

US EPA ARCHIVE DOCUMENT

**CHARACTERIZING THE SHORT-TERM TEMPORAL STABILITY OF
VOLATILE ORGANIC COMPOUNDS IN STAINLESS STEEL
CANISTERS USING PROFICIENCY TEST SAMPLES PREPARED FOR
THE NATIONAL AIR TOXICS TRENDS STATIONS NETWORK**

Revised Final Report

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Note

This report has been revised from the original (date April 3, 2013) so as to redact the names and locations of the participating laboratories.

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Executive Summary

Results are reported here on the investigation of the short-term temporal stability of trace-level concentrations of various volatile organic compounds (VOCs) collected in stainless steel canisters. To perform this work, laboratories participating in the National Air Toxics Trends Stations (NATTS) proficiency test program during the 1st quarter of calendar year 2013 were requested to perform three distinct analyses to measure the concentrations of VOCs in their PT sample canister. The first analysis occurred approximately seven days after the preparation of the PT sample, with each subsequent analysis targeted to occur approximately seven calendar days thereafter. The intent was to discern, by way of statistical analysis, the temporal trend in VOC recovery (if any) on a compound-specific basis in these three temporal replicate analyses within each participating laboratory so that the presence of any overall trend across all participating laboratories could be determined. Moreover, the effects of two specific variables on VOC recoveries, canister pressure at the time of analysis and canister type, were investigated.

The following observations and outcomes are reported:

- A total of 15 VOCs were measured, including acrolein, benzene, and tetrachloroethylene, among others.
- A total of 25 participating laboratories returned results.
 - Temporal trends could be assessed for at least some of the VOCs analyzed by 18 of these labs.
- For none of the 15 VOCs was the average percent change in VOC recovery over time across labs statistically significantly less than 0, indicating that there is insufficient evidence to conclude that VOC recoveries decreased over the approximately 30 days that elapsed during this study.
- For none of the 15 VOCs was a statistically significant difference observed in the percent change in concentration over time between canisters whose pressures were reduced compared to those canisters whose pressures were not reduced. There is insufficient evidence from these data that canister pressure at the time of analysis has an effect on VOC recovery over time.
- For none of the 15 VOCs was a statistically significant difference observed in the percent change in VOC concentrations over time between canister types. There is insufficient evidence from the study data that canister type has an effect on VOC recovery over time.
 - While some patterns in average percent change in VOC concentrations over time were noted between the two canister types (with the average percent change more likely to be positive for Summa canisters, and more likely to be negative for FSL canisters), these patterns were not statistically significant.

Although all three temporally-separated replicate canister analyses were requested to be completed within roughly a two-week period upon receipt of the canister at the participating laboratory, the actual total elapsed time between sample preparation and the final replicate analysis was occasionally as much as 30 days. From one-half to two-thirds of the laboratories showed no consistent decrease or increase in VOC concentrations across the three temporally-separated replicate analyses. For most of those remaining laboratories where a consistent decrease or increase in VOC concentrations was observed, the total change was typically within 25% of the target concentration for the given compound (i.e., within the acceptance limits for NATTS PT samples), and the change was about equally divided among laboratories with a decreasing trend and those with an increasing trend. Overall, the data generated by this study did not conclusively demonstrate that recoveries of VOCs collected in stainless steel canisters vary over time periods of about 30 days.

1. Introduction

Since 2003, EPA has operated the National Air Toxics Trends Stations (NATTS) ambient air monitoring program. This program generates long-term, quality assured, standardized ambient air toxics data that can be used to:

- Establish trends and evaluate the effectiveness of EPA's air toxics emissions reduction strategies;
- Characterize ambient concentrations/deposition of priority air toxics in local areas;
- Support, evaluate, and improve air quality models, and as input to source-receptor models; and
- Support scientific studies to better understand the relationship between ambient air toxics concentrations, human exposure, and health effects from these exposures.

Air samples collected in the NATTS network are analyzed at laboratories across the U.S., and EPA, as part of the NATTS Quality System, has mandated that NATTS laboratories analyze single-blind, proficiency test (PT) samples in order to provide a quantitative assessment of laboratory bias, i.e. the difference between a lab's result and a known 'true' target value. For the NATTS program the maximum acceptable bias, defined as the percent difference from the assigned true value, is 25%.

On a quarterly basis, Battelle prepares and distributes the PT samples to participating laboratories for determination of analytical bias.¹ The type of PT sample prepared (VOCs, carbonyls, metals, hexavalent chromium, polycyclic aromatic hydrocarbons [PAHs]) follows a pre-determined, cyclical schedule. Each participating laboratory has an obligation to perform a single analysis of the PT sample that it receives and report that result back to Battelle and EPA. As a result, the reported PT data are sufficient only for assessing trends in laboratory bias across PT cycles; trends in short-term temporal stability of spiked compounds cannot be assessed. For analytes such as VOCs collected in stainless steel canisters and analyzed by cryogenic preconcentration gas chromatography mass spectrometry (GC/MS) per Compendium Method TO-15 (US EPA, 1999), previous work (Kelly and Holdren, 1995) has shown many VOCs (e.g., benzene, tetrachloroethylene) to be relatively stable at trace (ppb) levels over 30 days, the maximum hold time specified in Method TO-15. However, EPA has recently promulgated guidance that VOC samples should be analyzed for acrolein "as soon as reasonably possible" following collection, indicating that its temporal stability is less than optimal (US EPA, 2010). Thus for some VOCs it is uncertain how a PT sample's short-term stability may affect the laboratory's measured and reported concentration, or percent difference from the assigned target concentration.

To add to the body of knowledge regarding the short-term stability of trace-level VOCs collected in stainless steel canisters, and how their stability affects the results reported for the NATTS PT program, EPA requested that 26 laboratories participating in the NATTS PT program perform three temporally-separated replicate analyses for 15 different VOCs spiked into the canister that each lab received in the 1st quarter (QTR1) of calendar year (CY) 2013 PT cycle. The first analysis occurred approximately seven calendar days after the preparation of the PT sample canister, with each subsequent analysis separated by approximately seven calendar days. Under Task B of Task Order # EP-G11D-00028 (Contract No. GS-10F-0275K), Battelle performed statistical analyses on the collected VOC data to assess temporal trends in the reported concentrations among the temporally-separated replicate analyses. This report presents the results of the assessment of observed temporal trends in the recoveries of the various VOCs. The influence of variables such as canister type (fused-silica line [FSL] or Summa [electropolished stainless

¹ Note that laboratories participating in the NATTS PT program may either be laboratories analyzing samples collected at field sites in the NATTS ambient air monitoring network (NATTS labs) or may be unaffiliated with a NATTS field site (non-NATTS labs).

steel]) and canister pressure at the time of analysis were tracked and considered to explain the observed trends in VOC recoveries.

1.1 Data Description

For QTR1 CY2013 within the NATTS PT program, Battelle prepared and shipped canisters at 30 psia containing 15 VOCs (the nominal spiked concentration of each VOC was 1.2 ppb, per EPA direction) to 15 NATTS laboratories and 11 non-NATTS laboratories. One canister was provided to each participating laboratory; two canisters were provided to a total of three reference laboratories. Reference laboratories included two EPA laboratories (US EPA National Exposure Research Laboratory [NERL, lab 11-03] and US EPA National Risk Management Research Laboratory [NRMRL, lab 04-09], both at EPA facilities in Research Triangle Park, NC, and indicated as) and a third-party commodity analytical laboratory (Eurofin Air Toxics). A list of laboratories receiving canisters is provided in Table 1.

For this temporal trends analysis, the laboratories were requested to analyze VOCs from each received canister a total of three times (representing three temporal replicate analyses):

- Temporal replicate #1: As soon as possible upon receipt (generally within three days of Battelle's shipment of the canister to the laboratory). This analysis was to represent the laboratory's official PT analysis results for this quarter.
- Temporal replicate #2: Approximately seven calendar days after the first analysis.
- Temporal replicate #3: Approximately seven calendar days after the second analysis.

(The actual number of days between canister receipt and the first analysis, and between the three replicate analyses, differed among the laboratories. Therefore, "elapsed number of days" between preparation of the canister in Battelle's laboratory – January 16, 2013 – and the analysis by the recipient laboratory is noted for each temporal replicate.) The two additional analyses (temporal replicates #2 and #3) allowed EPA to address the objective of this report, which was to investigate the short-term stability of various VOCs and its impact on the measurements being reported by the participating laboratories.

Table 2 provides information on the amount of data reported for each laboratory, the injection volume(s) analyzed, the pressure of the canister at the time of each analysis, the elapsed time(s) for each replicate analysis (i.e., the number of days between preparation of the canister in Battelle's laboratory and analysis), and the canister type. Some laboratories chose to intentionally reduce the canister pressure prior to analysis; pressure reduction was assumed to occur whenever a laboratory's first pressure reading was below 20 psia.

Battelle received data from 14 of the 15 NATTS laboratories (i.e., all but Lab 01-03), and for each of the non-NATTS laboratories receiving canisters. In addition, no data were received from one of the three reference laboratories (US EPA NERL, lab 11-03). Five laboratories (four NATTS and one non-NATTS laboratory) reported only one measurement (i.e., no replicate analyses were performed after the first analysis), and analyses performed by Eurofins Air Toxics represented two canisters analyzed on a single day. These single-day laboratory data were insufficient to address the objectives of the present work and were therefore excluded from further analysis.

One laboratory (Lab 09-08) performed analyses and reported results using two different instruments (designated as 09-08 MSF and 09-08 MSJ). As such, these two sets of results were treated as originating from two different laboratories (i.e., were not combined in any way).

As previously stated, reference laboratory 04-09 received two VOC canisters; when analyses of the canisters' contents were performed, the analyses were performed twice (in replicate). Replicate data for

both duplicate canisters were received for temporal replicate #1 (analyses performed on Day 2), but data for only one canister were reported for temporal replicates #2 and #3 (analyses performed on Days 9 and 16, respectively). Thus, data associated with the canister analyzed only once on Day 2 were excluded from this temporal trends analysis. For the remaining canister whose VOC concentrations were measured over three days, the two measurements were averaged and used for temporal replicates #1 and #2. However, for temporal replicate #3, the second reported measurement was unusually low for several different VOCs (1,3-butadiene, dichloromethane, and vinyl chloride), and therefore only the first reported measurement was used.

Table 3 lists the 15 VOCs that were included in the PT samples. Not all laboratories provided data for all 15 VOCs, and therefore, Table 3 also notes when a laboratory did not report results for certain VOCs.

Results from two reference labs, EPA NRMRL and Eurofins Air Toxics, were used as the confirmatory analyses, i.e., to make the final decision on whether to ship the PT canisters to the participating laboratories; canisters were shipped if measured percent recoveries were between 75% to 125%. Moreover, these confirmatory analysis results determined each VOC's assigned target concentration for the PT analysis, but were not designed to be used in this temporal trends analysis. The assigned target concentrations and percent recoveries are also shown in Table 3.

Appendix A provides detailed tables of the reported data which were included in this data analysis. Table A-1 lists the measurements for each of the three temporal replicates by laboratory for each VOC. Note that some laboratories occasionally reported two rather than three replicate measurements. As noted in Section 2, trend over time was characterized for a given laboratory (through calculating percent difference from the concentration result from temporal replicate # 1) only when data for the first and third temporal replicate were reported.

Reported results are plotted versus elapsed time from sample preparation to analysis in Appendix B for each VOC. Data are shown relative to the assigned target concentration and to $\pm 25\%$ of the target concentration, which is the currently established measurement quality objective (acceptance criterion) for laboratory bias for the NATTS program.

Table 1. List of Laboratories Provided with NATTS VOC PT samples for QTR1 CY2013

Lab ID	Affiliation	Lab ID	Affiliation
01-01	NATTS	05-04	Non-NATTS
01-03	NATTS ^a	05-07	Non-NATTS
01-04	NATTS	05-08	Non-NATTS
01-05	Non-NATTS	06-01	NATTS
02-01	NATTS	07-02	Non-NATTS
03-01	NATTS	09-03	NATTS
03-02	NATTS	09-06	Non-NATTS
03-03	Non-NATTS	09-08	NATTS
04-01	NATTS	09-09	Non-NATTS
04-02	NATTS	09-10	Non-NATTS
04-04	NATTS	10-02	NATTS
04-06	Non-NATTS	11-01	NATTS
04-08	Non-NATTS	11-03	Reference Lab ^b
04-09	Reference Lab ^b	N/A	Reference Lab ^b
05-03	NATTS		

^a PT sample delivered to lab but no analysis results received.

^b Reference labs included 04-09, US EPA NRMRL, and 11-03, US EPA NERL, both in Research Triangle Park, NC. The remaining reference lab was Eurofins Air Toxics in Folsom, CA. Reference laboratories received two canisters each. All other laboratories received a single canister. No analytical results were received from US EPA NERL.

