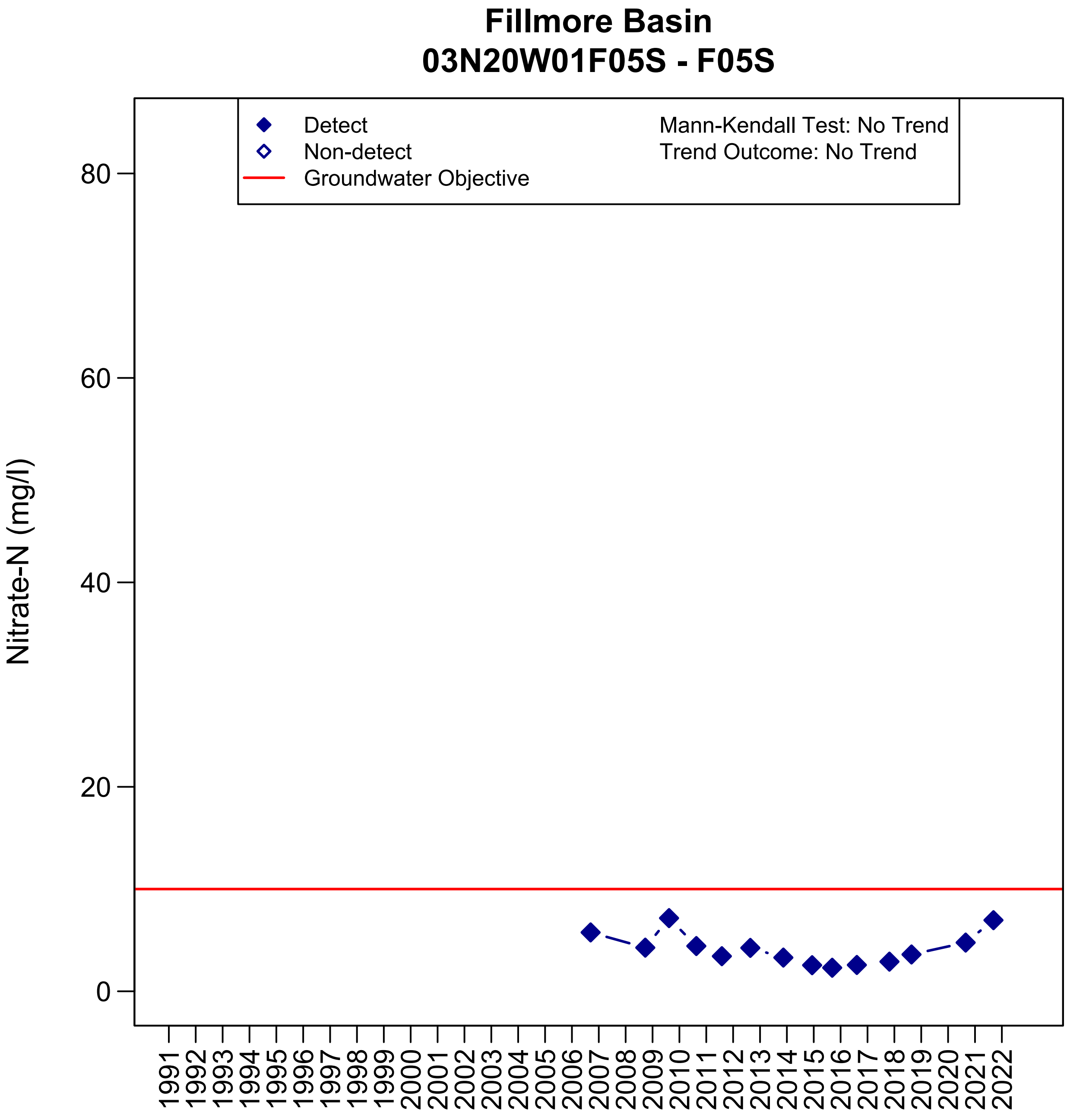
Fillmore Basin
03N20W01F05S - F05S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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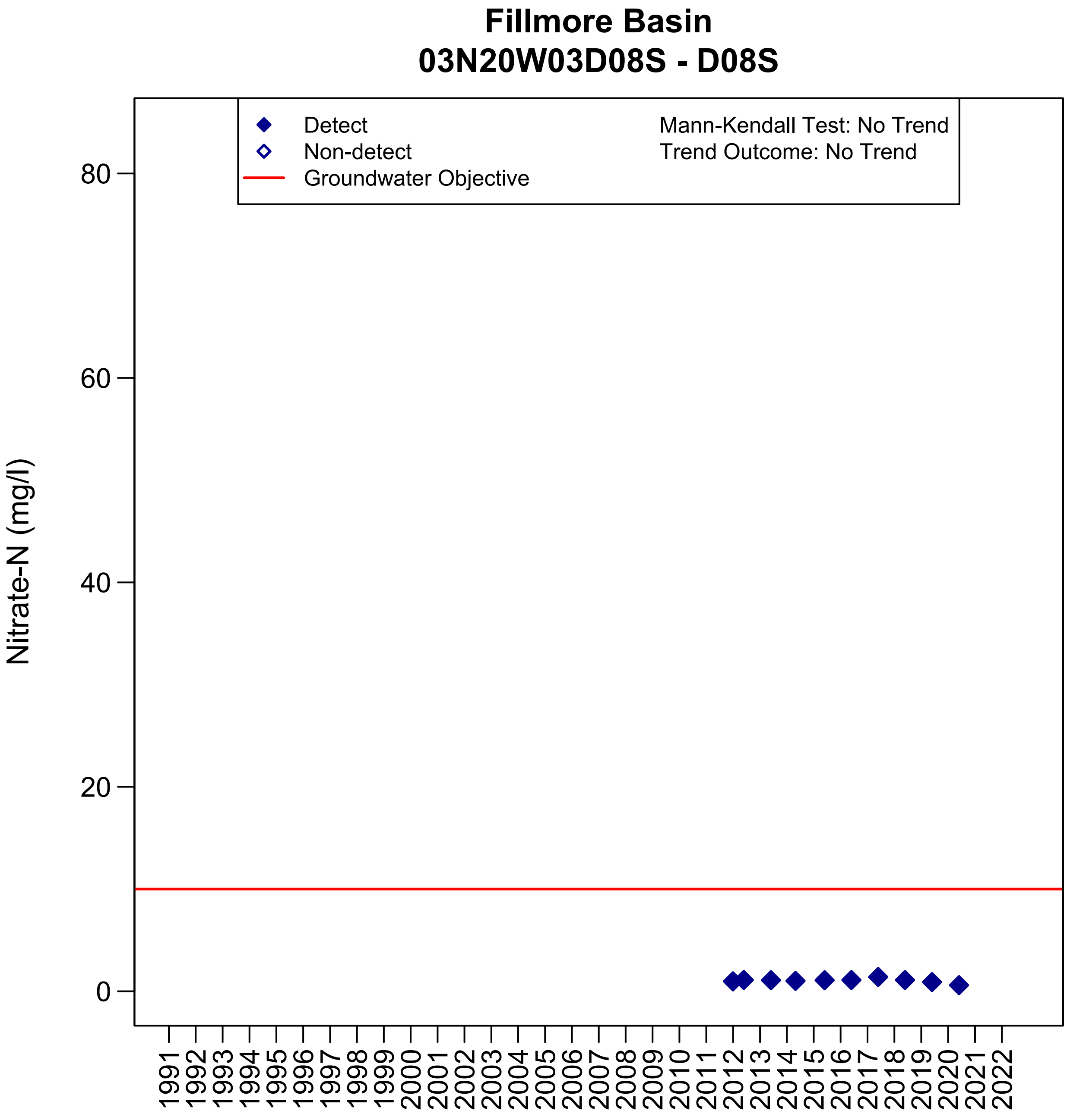

