EFFECTS OF ENVIRONMENTAL CONDITIONS ON PARTICULATE NITRATE STABILITY DURING POST SAMPLING PHASE

Gerhard H. Achtelik Jr., Jim Omand
Monitoring and Laboratory Division
California Air Resources Board
1927 13th Street, P.O. BOX 2815
Sacramento, California 95812

ABSTRACT

This study was designed to evaluate the stability of $PM_{2.5}$ particulate nitrate during the post sampling period. Four samples were collected per sampling run following instrument guidelines similar to those described in the particulate matter federal reference method. One of the four samples was extracted on-site and was used to represent a "no losses" category against which one could compare the effect of different post sampling environmental conditions. The remaining samples were exposed to various environmental conditions prior to extraction. The post sampling test conditions were storage temperature, storage time, and open versus closed container. The post sampling test conditions were among those permitted in the operating parameters for filter handling described in the U.S. EPA's $PM_{2.5}$ NAAQS regulations. The nitrate values were evaluated by regression analysis for similar environmental conditions. This study suggests that particulate nitrate losses occur if filters remain on samplers for prolonged periods of time after sampling. Losses increase as the filters are exposed to increased temperature. The study suggests that placing filters in closed containers and a cool environment can significantly reduce nitrate losses.

INTRODUCTION

This study was designed to evaluate the stability of particulate nitrate during the post-sampling period for samples collected on low volume samplers using Teflon filters. In part, the study originated to support California Air Resources Board’s (CARB) comments regarding the changes of the Particulate National Ambient Air Quality Standard (NAAQS). The sampler for the new NAAQS is designed to collect 2.5 µm particulate on a 47mm Teflon filter at a sample flow rate of 16.7 lpm. Since the intent of this study is to evaluate nitrate stability after sample collection, the sample flow rate and sampling media used in the study matched those specified by the U.S. EPA for the reference sampler.

The samples were collected at the CARB operated site in Bakersfield, located on California Avenue. The study was conducted in the winter time, normally the season with the highest particulate concentrations. High historic fine particulate ($PM_{2.5}$) concentrations and predominant concentrations of volatile compounds made this a good $PM_{2.5}$ site for the study.

The study attempted to assess the effect weathering (environmental exposure in field and transit) has on particulate nitrate concentrations during the post-sampling period. For our purposes, weathering was accomplished by varying the temperature the filter was exposed to and/or the number of days between the end of sampling and the date of filter extraction. In actuality, all filters were weathered in the laboratory. The conditions were identical until the filters were received in Sacramento.

STUDY DESIGN

Study period - Sample collection began in the field the week of November 17, 1996 and ended during the last week of January 1997.

Sampler - A modified $PM_{2.5}$ California Acid Deposition Monitoring Program (CADMP) Dry Deposition sampler was chosen for the study. The CADMP sampler uses a PFA Teflon-coated Bendix 240 cyclone operating at 113 liters per minute. The particle stream is directed into a conical shaped plenum that contains an eight port manifold. The sampler was configured to allow four samples to be collected simultaneously on 47 mm Teflon filters each at a flow rate of 16.7 lpm.

Filter and Holder - The filters used were 47 mm diameter with a 2 µm pore size made out of Teflon manufactured by Gelman Sciences. The filters were installed into a Teflon filter holder in the laboratory in Sacramento. The filter holder is of tubular design, with a 5 cm diameter and 9 cm height. Prior to sampling the field operator installed the filter holder assembly into the sampler. Post sampling the field operator would remove the filter holder assembly, cap both the inlet and outlet and ship the whole assembly. The field operator removed only the field extraction sample filters from the filter holders.

Sampler Precision - The sampler precision was evaluated during the study by extracting all four filter samples in the field immediately after the completion of a test sampling run. The extracted sample was analyzed for nitrates and sulfates. Analyses for sulfate were included since sulfate samples are likely to be more stable than nitrate samples and therefore can serve as a measure of the samplers operation.

Sampling Schedule - The sampling runs started at 9 a.m and ended 24 hours later. Typically runs were started on Sunday, Monday, Tuesday, and Wednesday. The sampling schedule was designed to minimize the amount of time a filter was in an uncontrolled environment. All samples were removed from the sampler and either extracted at the site or shipped on blue ice using next day delivery.

Extraction Schedule - Nitrate and sulfate were extracted from the filter for subsequent analysis by ion chromatography. The extraction process stabilizes the pollutants from further loss. Sample or filter weathering was replicated by varying the amount of time between the end of a sample run and the sample extraction. The samples were extracted at intervals of 0, 2, and 7 days after sampling completion. A same day field extraction was performed on at least one filter for every sample run. The field extraction was used as a reference point for the remaining three filter samples. The two-day scenario represented the optimum normal sample collection scenario, i.e., the sample filter was removed shortly after the completion of the sampling run, the filter holder was closed and shipped on blue ice. The sample filter arrived at the laboratory the following day and was weathered for 24 hours and extracted. (For regulatory monitoring the sample would be weighed first then extracted.) The seven-day scenario approximated a longer post-sampling period allowed in the $PM_{2.5}$ regulations.

Filter Storage Environments - The variables evaluated were selected from operating parameters currently in place and from those described in the $PM_{2.5}$ NAAQS. Filter samples were stored refrigerated, at room temperature, and heated. The refrigerated samples were stored in a standard laboratory refrigerator at 4º C (39º F). The room temperature conditions are those currently required for the PM_{10} program and represent the filter conditioning and weighing environments. The balance room was held at 23.0 +/- 3º C (73.4 +/- 5º F) and at a relative humidity of 40.0 +/-5%. The elevated temperature represents the maximum allowable filter temperature stated in the proposed NAAQS. Heated samples were held in a small oven at 32º C (90º F). The various filter storage conditions are shown in Table 1.