Table 2. Information on Replicate Analyses Performed by Each Laboratory Receiving VOC Canisters

Lab ID	# Analytes Reported	# Temporal Replicates	Volume Injected (mL) ^a	Canister Pressure for each temporal replicate analysis (psia)	Pressure Reduced? ^b	Elapsed Time to Analysis (# Days) ^c	Canister Type
01-01	15	3	500	17.0, 11.7, 8.5	Yes	7, 19, 27	FSL
01-04	14	1	500	17.89	Yes	29	FSL
01-05	10	3	400, 200, 200	14.4, 9.0, 8.4	Yes	8, 19, 29	Summa
02-01	15	3	400	24.12, NR, NR	No	7, 22, 28	FSL
03-01	15	3	400	28.8, 24.2, 18.7	No	8, 15, 22	FSL
03-02	15	2	200	20.66, 29.19	No	28, 35	FSL
03-03	15	1	500	29.6	No	19	Summa
04-01	15	3	400	33.8, 24.2, 22.2	No	10, 17, 27	FSL
04-02	15	3	400	15.0, 13.0, 9.0	Yes	14, 22, 29	FSL
04-04	15	3	500	30.9, 28.3, 26.9	No	9, 16, 23	Summa
04-06	15	2	500	29.9, 29.5	No	9, 19	Summa
04-08	15	3	400	36.4, 28.72, 23.65	No	8, 14, 23	Summa
04-09 ^d	15	3	400	29.2, 24.8, 17.1	No	2, 9, 16	FSL
05-03	15	1	500	7.5	Yes	26	Summa
05-04	15	3	400	7.0, 4.5, 2.0	Yes	8, 17, 22	Summa
05-07	14	1	400	NR	--	29	FSL
05-08	15	2	200	29.1, 26.0	No	8, 15	FSL
06-01	15	3	250	27.93, 26.4, 23.84	No	12, 21, 26	Summa
07-02	15	3	500	30.3, 28.8, 25.8	No	20, 29, 35	FSL
09-03	11	3	600	16.0, 14.0, 11.0	Yes	8, 15, 28	FSL
09-06	15	3	400	15.0, 11.0, 8.0	Yes	10, 18, 29	FSL
09-08 MSF	15	3	600	15.0, 7.5, 0.0	Yes	13, 20, 27	FSL
09-08 MSJ	15	3	600	19.0, 10.5, 4.0	Yes	9, 16, 23	FSL
09-09	10	3	500	15.0, 10.0, 8.0	Yes	8, 15, 22	Summa
09-10	10	3	150	15.0, 10.0, 9.0	Yes	12, 19, 26	Summa
10-02	15	1	1,000	24.1	No	28	FSL
11-01	15	3	250	27.7, 13.5, 9.6	No	8, 15, 22	Summa

NR = not reported

^a If the injection volume differed between the replicate temporal analyses, the pressure values are specified for each temporal replicate.

^b “Yes” indicates the first pressure reading (for temporal replicate #1) was below 20 psia, indicating that the canister’s pressure was reduced from 30 psia to a lower pressure prior to analysis; “No” indicates that no such pressure reduction occurred.

^c Number of days between preparation of the canister in Battelle’s laboratory and the analysis by the participating laboratory (reported for each temporal replicate).

^d This reference laboratory performed two analyses at each time point. Pressure readings for the analysis at each time point are the average of the two pressure readings associated with the two replicate analyses at that time point. While this reference laboratory was provided two canisters, results are reported only for the canister for which results were reported for each of the three replicate time points. Moreover, only results from the first replicate analysis on day 16 are reported as the lab reported spurious results for the second replicate analysis performed that day.

Table 3. Summary of VOCs Analyzed by Laboratories Participating in the NATTS PT program for QTR1 CY2013

Analyte	Laboratories <u>NOT</u> Reporting Analysis Results for This Analyte	Target concentration, ppb ^a	% recovery ^b
Acrolein	01-04 ^c , 05-07 ^c , 09-09, 09-10	1.39	116
Benzene	None	1.16	96
1,3-Butadiene	None	1.22	102
Carbon Tetrachloride	None	1.29	107
Chloroform	None	1.28	107
1,2-Dibromoethane	01-05, 09-10	1.13	94
1,3-Dichloropropene - <i>cis</i>	01-05, 09-03, 09-09	1.03	86
1,3-Dichloropropene - <i>trans</i>	01-05, 09-03, 09-09	1.15	96
1,2-Dichloropropane	01-05, 09-03, 09-09, 09-10	1.16	97
1,2-Dichloroethane	09-10	1.13	94
Dichloromethane	None	1.34	112
1,1,2,2-Tetrachloroethane	01-05, 09-03, 09-09, 09-10	1.14	95
Tetrachloroethylene	None	1.12	93
Trichloroethylene	None	1.11	93
Vinyl chloride	None	1.29	108

^a Target concentration determined as the following, using results from NRMRL’s analysis on Day 2 and Air Toxics’s analysis:

Acrolein: [(NRMRL Can 1 Replicate 1 + NRMRL Can 1 Replicate 2)/2 + (NRMRL Can 2 Replicate 1 + NRMRL Can 2 Replicate 2)/2]/2

All other VOCs: {[Air Toxics’s Can 1 + (Air Toxics’s Can 2 Replicate 1 + Air Toxics’s Can 2 Replicate 2)/2]/2 + [(NRMRL Can 1 Replicate 1 + NRMRL Can 1 Replicate 2)/2 + (NRMRL Can 2 Replicate 1 + NRMRL Can 2 Replicate 2)/2]/2}/2

^b % recovery = target concentration/nominal concentration; nominal concentration = 1.2 ppb

^c Only reported data for one temporal replicate (replicate #1), and thus were excluded from the subject temporal trends analysis for this VOC.

2. Data Analysis

The temporal trends analysis consisted of two parts:

- *Part 1.* For each laboratory and VOC, the primary measure of temporal trend was percent change between the final measurement (from temporal replicate #3) and the initial measurement (from temporal replicate #1). Percent change was calculated as follows:

$$\% \text{ Change} = (\text{TempRep}\#3 - \text{TempRep}\#1) * 100 / \text{TempRep}\#1 \quad (1)$$

where *TempRep#3* and *TempRep#1* corresponded to the reported measurements for the third and first temporal replicates, respectively. This analysis investigated how percent change may differ among canister types and whether or not canister pressure reduction occurred before analysis, along with whether a constant decline (or constant increase) in the reported measurement occurred from the first to the last temporal replicate.

- *Part 2.* For each VOC, an analysis was performed to assess the presence of a significant relationship between the measured concentration and the number of days that have elapsed since the canister was prepared.

All statistical analyses were performed using Version 9.3 of the SAS® System.

2.1 Analysis Approach

Analysis Part 1- Effect of Canister Type and Pressure: An analysis of variance (ANOVA) was performed by VOC to determine if either the canister type (FSL or Summa) or an indicator of canister pressure reduction before analysis had a significant effect on average percent change in concentration from temporal replicate #1 to temporal replicate #3 (i.e., equation (1)).

Using the GLM procedure in SAS, the following model was initially fit to the percent change values (y_{ijk}) for the reporting laboratories (noted by the subscript k):

$$y_{ijk} = \mu + \alpha_i + \beta_j + \delta_{ij} + \varepsilon_{k(ij)} \quad (2)$$

where

- μ is the overall intercept term,
- α_i is the fixed effect of reducing canister pressure ($i=1$ if canister pressure was reduced, and $i=2$ if canister pressure was not reduced),
- β_j is the fixed effect of canister type ($j=1$ if canister type was FSL, and $j=2$ if canister type was Summa),
- δ_{ij} is the interaction between the canister pressure reduction effect and the canister type effect, and
- $\varepsilon_{k(ij)} \sim iid N(0, \sigma^2)$

Within each model fit, the significance tests associated with each model parameter were performed at an overall 0.05 significance level across VOCs. This was done by applying a Bonferroni adjustment to the significance level for each VOC-specific test (i.e., significance was determined at the $0.05/15 = 0.0033$ level in order to keep the overall type I error rate across the 15 tests to within 0.05).

In preliminary fits of model (2), the interaction term δ_{ij} between pressure bleed and canister type effects was not statistically significant for any of the VOCs. Therefore, the following two reduced models (using the same notation as above) were each fit to the percent change values by VOC in order to test for the effects of canister pressure reduction before analysis and canister type, respectively:

$$y_{ik} = \mu + \alpha_i + \varepsilon_{k(i)} \quad (3)$$

and

$$y_{jk} = \mu + \beta_j + \varepsilon_{k(j)} \quad (4)$$

For each reduced model, tests for significance of the α_i and β_j parameters (i.e., representing the effects of pressure bleed and canister type, respectively) were each performed at an overall 0.05 significance level, with significance levels for the tests for individual VOCs adjusted as described for model (2).

Also within the fitted reduced models for each VOC (i.e., models (3) and (4)), a test of the interaction term μ was performed to determine whether the overall average percent change for the given VOC is significantly less than 0% (i.e., a significant decline occurs in the percent change on average across laboratories, from temporal replicate #1 to temporal replicate #3). Because 15 individual tests were performed, one for each VOC, the significance level for each individual test was adjusted to ensure a Type I error rate of no higher than 0.05 across all 15 tests.

Analysis Part 2 – VOC Recovery over Time: To assess the effect that the number of days elapsed from sample preparation to analysis may have on the reported concentration (denoted by y_{ijk}), a mixed-effects model was fitted (using the MIXED procedure in SAS) to the reported concentrations, with number of days elapsed since sample preparation (*Day*) as a continuous variable, indicator of canister pressure reduction before analysis (α_i) and canister type (β_j) as fixed effects, and laboratory as a random effect (denoted by subscript k). This model took the following form:

$$y_{ijk} = \mu + \delta(\text{Day}) + m_k + b_k(\text{Day}) + \alpha_i + \beta_j + \varepsilon_{k(ij)} \quad (5)$$

where

- μ is the overall intercept term,
- δ is the overall average slope factor (across labs) associated with the number of elapsed days,
- m_k is the random addition to the intercept term for the k^{th} lab,
- b_k is the random additional to the slope factor for the k^{th} lab,
- α_i is the fixed effect of reducing canister pressure ($i=1$ if canister pressure was reduced, and $i=2$ if canister pressure was not reduced),
- β_j is the fixed effect of canister type ($j=1$ if canister type was FSL; $j=2$ if canister type was Summa), and
- $\varepsilon_{k(ij)} \sim N(0, \sigma^2)$ represents random error, where the errors associated with measurements taken by the same laboratory on different days are assumed to follow a pre-specified correlation structure, and errors associated with measurements taken by different laboratories are independent.

Thus, this model accounts for the inherent correlation that may be present among repeated measurements taken at a given laboratory. The significance level of tests within an individual model fitting (i.e., for a particular VOC) were adjusted as in the Part 1 analysis to control the overall Type 1 error rate across all 15 tests to no higher than 0.05.

The fixed effects of canister pressure reduction before analysis (α_i) and canister type (β_j) in model (5) were not statistically significant for any of the model fittings. Therefore, the following reduced model was adopted (using the same notation as before):

$$y_{ijk} = \mu + \beta(\text{Day}) + m_k + b_k(\text{Day}) + \varepsilon_{k(ij)} \quad (6)$$

If the concentration of a VOC decreases over time, then the overall slope factor (β) should be less than 0. Therefore, a test was performed within the mixed model ANOVA of whether the slope term β was significantly less than zero. As with the other tests, the significance levels for the VOC-specific tests were properly adjusted to control the overall Type 1 error rate to no higher than 0.05 across all 15 tests.

2.2 Results

The models introduced in Section 2.1 were fitted to data on the percent change from temporal replicate #1 (Part 1) and on reported concentration (Part 2). For each of the 15 VOCs, none of the tests performed in the model fittings showed significance:

- There were no statistically significant differences in average percent change between canisters with reduced pressure and those that were not reduced (model (3)).
- There were no statistically significant differences in average percent change between the two canister types (model (4)).
- Average percent change across labs was not significantly less than 0 (models (3) and (4)).
- No significant relationship was observed between the reported concentration and time (based upon testing the significance of the overall slope factor in model (6)). This indicates that there is no statistical evidence of degradation of the concentration of any of the VOCs over the elapsed time covered by the three replicate analyses.

The plots in Appendix B show that trends in VOC concentration over time appear to be minor in nature and are generally consistent between laboratories with some exceptions. (These plots exclude data for Lab 03-02, which provided analysis results for only two replicate time points, where the measurement at the first time point was typically very high.) Laboratory 04-02 also has a different trend for certain VOCs (e.g., 1,3-butadiene). Otherwise, similar results and lack of obvious temporal trend in VOC concentrations are seen across the laboratories, a qualitative observation supporting the quantitative statistical determination of lack of observed decrease in VOC recovery over time. It is clear from inspection of the acrolein results that there exists more variability in its reported concentrations among the laboratories than for the other 14 VOCs.

Table 4 documents the percent change values for each laboratory and VOC. These values are summarized across laboratories in Table 5, by VOC and the canister type used. More laboratories used FSL canisters than Summa canisters. The average (and median) percent change value, calculated across laboratories, was consistently positive for the Summa canister laboratories and consistently negative for the FSL canister laboratories. In addition, the range of percent change values covered more of a positive range for laboratories using Summa canisters compared to laboratories using FSL canisters. While this is evidence that the type of canister may be an important factor in determining percent difference over time, the outcome of the statistical modeling did not find the canister type effect as statistically significant for any VOC. Note that conclusions drawn from the plots and Table 4 are qualitative in nature, and their lack of supporting a definite trend in measurements over time for analyses originating from the same canister implies that any temporal trend is minor or may be non-significant from a statistical or practical standpoint. Note that the p-values for the statistical tests of the effect of canister on percent change in concentration ranged from 0.0858 (chloroform) to 1.0 (acrolein), and the cutoff for statistical significance was set conservatively (maximum Type I error rate < 0.05). If the Type I error rate was allowed to be as high as 0.1, the effect of canister type on compound recovery for chloroform ($p < 0.1$) would have been found to be statistically significant. Also, the current model tested the trend in each VOC's recovery individually. Each individual test likely did not have enough statistical power to demonstrate statistical significance in the increasing recovery trend observed across VOCs collected in Summa cans and decreasing recovery trend observed across VOCs collected in FSL cans. To detect such trends, a more sophisticated method such as multivariate modeling would be needed in order to perform a single analysis incorporating all VOCs.

As defined in equation (1), percent change depends only on the first and third replicate values, and not the second value. The plots in Appendix B show when the observed temporal trends are always in the same

direction from one replicate to another within a given laboratory (i.e., always decreasing, or always increasing, over time). It was of interest to determine how many laboratories had such steady (“definitive”) trends over time, versus a mix of results (i.e., an increase from temporal replicate #1 to temporal replicate #2, followed by a decrease to temporal replicate #3; or a decrease from temporal replicate #1 to temporal replicate #2, followed by an increase to temporal replicate #3). Table 4 also indicates when these types of trends occur. This table shows that for each VOC, about one-half to two-thirds of the laboratories do not have a definitive increasing or decreasing trend across the three replicates. Of those laboratories that do have a definitive trend, they are about equally divided among laboratories with a decreasing trend and those with an increasing trend. (Some exceptions exist, such as for tetrachloroethylene, where only one laboratory noted a definitive negative trend, and for 1,2-dibromoethane, where only one laboratory noted a definitive positive trend.)