Fillmore Basin
03N20W03D08S - D08S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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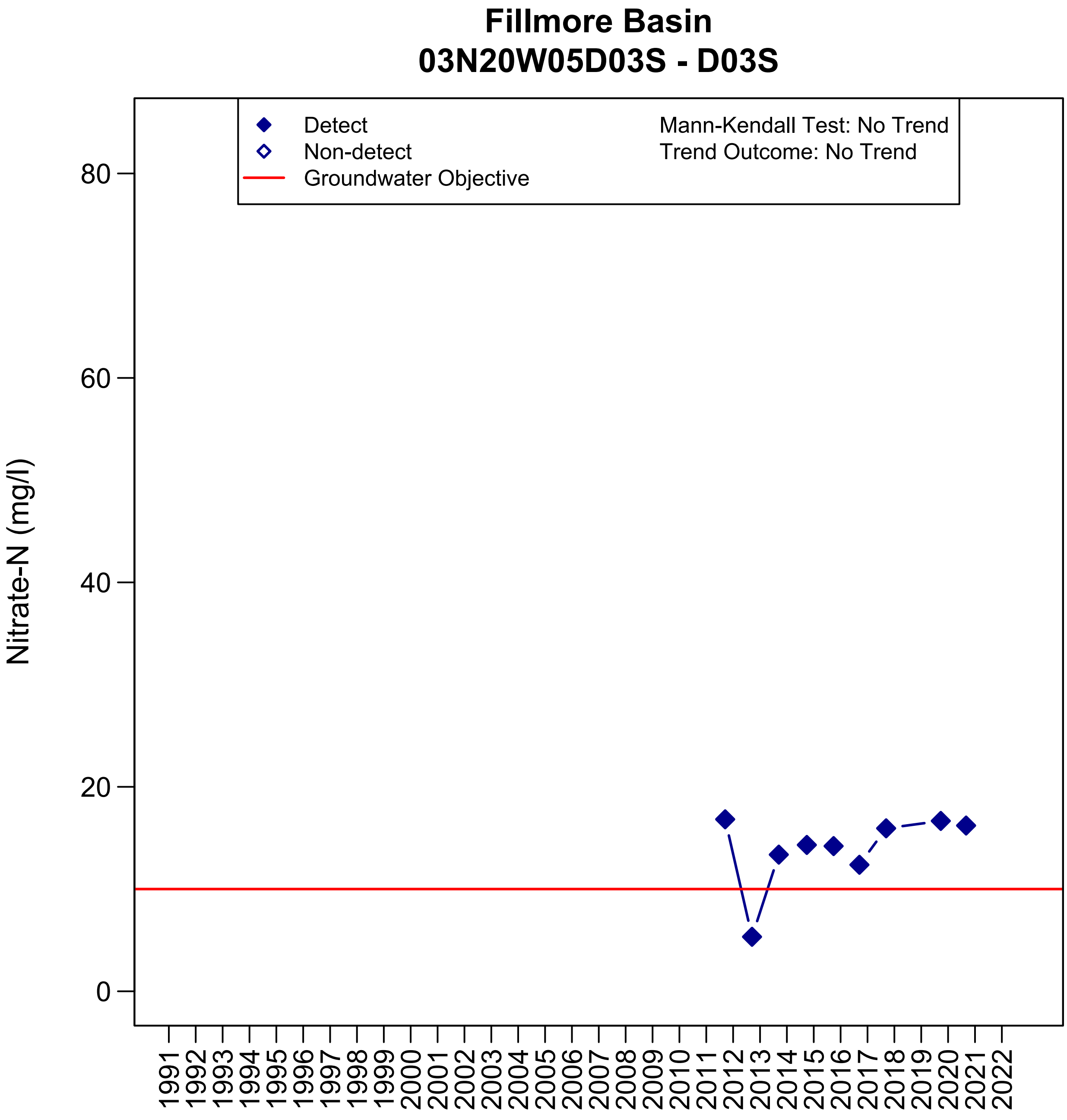