Table 1 Sample Storage

Storage time*	Storage conditions	filter holder
24 hours	refrigerated	closed
24 hours	heated	closed
24 hours	balance room	closed
24 hours	balance room	open
6 days	refrigerated	closed
6 days	heated	closed
6 days	heated	open
6 days	balance room	closed
6 days	balance room	open

* The sample storage conditions do not include the shipping time.

Sample Analyses - The filter analyses were performed by first wetting the filter with 50 microliters of ethanol then extracting with 20 milliliters of deionized water. The extracted solution was stored and refrigerated. The extract was analyzed for nitrate and sulfate by ion chromatography. Filter samples that were extracted in the field were placed on blue ice and shipped via overnight delivery to the laboratory.

RESULTS

The various field extraction and sample filter storage conditions are plotted on X, Y graphs. The x axis represents the field extraction value and the y axis represents the concentration that resulted from the filters being exposed to one of the filter sample handling variables. The primary x and y axis display the data in units of micrograms per filter (µg/filter), the secondary axes are in ambient concentration units of micrograms per cubic meter ($\mu g/m^3$). The ambient concentration are derived by dividing the filter mass value by the total flow to obtain $\mu g/m^3$. The conversion factor was based on a standard sampling time of 1440 minutes and flow rate of 16.7 lpm. Due to limitations of the study it was not possible to collect the same number of samples for each storage condition. Graphs with sulfate data are included for some storage conditions to show that sample losses were limited to nitrates.

Sampler Precision - The sampler precision was evaluated during the study by extracting all four filter samples in the field immediately after the completion of a test sampling run. The extracted sample was analyzed for nitrates and sulfates. Throughout the study seven precision runs were performed. The sampler precision (sample standard deviation divided by the sample mean) based on sulfate analyses ranged from 2.6% to 7.8% with the average being 4.4%. The filter mass and standard deviation for each precision run are given on Table 2. The sample analyses were performed at the Inorganics Laboratory in Sacramento.

Table 2 Sampler Precision

Run end date	SO_4^- (µg/filter)				SO_4^-	Percent STD/
	5	**6**	**7**	**8**	STDS(µg)	Mean
11/21/96	17.24	17.48	17.32	16.48	0.44	2.60
12/04/96	41.46	47.00	43.40	39.16	3.32	7.76
12/13/96	14.94	16.02	14.58	16.60	0.94	6.03
12/24/96	13.30	14.24	12.80	12.74	0.69	5.23
12/31/96	24.30	25.30	24.70	23.70	0.67	2.75
01/09/97	22.66	23.82	22.68	22.14	0.71	3.11
01/31/97	63.04	64.36	67.96	65.30	2.08	3.19
Average Standard Deviations						4.38

Graph 1 represents the minimum weathering conditions a filter sample could be exposed to. The filter samples were stored in a closed filter holder, in the balance room for 24 hours and extracted. This storage condition resulted in a nearly 1 to 1 fit with the field extraction. The 24 hour closed scenario was used to help identify losses due to filter conditioning. A typical filer sample would be conditioned by being placed in the balance room in an open container for 24 hours before mass weighing and extraction.

Graph 2 represents the best possible routine sample analyses scenario, i.e., minimal weathering. The filters were removed from the sampler, packed on blue ice and shipped using an overnight delivery service. Upon arrival at the laboratory the filters were conditioned for twenty-four hours in an open filter holder in the balance room and then extracted. This storage condition resulted in a nearly 1 to 1 fit with the field extraction.

For **Graph 3** the filter sample was exposed to short term weathering by storing the filter sample for 24 hours in a closed filter holder at 32º C before extracting. This condition could represent transport conditions. Due to limited data this graph is inconclusive. One of three samples indicated some loss. Short term elevated temperature conditions in a closed environment could cause nitrate losses.

Other one-day scenarios included 24 hour refrigerated in a closed container and 24 hour heated in an open container. The 24 hour refrigerated sample indicated no sample loss. Unfortunately the samples for the 24 hour heated open condition were invalidated due to handling errors.

Graph 4 represents long term protected storage. The filter samples were stored for six days in a closed filter holder in the balance room and extracted. This storage condition resulted in a good fit with the field extraction. The concentrations collected below 160 µg/filter show almost a 1 to 1 fit with ideal. The calculated slope regression equations is $y = 0.993x – 4.712$ with a correlation coefficient of .996. Storing the filter for 6 days at moderate temperature (23º C) revealed almost no detectable nitrate loss.

For **Graph 5** the filter sample was weathered for six days. The filter sample was stored for six days in an open filter holder in the balance room and extracted. Only four samples are available but they indicate a clear loss of nitrate. Of interest is that the nitrate loss appeared to be constant regardless of concentration. The loss averages around 12 µg/filter. The sulfate analyses for this storage condition is shown on **Graph 6** and indicates no sample loss.

Graph 7 represents the extreme weathering conditions for this study. This could represent a filter that was left on a sampler for an extended period. The filter sample was stored for six days in an open filter holder at 32º C and extracted. As expected, storing the filter sample for six days in an open filter holder in a heated environment created the largest nitrate loss. Again, the amount of nitrate loss was constant averaging around 20 µg/filter throughout the range of concentration. The sulfate analyses for this storage condition is shown on **Graph 8** and indicates no sample loss.