3.0 Conclusions

This study demonstrated that for the 15 VOCs analyzed by the laboratories within a single cycle of the NATTS PT program, no significant decrease in reported VOC concentrations was observed on average across laboratories over the period of time that elapsed between when the canister samples were prepared by Battelle and when the last of the three temporally-separated replicate analyses was completed (generally within 30 days). Statistical modeling efforts suggested that average values of the percent change in VOC concentrations between the first temporal replicate and the last (which was targeted to occur about two weeks following the first analysis) were not significantly impacted on average by the elapsed time from sample preparation (i.e., the percent change was not significantly less than zero), nor were they linked significantly to canister type or pressure reduction. While there exists qualitative trends in VOC recovery over time for certain laboratories and VOCs, there was insufficient statistical evidence to indicate a statistically significant trend in VOC concentrations over a 30-day period for a typical laboratory.

All tests for statistical trend were applied independently to data for each of the 15 VOCs. Any patterns in trends across VOCs (e.g., higher percent changes among Summa canisters versus FSL canisters) were identified qualitatively; more formal statistical testing of the significance of these patterns would require more sophisticated multivariate statistical modeling techniques. Such could be the subject of future work.

Table 4. Percent Change in Reported Concentration from First to Third Temporally-Separated Replicates, and Observed Trend in Concentrations Among the Three Replicates^{a,b,c}

Lab ID	Acrolein		Benzene		1,3-Butadiene		Carbon Tetrachloride		Chloroform	
	% Change	Trend	% Change	Trend	% Change	Trend	% Change	Trend	% Change	Trend
01-01	4.2%	Mix	0.6%	Mix	-5.0%	Mix	-2.4%	Mix	-1.3%	Mix
01-05	-0.6%	Mix	-3.8%	Mix	-2.0%	Mix	-1.5%	Mix	2.8%	Mix
02-01	24.6%	>	0.8%	Mix	-11.4%	<	0.0%	Mix	-0.9%	Mix
03-01	37.0%	>	5.5%	Mix	0.0%	Mix	2.7%	Mix	0.0%	Mix
04-01	9.8%	Mix	-6.1%	<	-5.2%	<	-14.3%	<	-9.9%	<
04-02	-36.1%	<	-6.7%	<	-47.0%	<	9.0%	>	1.1%	Mix
04-04	6.3%	Mix	5.8%	Mix	8.8%	>	15.5%	>	18.5%	>
04-08	17.0%	Mix	11.8%	>	19.4%	>	15.0%	>	22.7%	>
04-09	2.9%	Mix	6.8%	>	2.4%	Mix	6.0%	Mix	6.0%	Mix
05-04	3.9%	Mix	16.6%	>	11.9%	Mix	19.5%	Mix	15.3%	>
06-01	-16.4%	<	8.3%	Mix	-7.7%	Mix	-14.3%	Mix	-7.7%	Mix
07-02	-3.1%	Mix	19.1%	>	7.7%	Mix	6.6%	>	0.2%	Mix
09-03	12.7%	>	-3.2%	Mix	-20.0%	Mix	-10.9%	<	-11.4%	Mix
09-06	-6.6%	Mix	-6.2%	Mix	-10.5%	<	-5.5%	<	-6.3%	<
09-08 MSF	3.6%	Mix	-2.4%	Mix	-2.5%	Mix	-8.5%	<	-9.6%	Mix
09-08 MSJ	-0.8%	Mix	-5.6%	<	-9.5%	<	0.0%	Mix	-15.4%	<
09-09	--		0.0%	Mix	8.3%	Mix	0.0%	Mix	0.0%	Mix
09-10	--		-1.4%	Mix	-2.6%	Mix	-2.8%	<	0.8%	Mix
11-01	31.2%	>	-1.9%	Mix	-10.9%	<	-8.7%	<	12.6%	>

Lab ID	1,2-Dibromoethane		1,3-Dichloropropene - cis		1,3-Dichloropropene - trans		1,2-Dichloropropane		1,2-Dichloroethane	
	% Change	Trend	% Change	Trend	% Change	Trend	% Change	Trend	% Change	Trend
01-01	-2.7%	Mix	-3.2%	Mix	-4.5%	Mix	-0.3%	Mix	-0.4%	Mix
01-05	--		--		--		--		1.5%	Mix
02-01	1.6%	Mix	2.0%	Mix	0.0%	Mix	1.6%	Mix	-0.8%	Mix
03-01	5.1%	Mix	17.1%	>	18.0%	>	10.5%	Mix	-2.5%	<
04-01	-7.9%	<	-6.6%	<	-9.2%	Mix	-8.5%	<	-9.9%	Mix
04-02	-5.4%	Mix	-25.8%	Mix	-27.6%	Mix	-41.7%	Mix	9.5%	Mix
04-04	7.8%	>	4.5%	Mix	6.0%	>	7.0%	>	13.8%	>
04-08	2.4%	Mix	2.7%	>	2.0%	Mix	7.7%	>	8.8%	>
04-09	-0.7%	Mix	5.2%	>	1.5%	Mix	4.4%	Mix	10.7%	>
05-04	7.7%	Mix	8.7%	Mix	9.6%	Mix	18.2%	Mix	15.7%	Mix
06-01	0.0%	Mix	-5.9%	Mix	-5.3%	Mix	0.0%	Mix	-7.7%	Mix
07-02	11.0%	Mix	29.3%	>	11.2%	Mix	29.4%	>	39.7%	>
09-03	-33.5%	<	--		--		--		6.5%	Mix
09-06	-3.6%	Mix	-5.5%	Mix	-7.8%	Mix	-5.0%	Mix	-5.6%	<
09-08 MSF	-12.5%	<	-5.3%	<	-14.4%	<	-2.4%	Mix	-12.6%	<
09-08 MSJ	-7.8%	<	-7.3%	<	-19.7%	<	-4.8%	<	-16.7%	<
09-09	0.0%	Mix	--		--		--		0.0%	Mix
09-10	--		6.4%	Mix	-3.0%	<	--		--	
11-01	2.4%	Mix	-4.4%	Mix	-0.5%	Mix	-3.4%	<	12.4%	>

Table 4. (cont.)

Lab ID	Dichloro-methane		1,1,2,2-Tetra-chloroethane		Tetrachloro-ethylene		Trichloro-ethylene		Vinyl chloride	
	% Change	Trend	% Change	Trend	% Change	Trend	% Change	Trend	% Change	Trend
01-01	-0.8%	Mix	-5.9%	Mix	-2.2%	Mix	-2.1%	Mix	-0.7%	Mix
01-05	8.5%	Mix	--		9.6%	Mix	-0.2%	Mix	8.8%	Mix
02-01	8.0%	Mix	-7.4%	Mix	1.7%	Mix	1.7%	Mix	0.0%	Mix
03-01	5.5%	Mix	2.6%	Mix	9.3%	Mix	6.7%	Mix	5.5%	Mix
04-01	-8.3%	<	-8.9%	<	-11.7%	Mix	-11.4%	Mix	-12.3%	<
04-02	-3.1%	Mix	-3.0%	Mix	-1.3%	Mix	-1.1%	Mix	-55.0%	<
04-04	11.3%	>	8.0%	>	6.6%	Mix	11.7%	Mix	17.1%	>
04-08	10.4%	>	9.7%	Mix	16.2%	>	5.7%	Mix	15.9%	>
04-09	15.6%	>	1.6%	Mix	3.4%	>	2.3%	>	4.9%	Mix
05-04	19.9%	>	10.5%	Mix	11.2%	Mix	13.7%	>	13.8%	Mix
06-01	9.1%	Mix	0.0%	Mix	0.0%	Mix	9.1%	Mix	-7.7%	Mix
07-02	10.0%	>	14.8%	>	8.1%	>	18.1%	Mix	-0.7%	Mix
09-03	-14.3%	Mix	--		7.4%	>	-3.3%	Mix	-15.1%	Mix
09-06	-5.7%	Mix	-4.2%	Mix	-5.7%	Mix	0.4%	Mix	-9.3%	Mix
09-08 MSF	-3.9%	Mix	-13.4%	Mix	-3.4%	Mix	-8.3%	Mix	-4.1%	Mix
09-08 MSJ	-2.6%	Mix	-18.4%	<	-5.1%	<	-17.5%	<	-3.4%	<
09-09	0.0%	Mix	--		0.0%	Mix	0.0%	Mix	0.0%	Mix
09-10	-0.4%	Mix	--		-0.7%	Mix	3.7%	Mix	-4.8%	Mix
11-01	-4.2%	<	-3.0%	<	2.6%	>	-5.1%	Mix	-7.4%	<

^a Only laboratories reporting measurements for at least three temporally-separated replicates are included in this table.

^b % change is calculated as in equation (1). No value for percent change is given if the measurement for either the first or third temporal replicate is unavailable.

^c Trend = '<' signifies that the reported values were non-increasing from Rep#1 to Rep#3.

Trend = '>' signifies that the reported values were non-decreasing from Rep#1 to Rep#3.

Trend = 'Mix' signifies that the reported values increased from Rep#1 to Rep#2 and decreased from Rep#2 to Rep#3, or decreased from Rep#1 to Rep#2 and increased from Rep#2 to Rep#3.

Table 5. Summary Statistics on Percent Change from Temporal Replicate #1, by VOC and Canister Type

VOC	Canister Type	# Labs	Percent Change from Temporal Replicate #1						
			Mean	Std. Error	Min.	25 th %ile	50 th %ile	75 th %ile	Max.
Acrolein	FSL	11	4.4	5.6	-36.1	-3.1	3.6	12.7	37.0
	Summa	6	6.9	6.6	-16.4	-0.6	5.1	17.0	31.2
Benzene	FSL	11	0.2	2.4	-6.7	-6.1	-2.4	5.5	19.1
	Summa	8	4.4	2.6	-3.8	-1.7	2.9	10.0	16.6
1,3-Butadiene	FSL	11	-9.2	4.4	-47.0	-11.4	-5.2	0.0	7.7
	Summa	8	3.1	3.7	-10.9	-5.2	3.2	10.3	19.4
Carbon Tetrachloride	FSL	11	-1.6	2.3	-14.3	-8.5	0.0	6.0	9.0
	Summa	8	2.8	4.4	-14.3	-5.8	-0.7	15.2	19.5
Chloroform	FSL	11	-4.3	2.0	-15.4	-9.9	-1.3	0.2	6.0
	Summa	8	8.1	3.8	-7.7	0.4	7.7	16.9	22.7
1,2-Dibromoethane	FSL	11	-5.1	3.5	-33.5	-7.9	-3.6	1.6	11.0
	Summa	6	3.4	1.4	0.0	0.0	2.4	7.7	7.8
1,3-Dichloropropene – <i>cis</i>	FSL	10	-0.0	4.7	-25.8	-6.6	-4.2	5.2	29.3
	Summa	6	2.0	2.4	-5.9	-4.4	3.6	6.4	8.7
1,3-Dichloropropene – <i>trans</i>	FSL	10	-5.3	4.3	-27.6	-14.4	-6.2	1.5	18.0
	Summa	6	1.5	2.3	-5.3	-3.0	0.8	6.0	9.6
1,2-Dichloropropane	FSL	10	-1.7	5.6	-41.7	-5.0	-1.4	4.4	29.4
	Summa	5	5.9	3.7	-3.4	0.0	7.0	7.7	18.2
1,2-Dichloroethane	FSL	11	1.6	4.6	-16.7	-9.9	-0.8	9.5	39.7
	Summa	7	6.4	3.3	-7.7	0.0	8.8	13.8	15.7
Dichloromethane	FSL	11	0.0	2.7	-14.3	-5.7	-2.6	8.0	15.6
	Summa	8	6.8	2.8	-4.2	-0.2	8.8	10.8	19.9
1,1,2,2-Tetrachloroethane	FSL	10	-4.2	2.9	-18.4	-8.9	-5.1	1.6	14.8
	Summa	5	5.0	2.7	-3.0	0.0	8.0	9.7	10.5
Tetrachloroethylene	FSL	11	0.1	2.0	-11.7	-5.1	-1.3	7.4	9.3
	Summa	8	5.7	2.2	-0.7	0.0	4.6	10.4	16.2
Trichloroethylene	FSL	11	-1.3	2.8	-17.5	-8.3	-1.1	2.3	18.1
	Summa	8	4.8	2.3	-5.1	-0.1	4.7	10.4	13.7
Vinyl chloride	FSL	11	-8.2	5.1	-55.0	-12.3	-3.4	0.0	5.5
	Summa	8	4.5	3.8	-7.7	-6.1	4.4	14.8	17.1

4.0 References

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**APPENDIX A
DETAILED DATA TABLES**

Table A-1. Temporally-Separated Replicate Measurements (ppb) for VOCs by Laboratory