Fillmore Basin
03N20W05D03S - D03S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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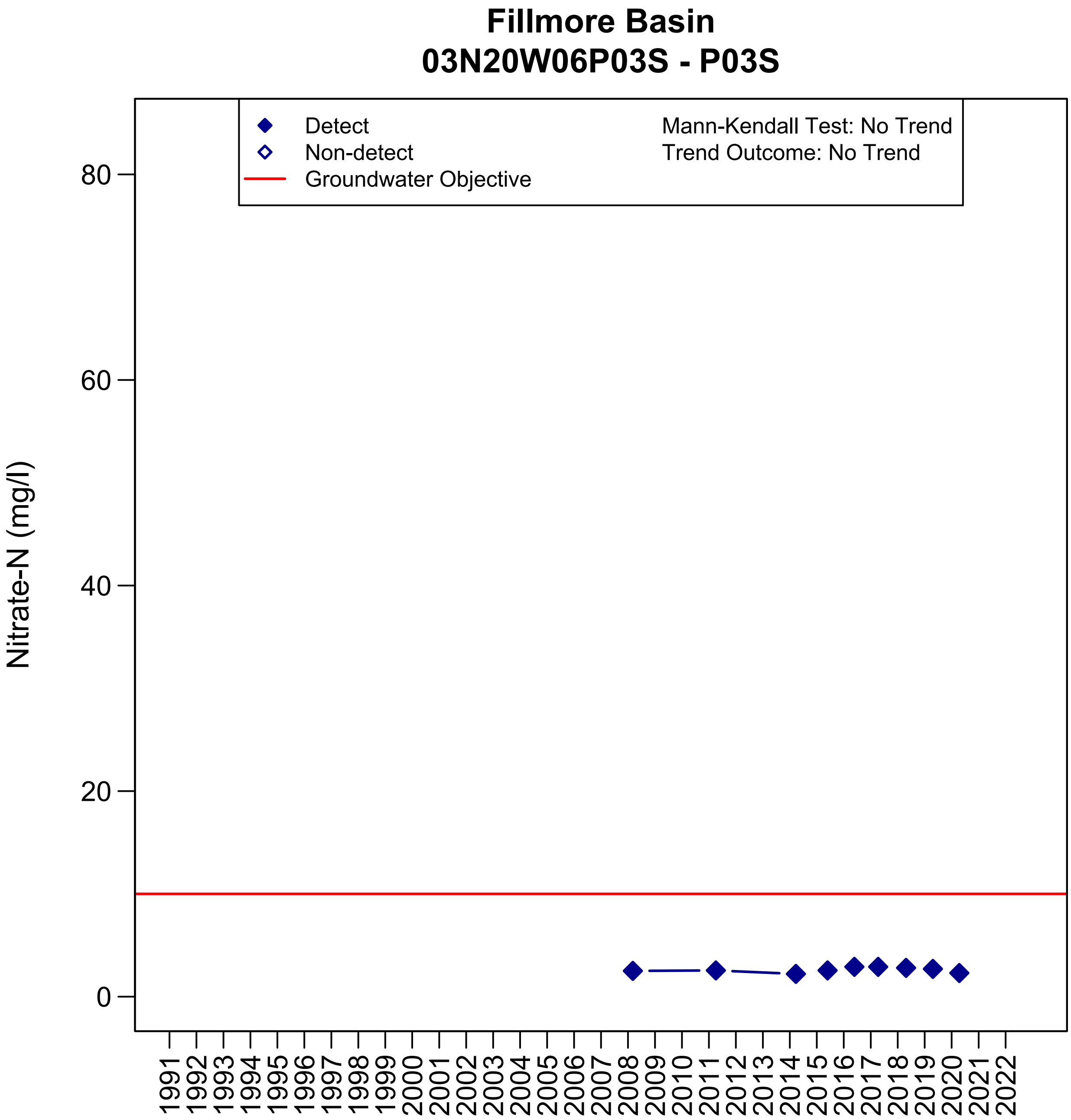

Fillmore Basin
03N20W06P03S - P03S
Detect
Non-detect
Groundwater Objective
Mann-Kendall Test: No Trend
Trend Outcome: No Trend
Nitrate-N (mg/l)
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