Graph 9 represent long term protected storage at an elevated temperature. This condition could describe transport conditions and/or conditions found in a multi-filter sampler if the filter was tightly enclosed after sampling. The filter sample was stored for six days in a closed filter holder in a heated environment. The graph indicates some nitrate loss below 160 µg/filter. At concentrations below 160 µg/filer the nitrate loss appears to average around 10 µg/filter. The sulfate analyses for this storage condition is shown on **Graph 10** and indicates no sample loss.

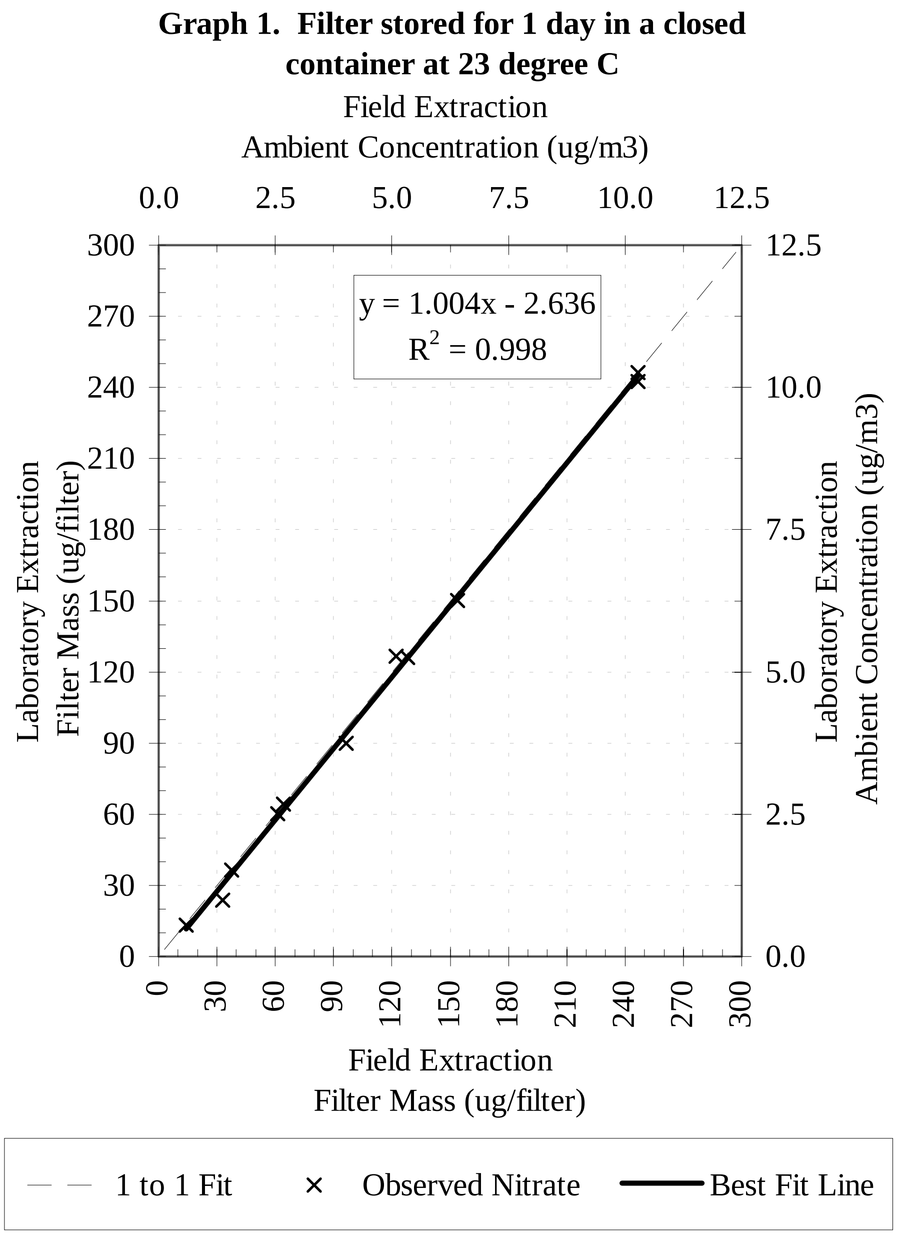
CONCLUSIONS

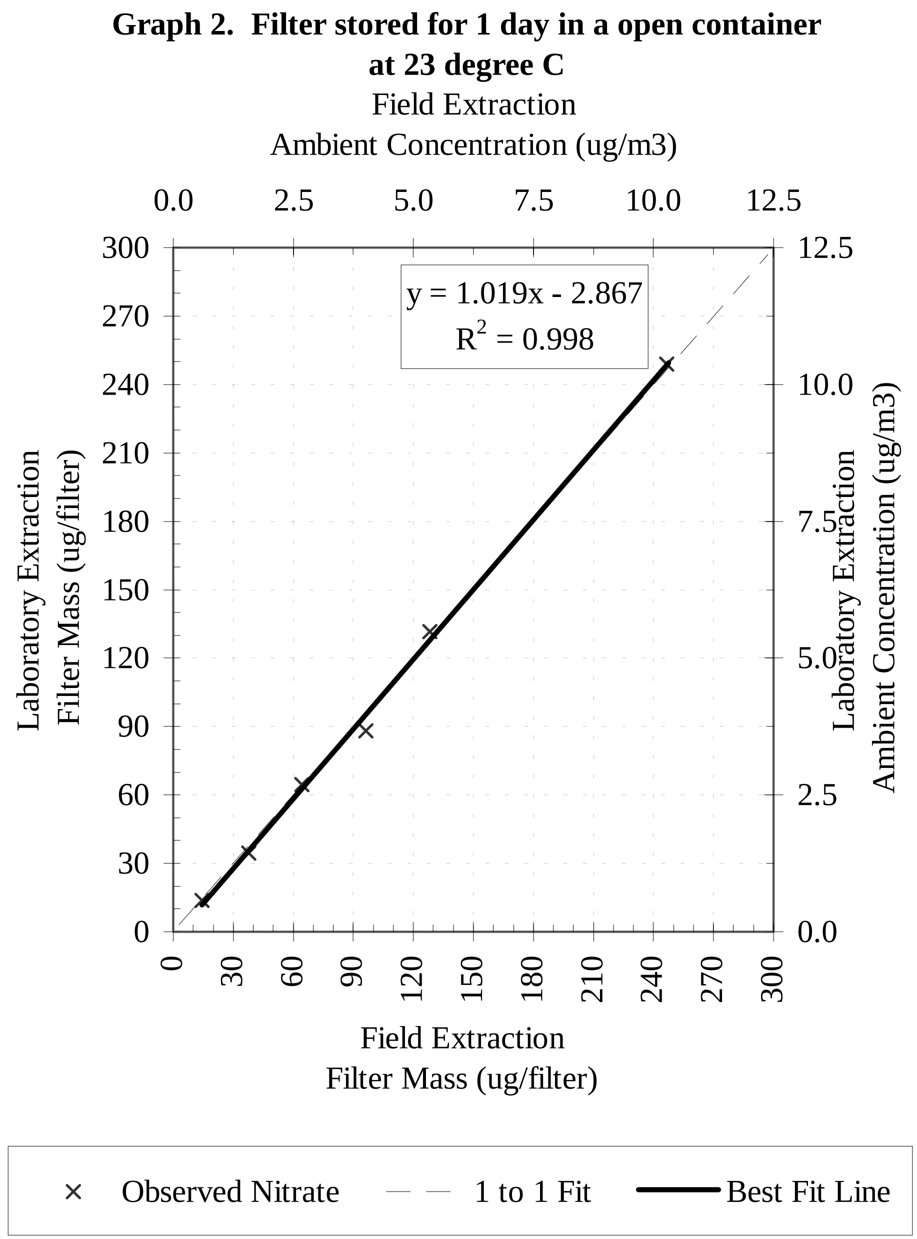
There is no apparent $PM_{2.5}$ nitrate loss from Teflon filters in the post-sampling period if the filter sample is stored in a closed container and at room temperature or lower. Significant nitrate