Lab ID	Acrolein			Benzene			1,3-Butadiene		
	Rep #1	Rep #2	Rep #3	Rep #1	Rep #2	Rep #3	Rep #1	Rep #2	Rep #3
01-01	1.08	1.19	1.13	1.27	1.36	1.28	1.19	1.22	1.13
01-05	1.26	1.12	1.25	1.26	0.99	1.22	1.35	1.07	1.32
02-01	1.38	1.61	1.72	1.22	1.19	1.23	1.14	1.03	1.01
03-01	2.11	2.20	2.89	1.10	1.18	1.16	1.13	1.03	1.13
03-02	3.44	1.18	--	2.06	1.08	--	2.00	1.42	--
04-01	1.30	1.45	1.43	1.16	1.15	1.09	1.07	1.04	1.02
04-02	1.33	1.11	0.85	0.90	0.89	0.84	2.53	2.12	1.34
04-04	1.91	2.08	2.03	1.20	1.29	1.27	1.14	1.22	1.24
04-06	1.33	1.37	--	1.08	1.14	--	1.10	1.23	--
04-08	1.65	1.61	1.93	1.36	1.51	1.52	1.24	1.35	1.48
04-09*	1.36	1.59	1.40	1.17	1.24	1.25	1.13	1.19	1.15
05-04	1.57	1.74	1.63	0.98	1.14	1.15	1.13	1.30	1.26
05-08	2.68	3.09	--	1.12	1.06	--	1.25	1.12	--
06-01	1.10	1.00	0.92	1.20	1.20	1.30	1.30	1.20	1.20
07-02	1.51	1.44	1.46	1.09	1.16	1.30	1.23	1.22	1.32
09-03	1.81	1.91	2.04	1.26	1.21	1.22	1.50	1.54	1.20
09-06	1.18	1.25	1.10	1.24	1.25	1.17	1.20	1.20	1.08
09-08 MSF	1.12	1.07	1.16	1.24	1.20	1.21	1.21	1.16	1.18
09-08 MSJ	1.21	1.22	1.20	1.26	1.25	1.19	1.16	1.11	1.05
09-09	--	--	--	1.30	1.30	1.30	1.20	1.30	1.30
09-10	--	--	--	1.26	1.27	1.24	1.33	1.22	1.29
11-01	1.22	1.53	1.60	1.09	1.11	1.07	1.17	1.08	1.04

Lab ID	Carbon Tetrachloride			Chloroform			1,2-Dibromoethane		
	Rep #1	Rep #2	Rep #3	Rep #1	Rep #2	Rep #3	Rep #1	Rep #2	Rep #3
01-01	1.17	1.21	1.15	1.11	1.18	1.10	1.15	1.24	1.12
01-05	1.44	1.26	1.42	1.48	1.35	1.52	--	--	--
02-01	1.26	1.20	1.26	1.15	1.08	1.14	1.24	1.16	1.26
03-01	1.10	1.16	1.13	1.16	1.13	1.16	0.78	0.73	0.82
03-02	2.22	1.32	--	2.04	1.24	--	3.02	1.84	--
04-01	1.20	1.17	1.03	1.16	1.15	1.05	1.22	1.22	1.13
04-02	0.89	0.93	0.97	0.95	0.97	0.96	0.93	0.99	0.88
04-04	1.16	1.22	1.34	1.30	1.47	1.54	1.16	1.22	1.25
04-06	1.14	1.25	--	0.86	0.95	--	1.28	1.32	--
04-08	1.27	1.42	1.46	1.54	1.68	1.89	1.65	1.73	1.69
04-09*	1.26	1.35	1.33	1.23	1.31	1.30	1.05	1.05	1.04
05-04	1.06	1.30	1.27	0.98	1.12	1.13	0.84	0.98	0.90
05-08	1.45	1.44	--	1.13	1.12	--	1.01	1.19	--
06-01	1.40	1.20	1.20	1.30	1.20	1.20	1.60	1.40	1.60
07-02	1.45	1.53	1.55	1.33	1.52	1.33	0.96	1.07	1.06
09-03	2.11	1.97	1.88	1.40	1.57	1.24	1.73	1.40	1.15
09-06	1.33	1.30	1.26	1.29	1.26	1.21	1.24	1.29	1.20
09-08 MSF	1.18	1.12	1.08	1.25	1.10	1.13	1.28	1.14	1.12
09-08 MSJ	1.18	1.17	1.18	1.23	1.13	1.04	1.28	1.27	1.18
09-09	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.30
09-10	1.28	1.25	1.24	1.25	1.22	1.26	--	--	--
11-01	1.39	1.27	1.27	1.18	1.23	1.33	1.02	1.01	1.04

Table A-1. (cont.)

Lab ID	1,3-Dichloropropene - <i>cis</i>			1,3-Dichloropropene - <i>trans</i>			1,2-Dichloropropane		
	Rep #1	Rep #2	Rep #3	Rep #1	Rep #2	Rep #3	Rep #1	Rep #2	Rep #3
01-01	1.13	1.19	1.09	1.18	1.23	1.13	1.14	1.21	1.14
01-05	--	--	--	--	--	--	--	--	--
02-01	1.02	0.96	1.04	1.12	1.06	1.12	1.26	1.25	1.28
03-01	0.82	0.94	0.96	1.00	1.17	1.18	1.05	1.18	1.16
03-02	2.32	1.06	--	2.48	1.30	--	2.38	1.34	--
04-01	1.25	1.24	1.17	1.41	1.41	1.28	1.21	1.15	1.10
04-02	0.31	0.33	0.23	0.29	0.30	0.21	0.72	0.80	0.42
04-04	1.10	1.20	1.15	1.34	1.39	1.42	1.15	1.18	1.23
04-06	1.37	1.51	--	1.00	1.07	--	1.27	1.34	--
04-08	1.46	1.49	1.50	1.99	2.11	2.03	1.55	1.63	1.67
04-09*	1.05	1.09	1.11	1.14	1.18	1.15	1.07	1.13	1.12
05-04	0.87	0.99	0.95	0.85	0.96	0.93	0.92	1.10	1.09
05-08	1.31	1.28	--	1.50	1.40	--	1.16	1.14	--
06-01	1.70	1.50	1.60	1.90	1.60	1.80	1.20	1.20	1.20
07-02	0.85	1.04	1.11	0.83	0.94	0.92	1.20	1.46	1.56
09-03	--	--	--	--	--	--	--	--	--
09-06	1.18	1.23	1.11	1.44	1.51	1.33	1.19	1.24	1.13
09-08 MSF	1.14	1.12	1.08	1.32	1.14	1.13	1.23	1.20	1.20
09-08 MSJ	1.24	1.22	1.15	1.32	1.20	1.06	1.26	1.25	1.20
09-09	--	--	--	--	--	--	--	--	--
09-10	1.34	1.46	1.43	1.52	1.48	1.47	--	--	--
11-01	1.10	1.04	1.05	1.11	1.08	1.11	1.12	1.12	1.08

Lab ID	1,2-Dichloroethane			Dichloromethane			1,1,2,2-Tetrachloroethane		
	Rep #1	Rep #2	Rep #3	Rep #1	Rep #2	Rep #3	Rep #1	Rep #2	Rep #3
01-01	1.13	1.21	1.13	1.15	1.23	1.14	1.15	1.25	1.08
01-05	1.50	1.28	1.52	1.29	1.20	1.40	--	--	--
02-01	1.28	1.20	1.27	1.13	1.05	1.22	1.49	1.24	1.38
03-01	1.19	1.17	1.16	1.10	1.05	1.16	0.76	0.72	0.78
03-02	2.26	1.32	--	1.96	1.18	--	2.62	1.80	--
04-01	1.16	1.16	1.04	1.09	1.04	1.00	1.18	1.13	1.07
04-02	0.42	0.74	0.46	0.96	1.03	0.93	0.99	1.02	0.96
04-04	1.23	1.35	1.40	1.33	1.46	1.48	1.13	1.14	1.22
04-06	1.05	1.10	--	1.21	1.34	--	1.32	1.20	--
04-08	1.59	1.67	1.73	1.35	1.41	1.49	1.45	1.21	1.59
04-09*	1.16	1.28	1.28	1.31	1.33	1.52	1.05	1.10	1.07
05-04	0.93	1.09	1.08	1.12	1.31	1.35	0.77	0.90	0.85
05-08	1.15	1.13	--	1.09	1.09	--	1.10	1.32	--
06-01	1.30	1.20	1.20	1.10	1.20	1.20	1.40	1.30	1.40
07-02	1.26	1.36	1.77	1.71	1.74	1.88	1.11	1.17	1.27
09-03	1.23	1.52	1.31	1.61	1.36	1.38	--	--	--
09-06	1.21	1.17	1.14	1.19	1.26	1.12	1.28	1.38	1.22
09-08 MSF	1.19	1.05	1.04	1.28	1.20	1.23	1.12	0.97	0.97
09-08 MSJ	1.20	1.12	1.00	1.17	1.18	1.14	1.25	1.14	1.02
09-09	1.30	1.30	1.30	1.20	1.10	1.20	--	--	--
09-10	--	--	--	1.20	1.20	1.20	--	--	--
11-01	1.14	1.19	1.28	1.27	1.24	1.22	1.04	1.02	1.01

Table A-1. (cont.)

Lab ID	Tetrachloroethylene			Trichloroethylene			Vinyl chloride		
	Rep #1	Rep #2	Rep #3	Rep #1	Rep #2	Rep #3	Rep #1	Rep #2	Rep #3
01-01	1.13	1.19	1.10	1.14	1.20	1.12	1.10	1.16	1.10
01-05	1.06	1.02	1.16	1.37	1.20	1.37	1.31	1.12	1.42
02-01	1.19	1.16	1.21	1.18	1.16	1.20	1.25	1.20	1.25
03-01	0.75	0.74	0.82	1.04	1.12	1.11	1.10	1.10	1.16
03-02	2.82	1.58	--	2.40	1.32	--	2.10	1.36	--
04-01	1.13	1.17	1.00	1.18	1.20	1.05	1.15	1.03	1.01
04-02	0.79	0.86	0.78	0.91	0.97	0.90	2.91	2.32	1.31
04-04	1.06	1.03	1.13	1.11	1.27	1.24	1.17	1.19	1.37
04-06	1.22	1.29	--	1.02	1.06	--	1.18	1.30	--
04-08	1.30	1.48	1.51	1.22	1.34	1.29	1.45	1.50	1.68
04-09*	1.03	1.05	1.06	1.02	1.03	1.05	1.19	1.26	1.25
05-04	0.94	1.09	1.05	1.05	1.18	1.19	1.09	1.26	1.25
05-08	0.94	1.12	--	1.08	1.06	--	1.28	1.23	--
06-01	1.20	1.10	1.20	1.10	1.20	1.20	1.30	1.20	1.20
07-02	1.17	1.18	1.26	1.08	1.35	1.28	1.36	1.37	1.35
09-03	1.48	1.54	1.59	1.23	1.33	1.19	1.52	1.52	1.29
09-06	1.18	1.19	1.11	1.22	1.30	1.22	1.26	1.31	1.14
09-08 MSF	1.17	1.13	1.13	1.21	1.07	1.11	1.23	1.17	1.18
09-08 MSJ	1.18	1.17	1.12	1.26	1.16	1.04	1.16	1.15	1.12
09-09	1.20	1.20	1.20	1.20	1.20	1.20	1.30	1.30	1.30
09-10	1.27	1.19	1.26	1.25	1.21	1.29	1.24	1.16	1.18
11-01	1.02	1.02	1.04	1.15	1.08	1.09	1.14	1.06	1.06

Notes: The nominal spiked concentration for each VOC is 1.2 ppb.

* Reference laboratory. Temporal replicates #1 and #2 each represent an average of two reported readings, while temporal replicate #3 represents one of two reported readings.

**APPENDIX B
TREND PLOTS**

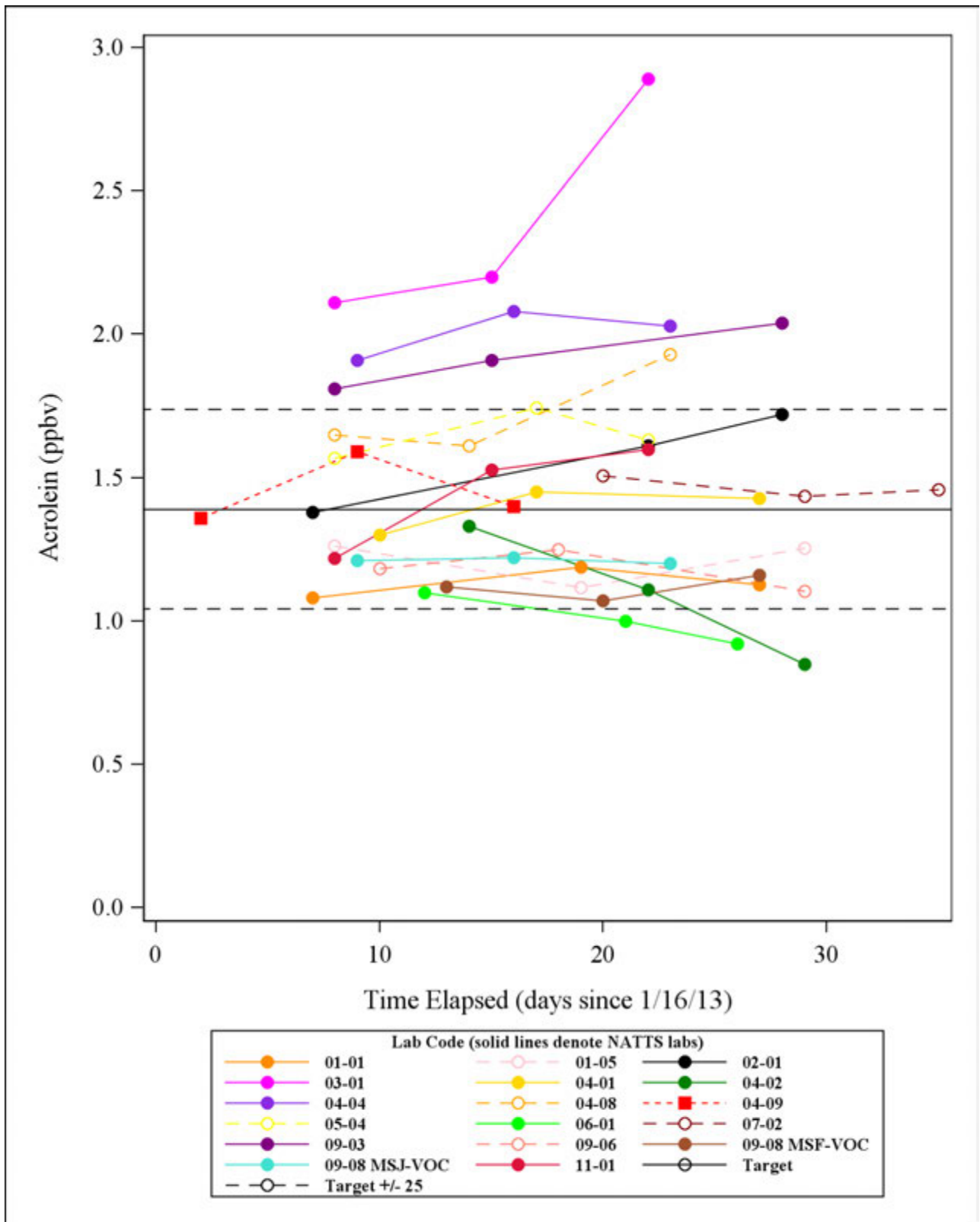


Figure B-1. Observed Trend in Acrolein Concentration among the 3 Replicate Testing Days, by Laboratory