losses occur when the filter is heated and/or is left in an open filter holder for six days. Losses appear when the filter is heated in a closed filter holder. In the heated closed filter holder a nitrate loss is noticeable at mass values below 160 µg/filter.

This study suggests that nitrate losses can be expected to occur if filters remain on samplers for prolonged periods after sampling. Losses increase as the filters are exposed to increased temperature. The study suggests that placing filters in closed containers and a cool environment can significantly reduce nitrate losses. Under these conditions, it may not be necessary to expedite filter transport to a laboratory for processing.

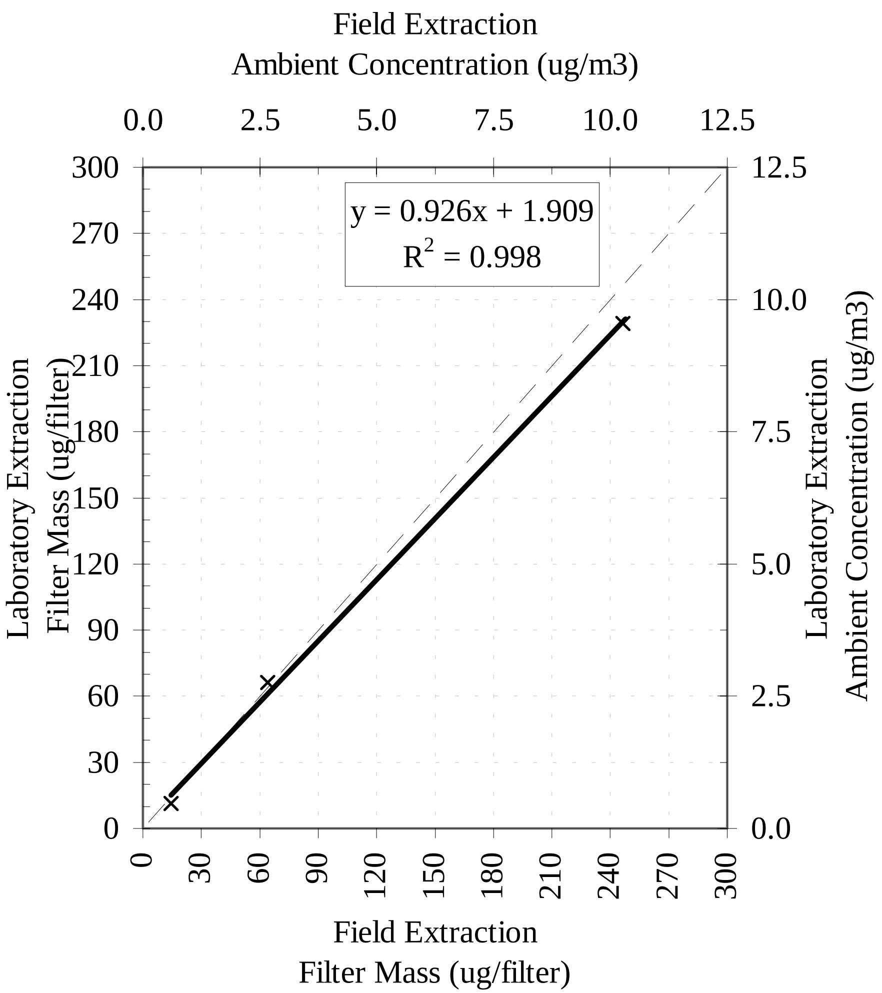
Lastly, the study found no adverse effect on nitrate levels attributed to the 24 hour equilibration process as the U.S. EPA proposed.

Acknowledgments This study was made possible through the combined efforts of the staff from the Monitoring and Laboratory Division. Their combined effort made it possible to obtain, calibrate and operate the sampler and to analyze the filters for this study in a very short time. Special thanks to Peter Ouchida, manager of the Air Quality Monitoring-Central Section, Jack Romans, and Ralph Robles for field sampling at the Bakersfield-California Ave. site; Dale A. Secord, manger of the Program Evaluation and Standards Section; Chas Cowell, manager of the Inorganics Laboratory, Samantha Kwan and Elpidio Perez for filter preparation and analyses.


Graph 1. Filter stored for 1 day in a closed container at 23 degree C
Field Extraction
Ambient Concentration (ug/m3)
0.0
2.5
5.0
7.5
10.0
12.5
y = 1.004x - 2.636
R^2 = 0.998
Laboratory Extraction
Filter Mass (ug/filter)
Laboratory Extraction
Ambient Concentration (ug/m3)
0
30
60
90
120
150
180
210
240
270
300
Field Extraction
Filter Mass (ug/filter)
1 to 1 Fit
Observed Nitrate
Best Fit Line

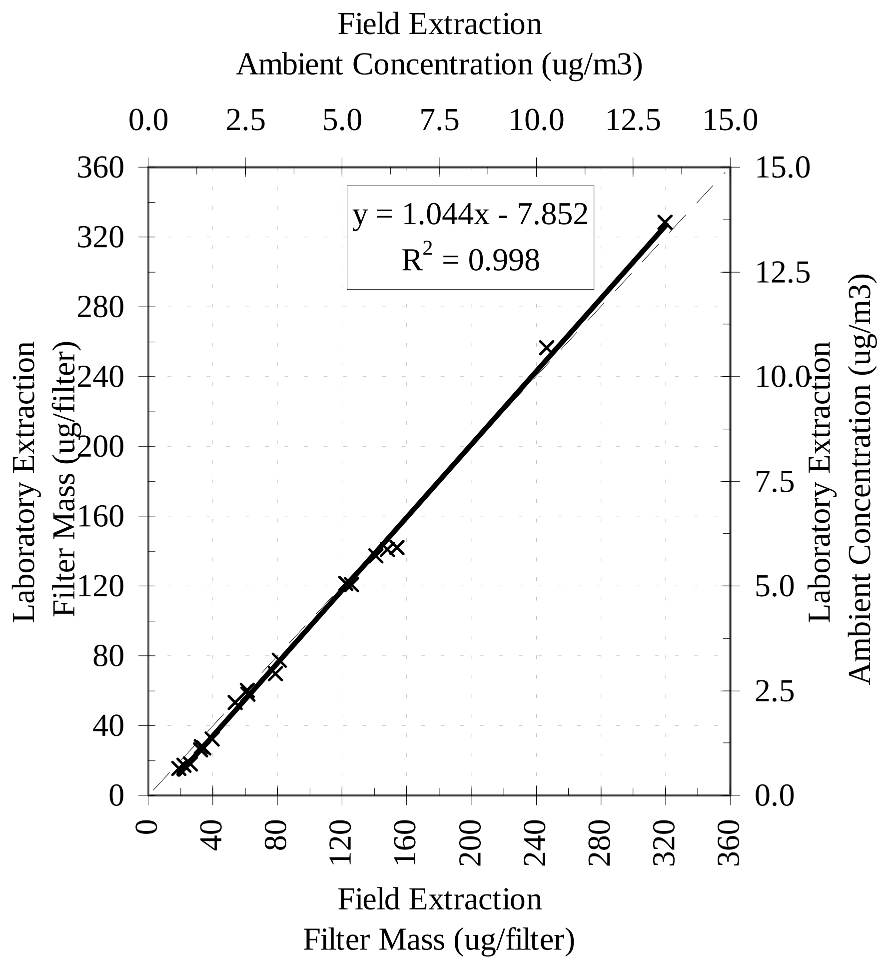

Graph 2. Filter stored for 1 day in a open container at 23 degree C
Field Extraction
Ambient Concentration (ug/m3)
0.0
2.5
5.0
7.5
10.0
12.5
y = 1.019x - 2.867
R^2 = 0.998
Laboratory Extraction
Filter Mass (ug/filter)
Laboratory Extraction
Ambient Concentration (ug/m3)
0
30
60
90
120
150
180
210
240
270
300
Field Extraction
Filter Mass (ug/filter)
Observed Nitrate
1 to 1 Fit
Best Fit Line