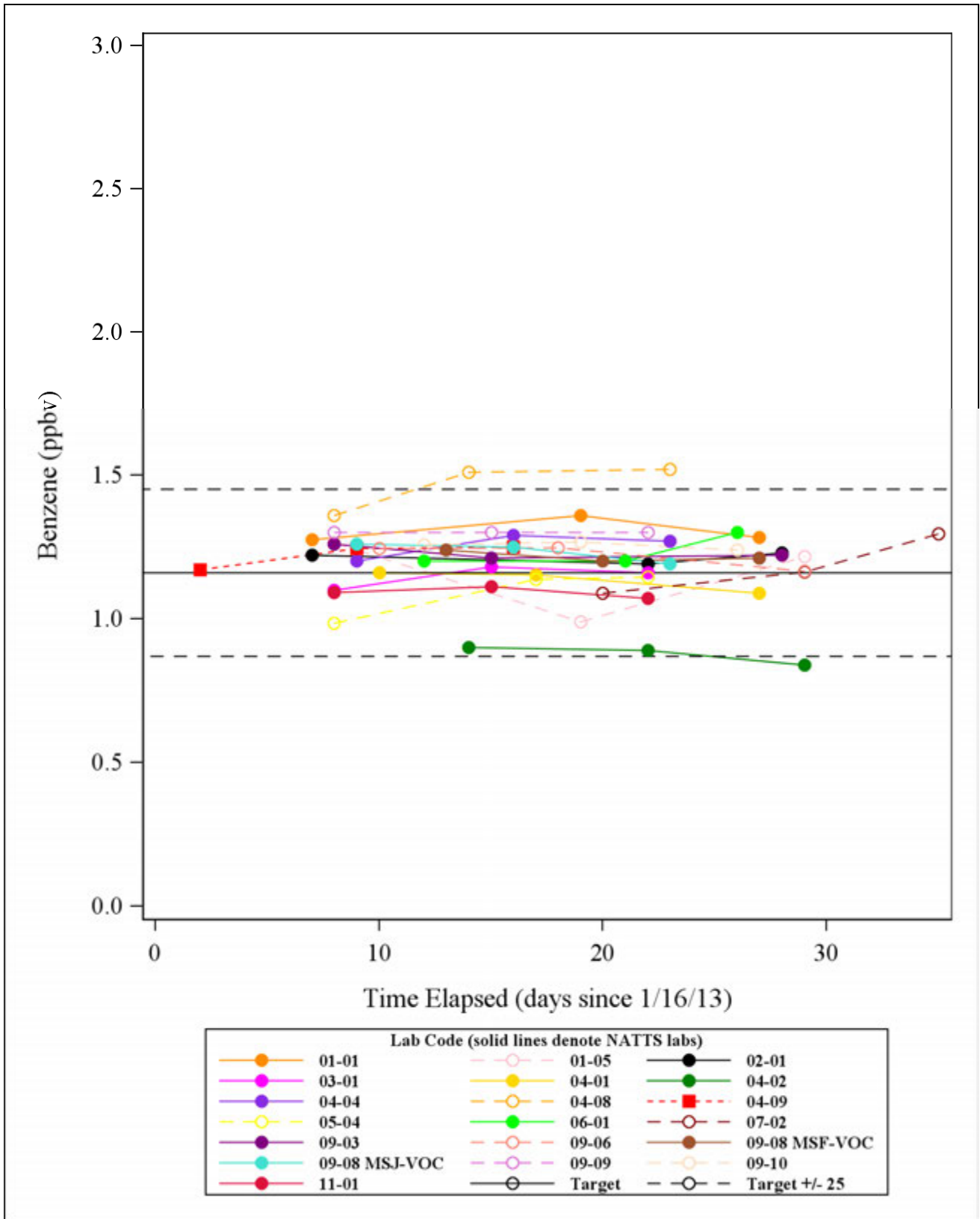


Figure B-2. Observed Trend in Benzene Concentration among the 3 Replicate Testing Days, by Laboratory

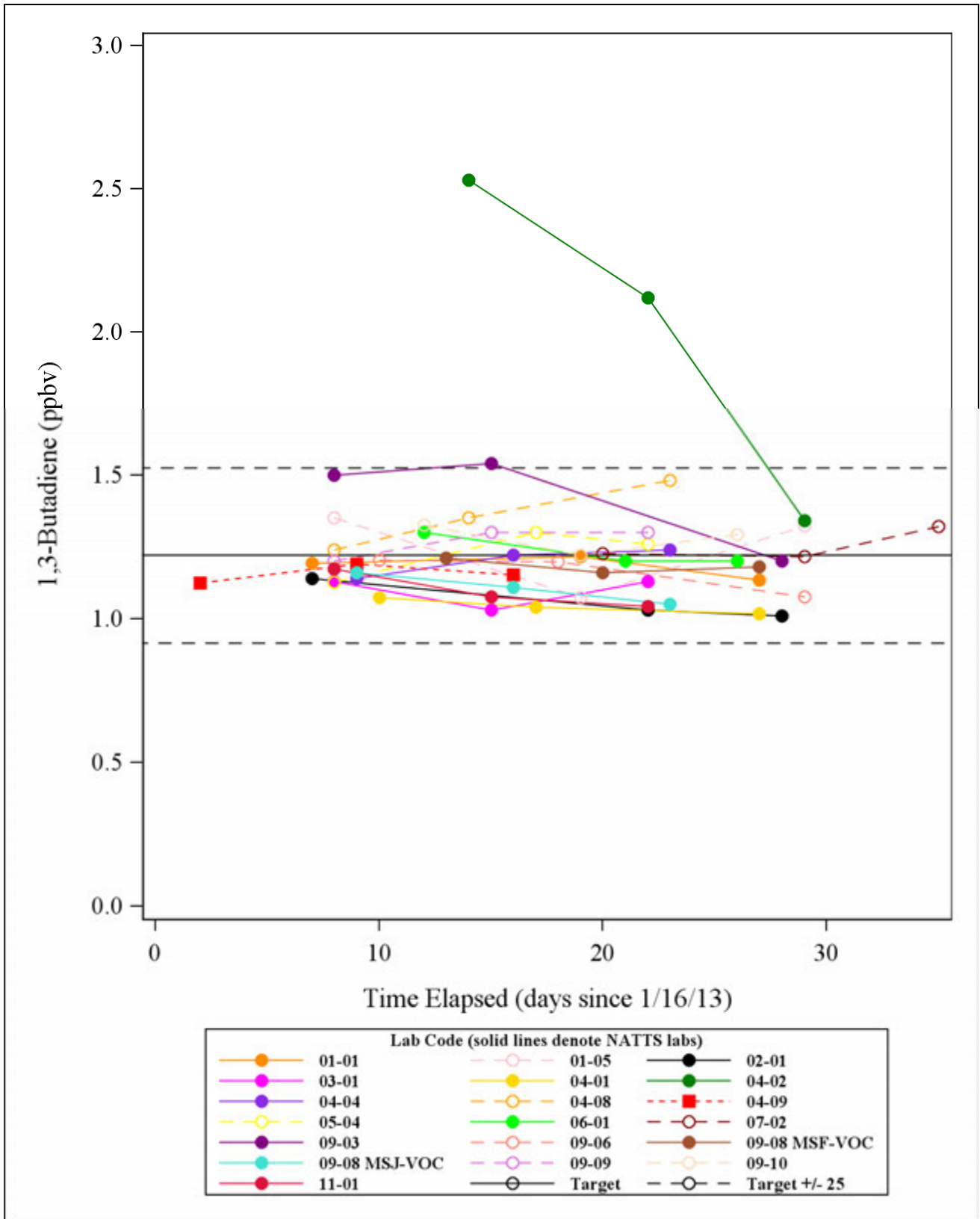


Figure B-3. Observed Trend in 1,3-Butadiene Concentration among the 3 Replicate Testing Days, by Laboratory

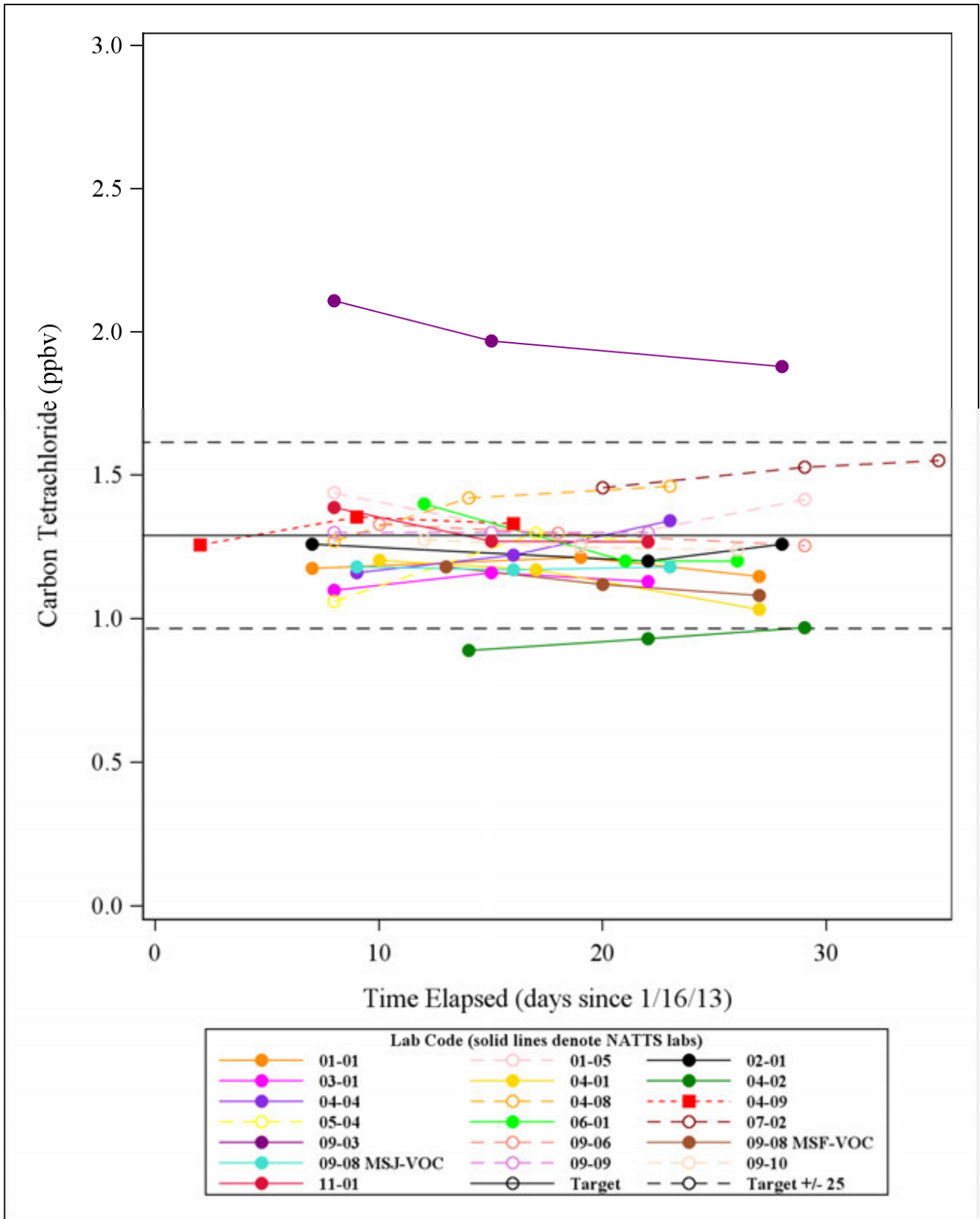


Figure B-4. Observed Trend in Carbon Tetrachloride Concentration among the 3 Replicate Testing Days, by Laboratory