Graph 3. Filter stored for 1 day in a closed container at 32 degree C



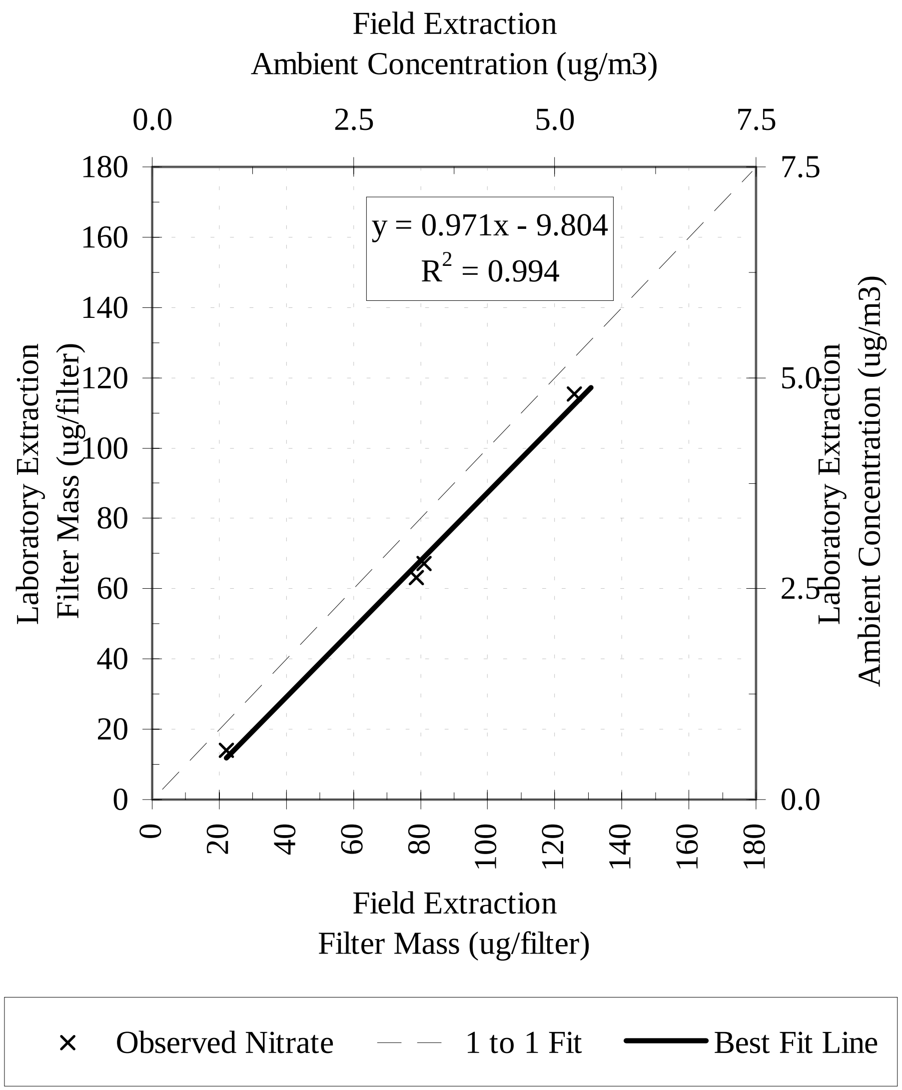
× Observed Nitrate — — 1 to 1 Fit ▬ Best Fit Line

Graph 4. Filter stored for 6 days in a closed container at 23 degree C

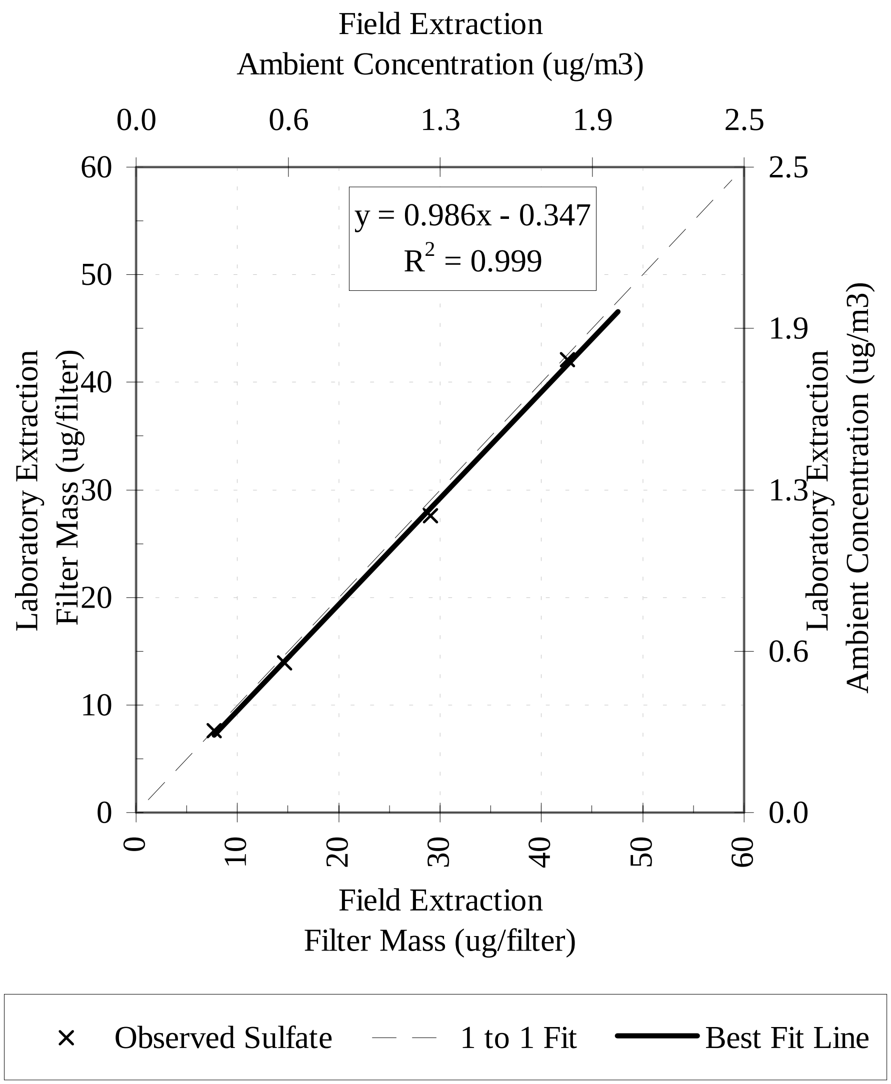


× Observed Nitrate — — 1 to 1 Fit ▬ Best Fit Line

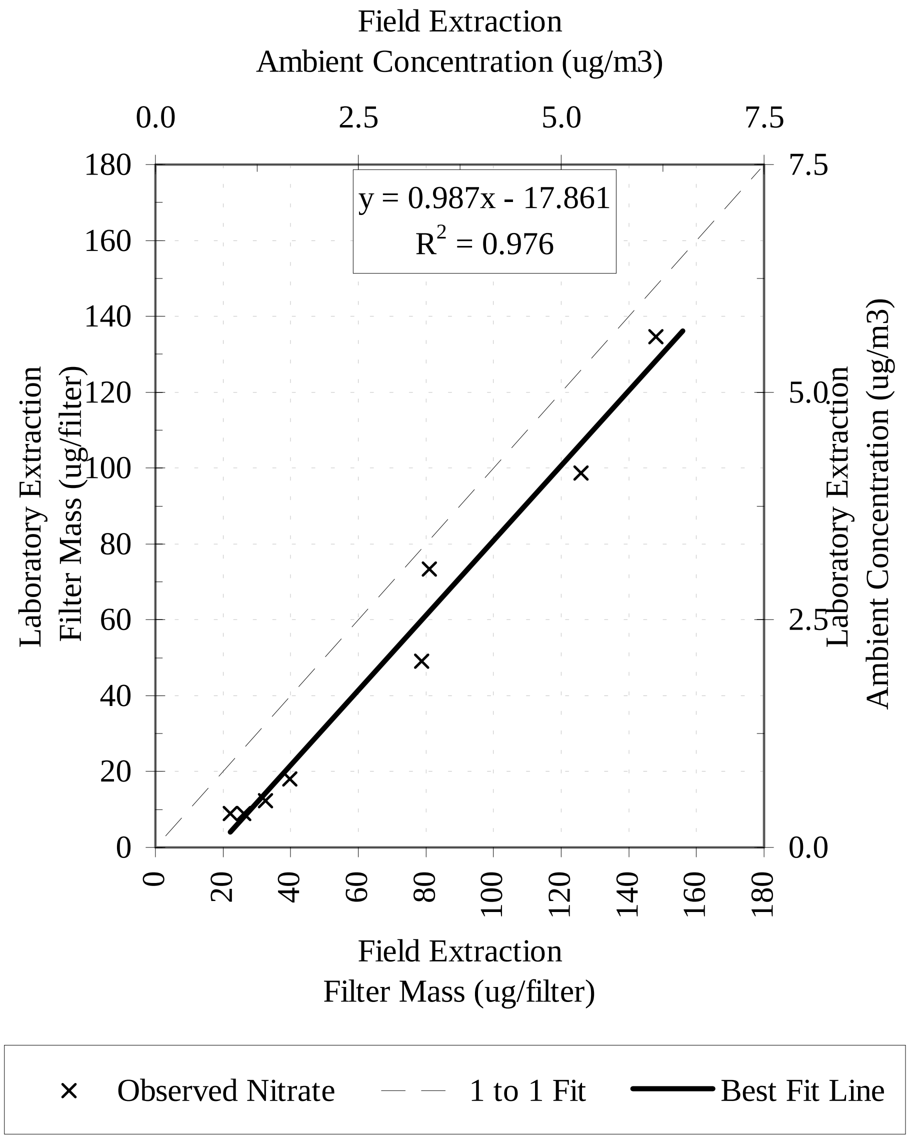
Graph 5. Filter stored for 6 days in an open container at 23 degree C



Sulfate Control
Graph 6. Filter stored for 6 days in a open container at 23 degree C