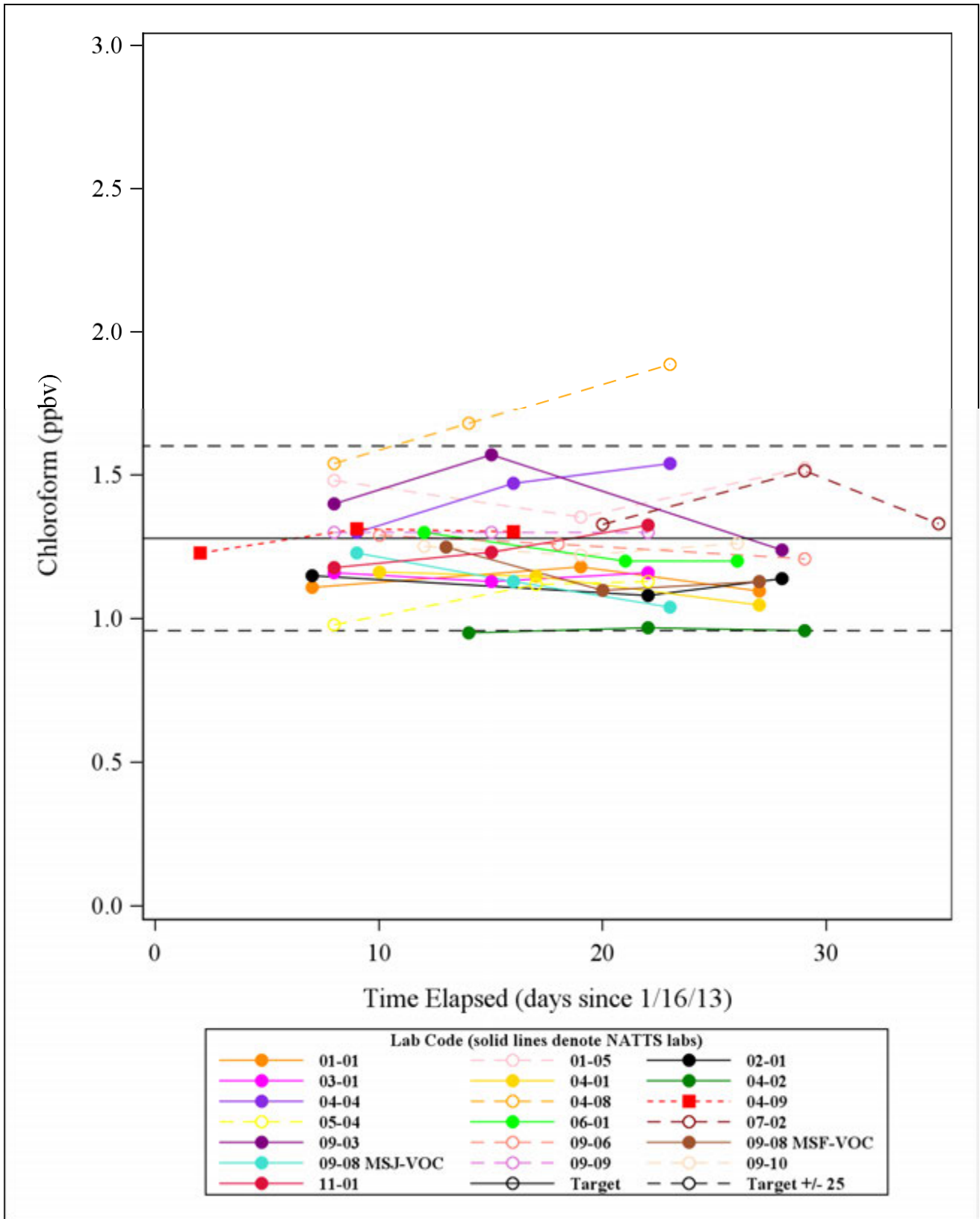


Figure B-5. Observed Trend in Chloroform Concentration among the 3 Replicate Testing Days, by Laboratory

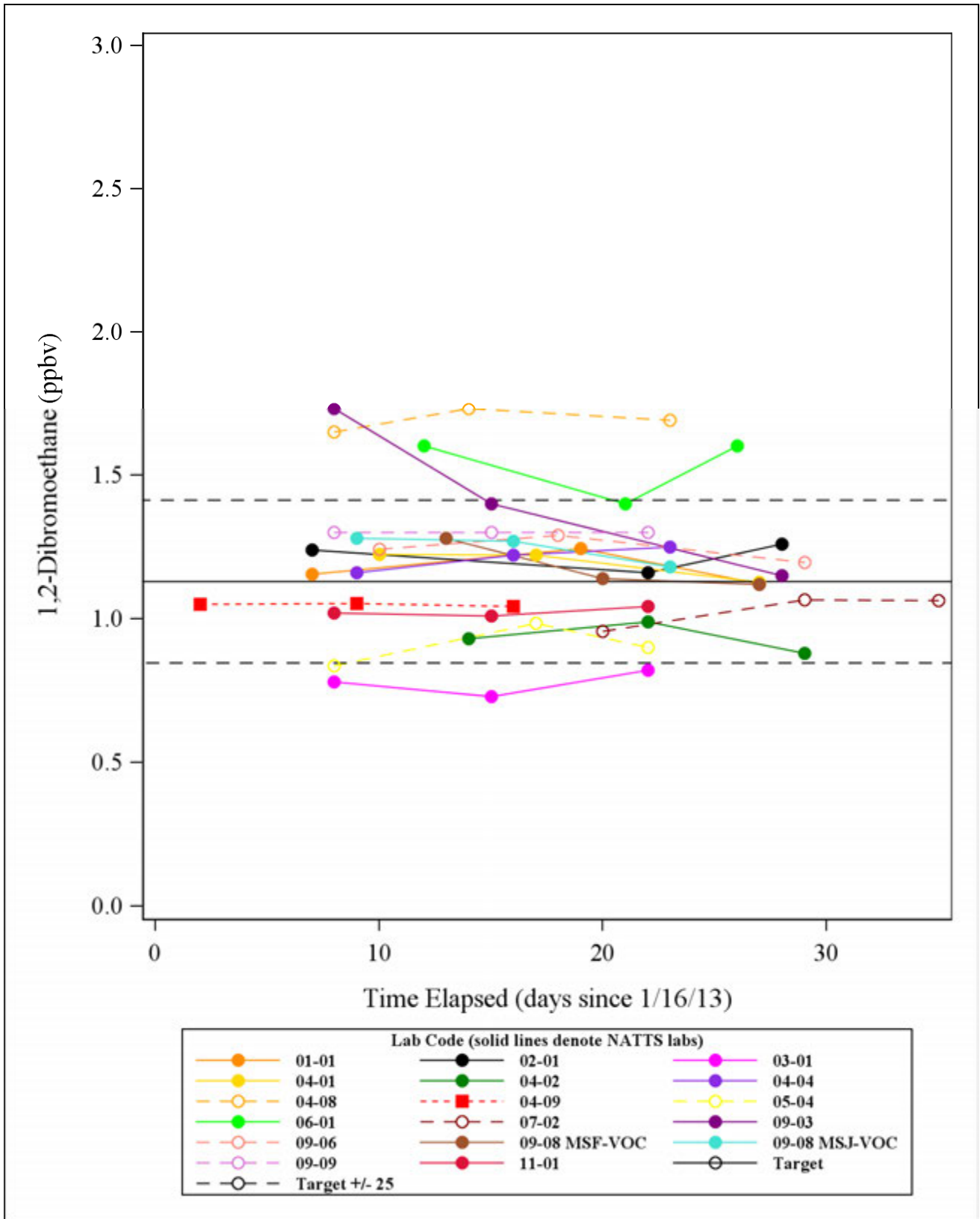


Figure B-6. Observed Trend in 1,2-Dibromoethane Concentration among the 3 Replicate Testing Days, by Laboratory

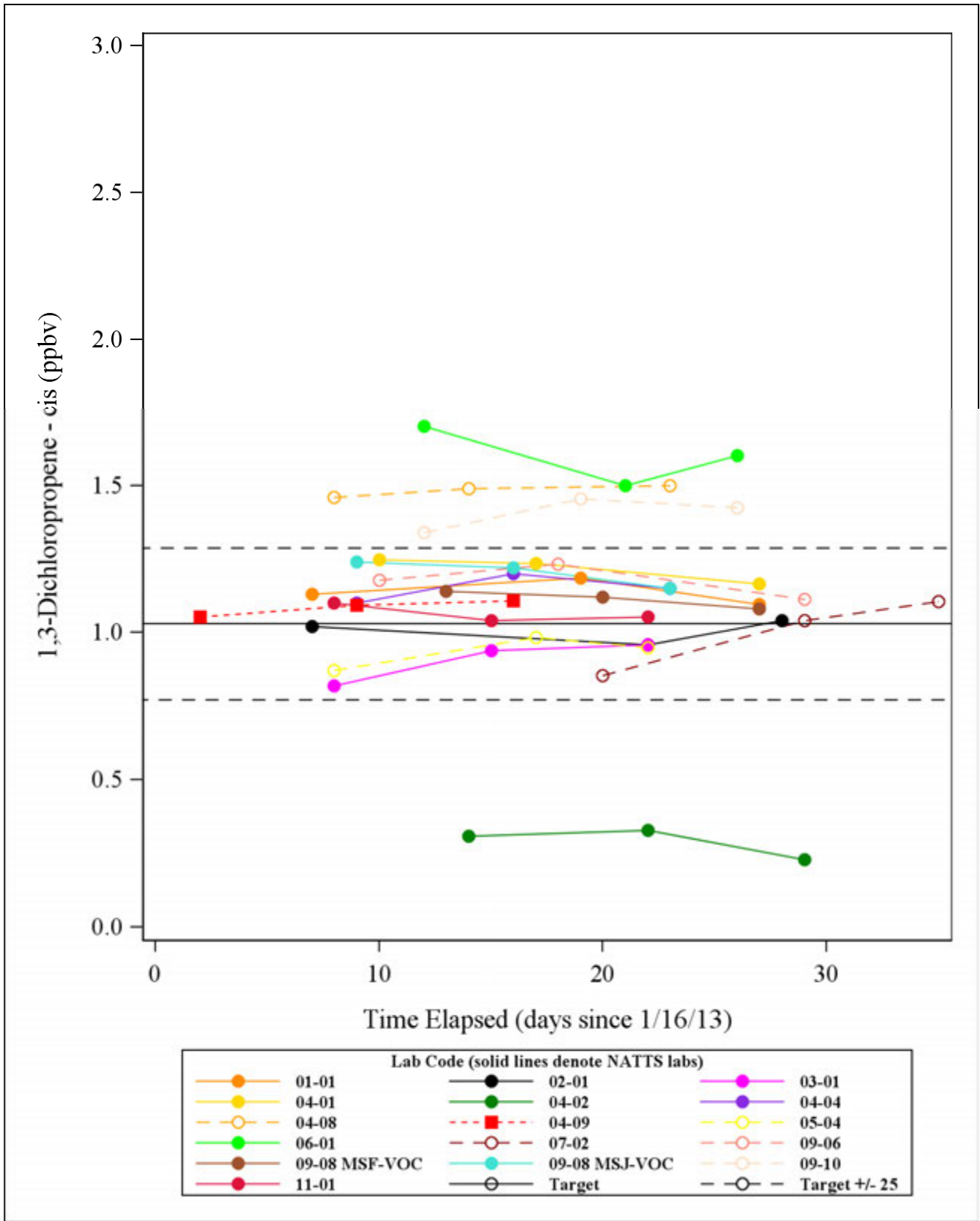


Figure B-7. Observed Trend in 1,3-Dichloropropene - cis Concentration among the 3 Replicate Testing Days, by Laboratory

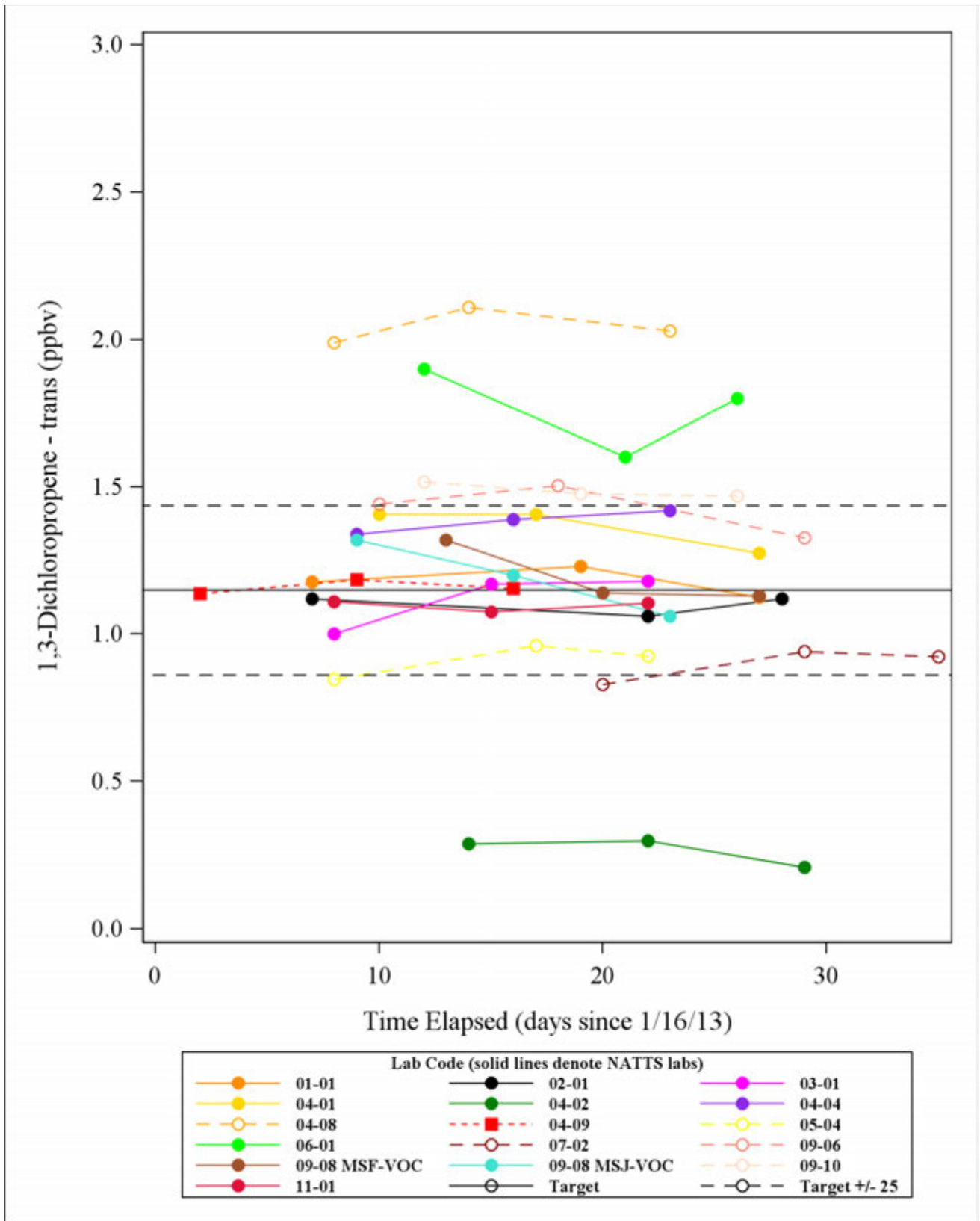


Figure B-8. Observed Trend in 1,3-Dichloropropene - trans Concentration among the 3 Replicate Testing Days, by Laboratory