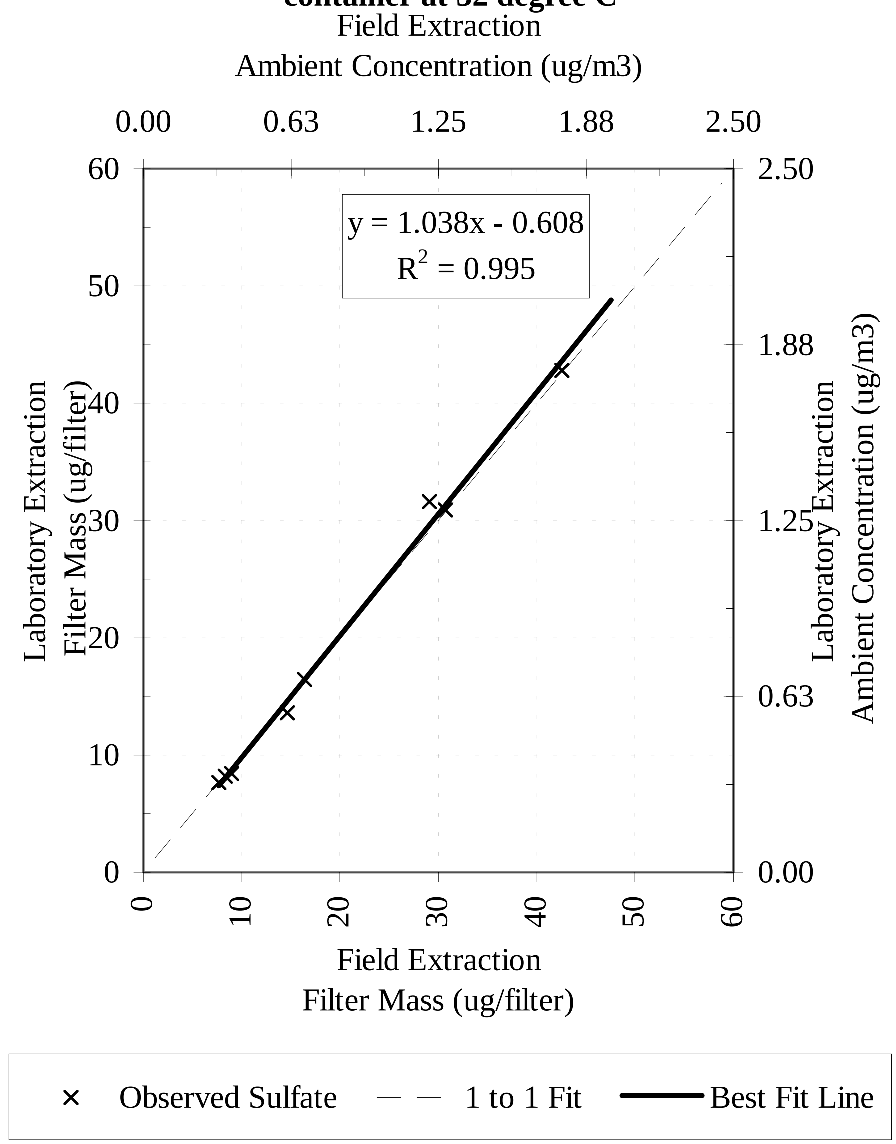


Graph 7. Filter stored for 6 days in an open container at 32 degree C

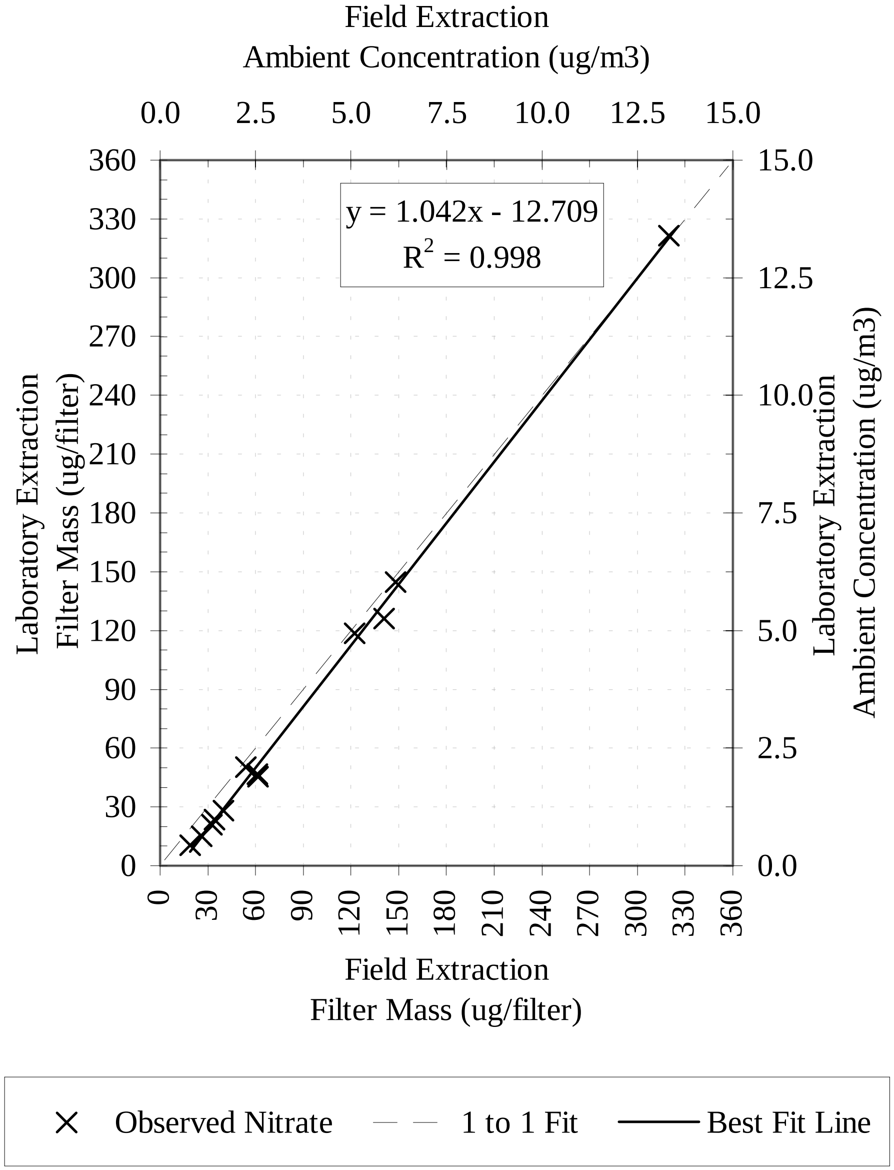


Sulfate Control

Graph 8. Filter stored for 6 days in an open container at 32 degree C



Graph 9. Filter stored for 6 days in a closed container at 32 degree C



Sulfate Control

Graph 10. Filter stored for 6 days in a closed container at 32 degree C