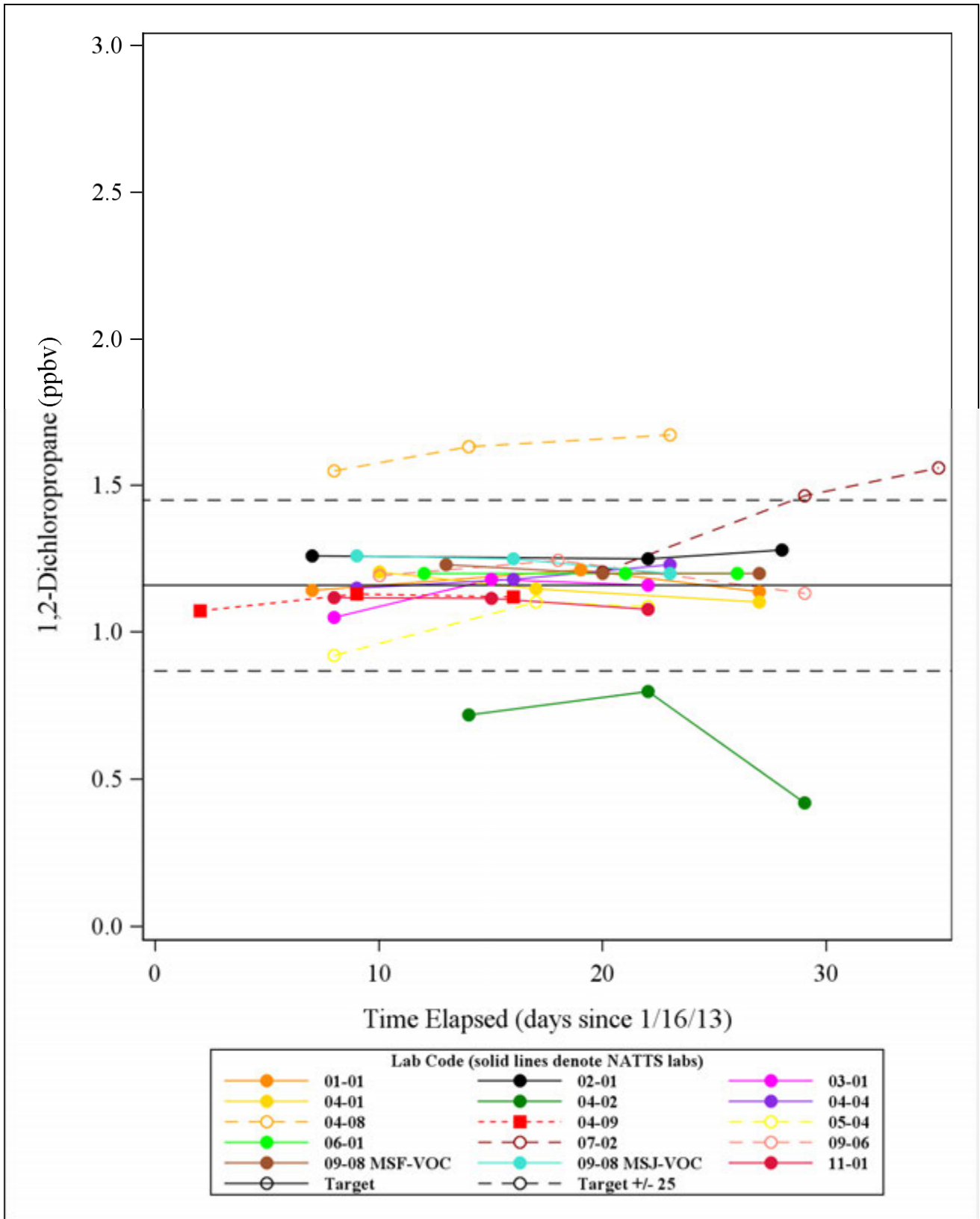


Figure B-9. Observed Trend in 1,2-Dichloropropane Concentration among the 3 Replicate Testing Days, by Laboratory

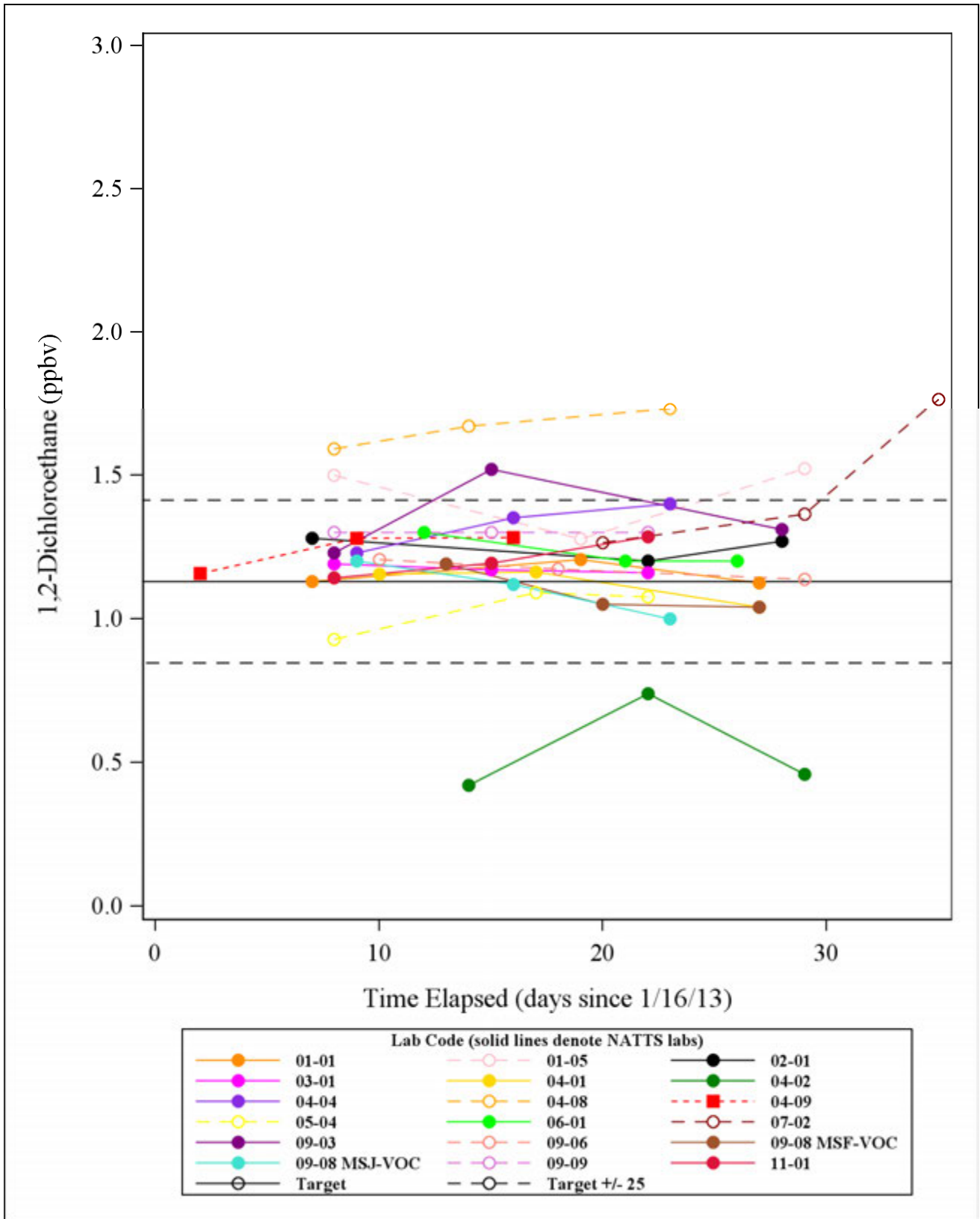


Figure B-10. Observed Trend in 1,2-Dichloroethane Concentration among the 3 Replicate Testing Days, by Laboratory

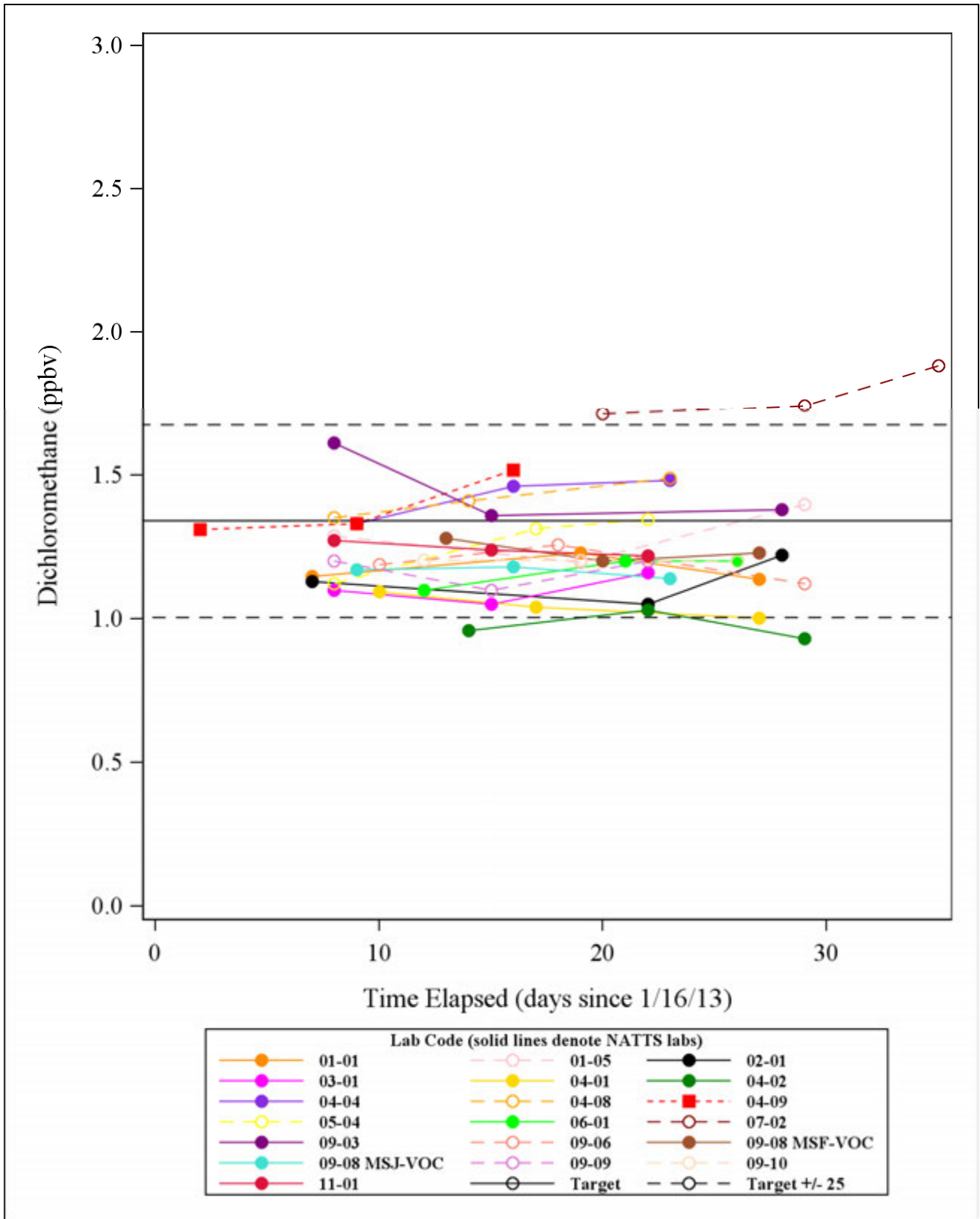


Figure B-11. Observed Trend in Dichloromethane Concentration among the 3 Replicate Testing Days, by Laboratory

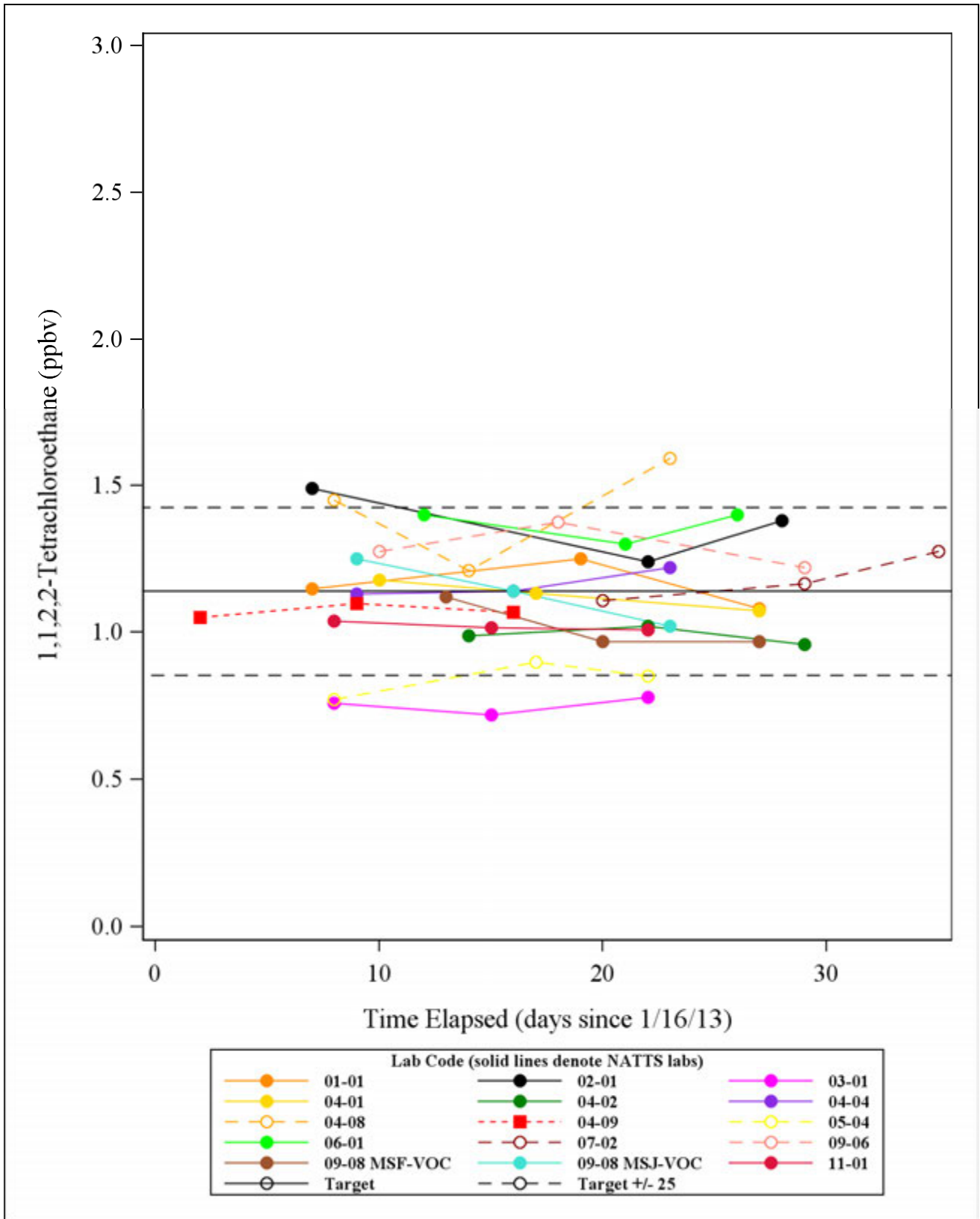


Figure B-12. Observed Trend in 1,1,2,2-Tetrachloroethane Concentration among the 3 Replicate Testing Days, by Laboratory

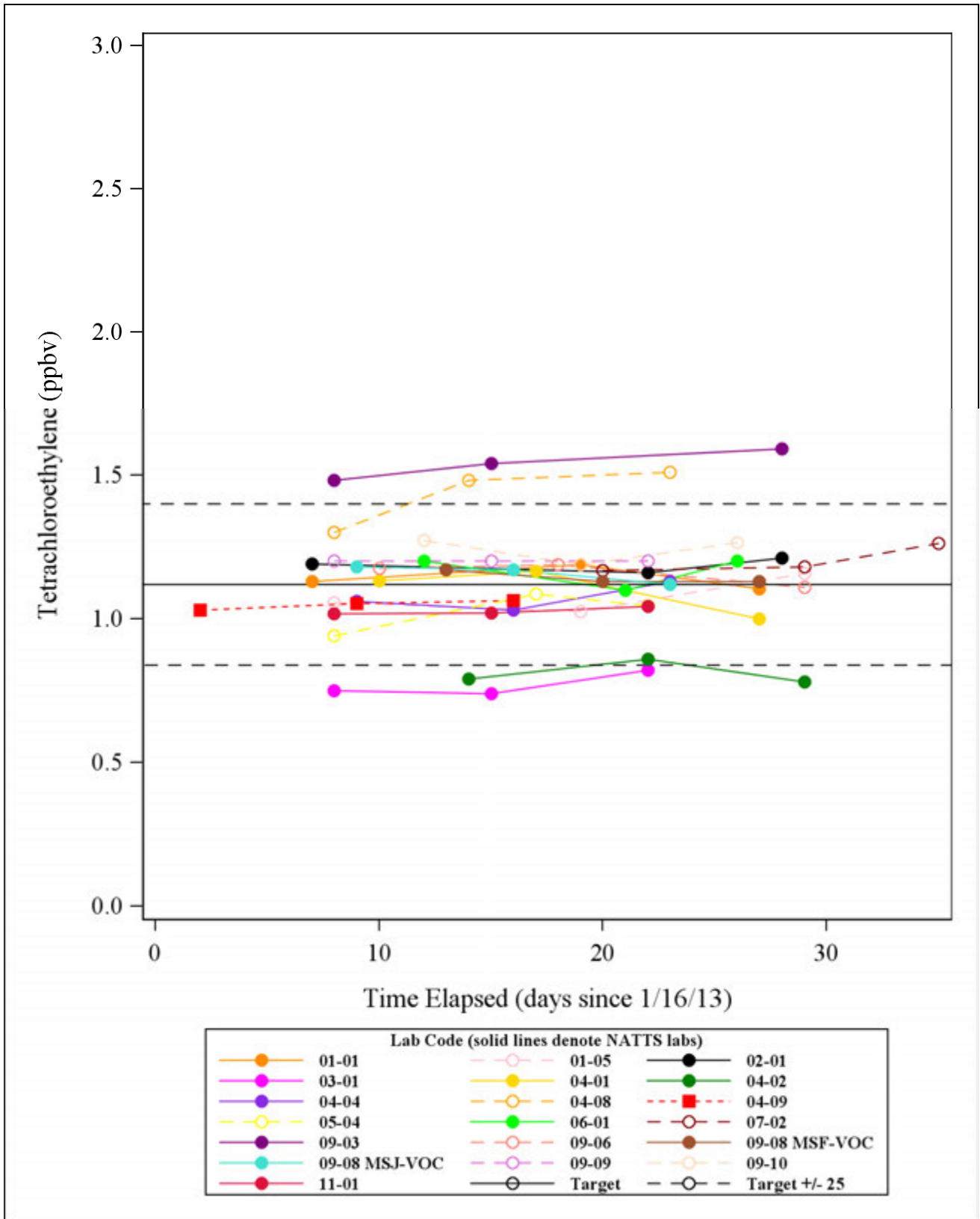


Figure B-13. Observed Trend in Tetrachloroethylene Concentration among the 3 Replicate Testing Days, by Laboratory

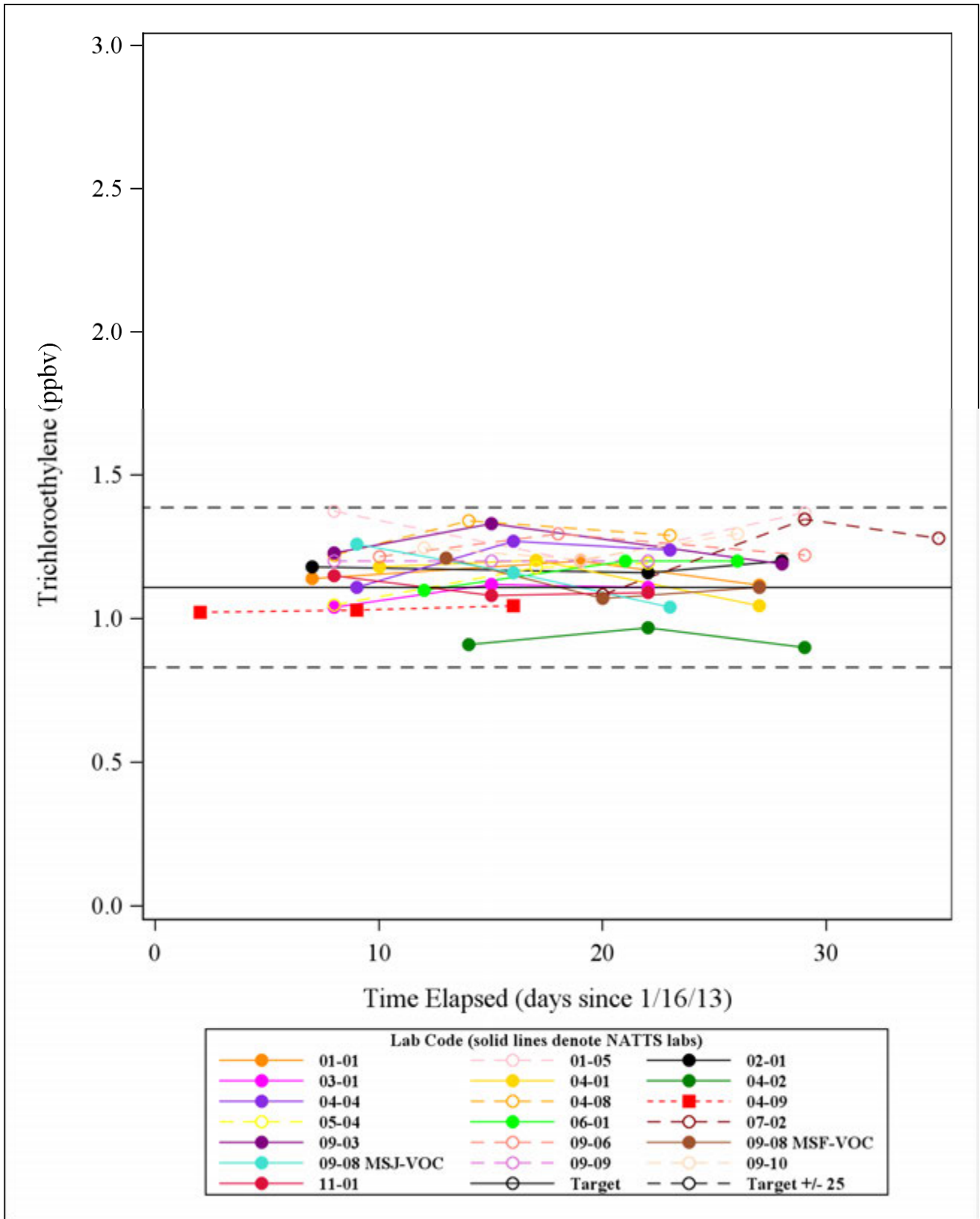


Figure B-14. Observed Trend in Trichloroethylene Concentration among the 3 Replicate Testing Days, by Laboratory

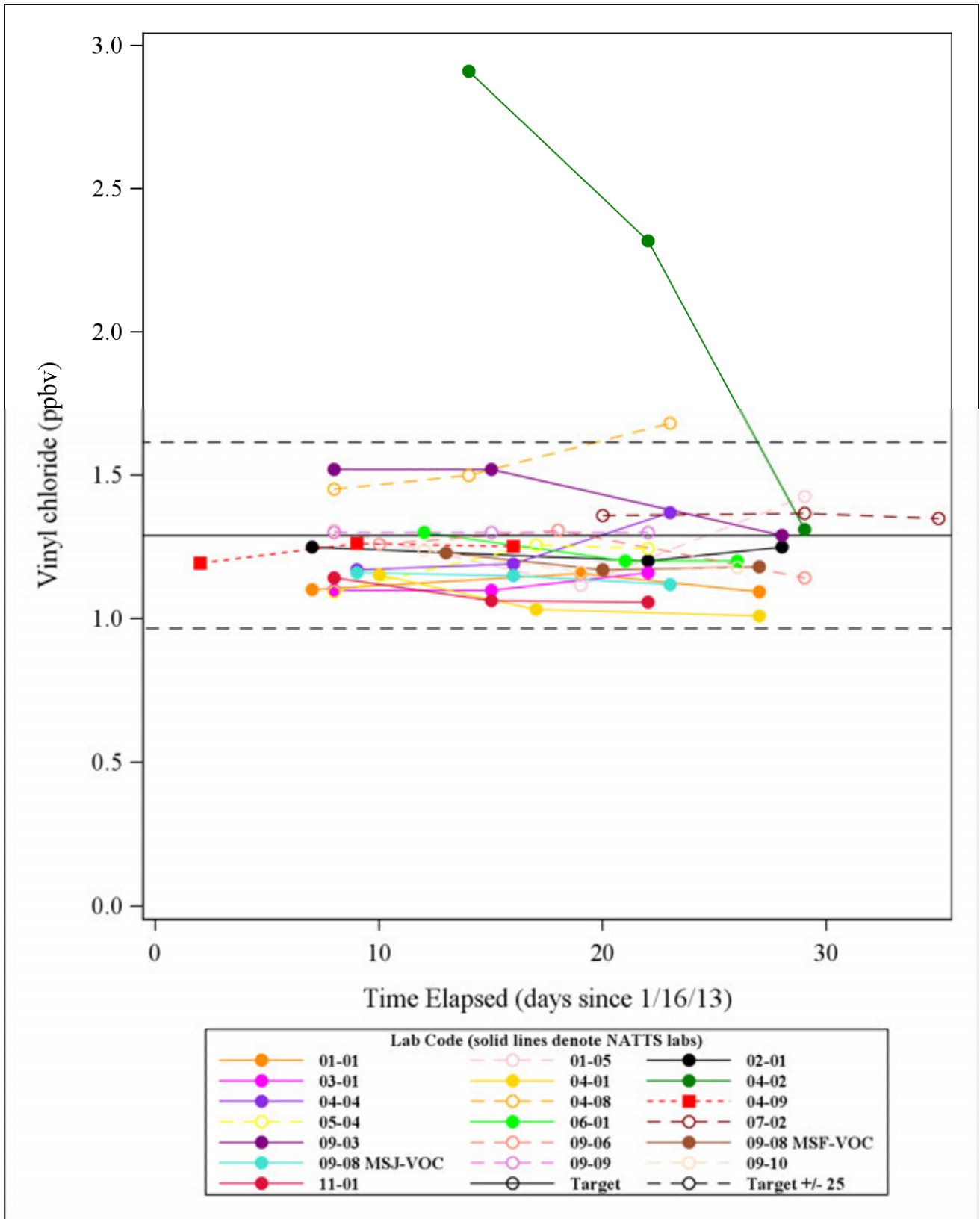


Figure B-15. Observed Trend in Vinyl Chloride Concentration among the 3 Replicate Testing Days, by Laboratory