Centre County

Pennsylvania

Senior Environmental Corps

The mission of the Centre County Pennsylvania Senior Environmental Corps (CCPaSEC) is to develop and to support teams of senior citizens who gather and publish data on the quality of water in the streams of Centre County. Through public outreach, with the assistance of the ClearWater Conservancy, the Centre County Conservation District, Nature Abounds, and other environmentally concerned organizations, CCPaSEC seeks to keep the public informed of the importance of clean water and how the management of our civil and natural resources affects the quality of streams in the county.

2016 Quality Report

Ken Johnson Dec 2016

We value the Quality of our data published on our WEB site.

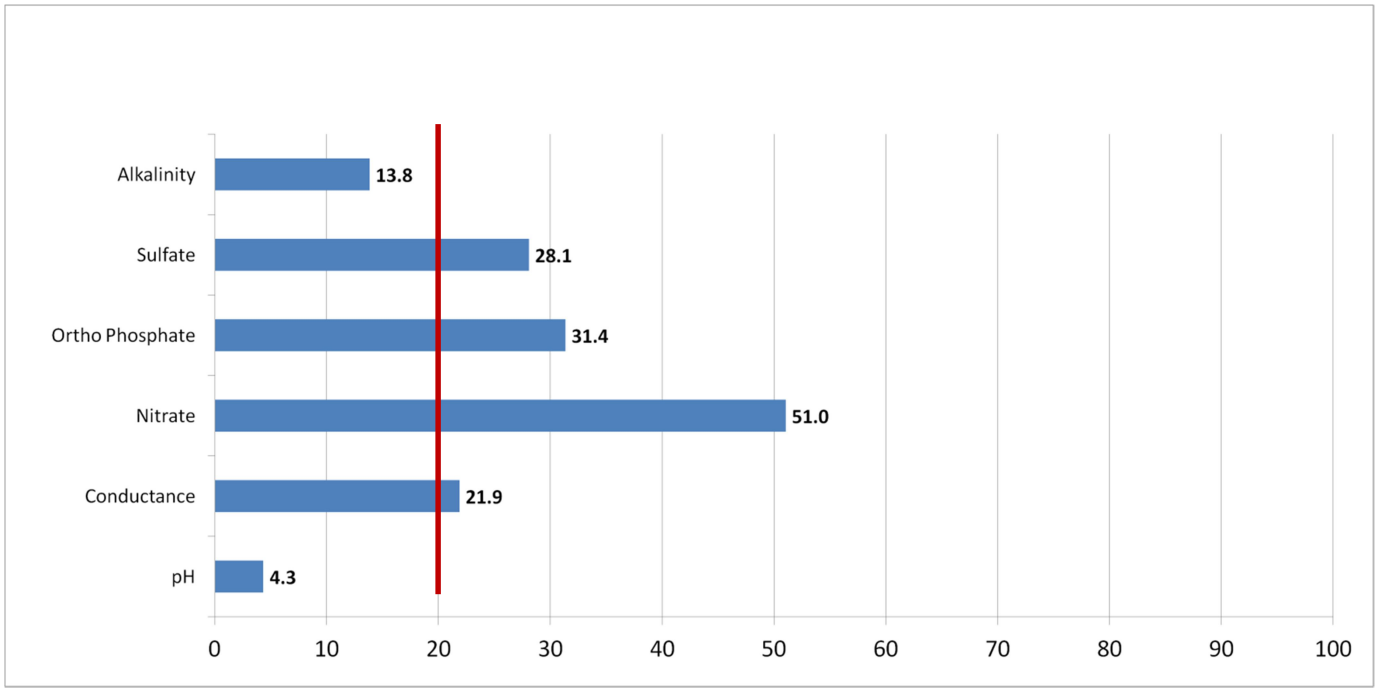
http://www.ccpasec.org/index.php

CCPaSEC has implemented a Quality Assurance Plan in preparation for the Nature Abounds plan distributed at the May Training Session. Basically our plan calls for our Quality Team to conduct Team field reviews, perform duplicate test to determine our collective Relative Percent Deviation (RPD) and a yearly Equipment check including a report on instrument Percent Deviation (PR).

Relative Percent Deviation (RPD): The RPD is one measure of the quality of our posted data. We are not using Laboratory certified equipment and we cannot expect Laboratory level results The Nature Abounds Quality Plan set a goal for the RPD to be less than 20%. It is incumbent on us to report the CCPaSEC RPD of our data to all users.

The CCPaSEC RPD was determined from duplicate testing between eleven (11) of our Field teams and the Quality team. The individual team RPD's were combined (averaged) and presented here.

Relative Percent Deviation (RPD)

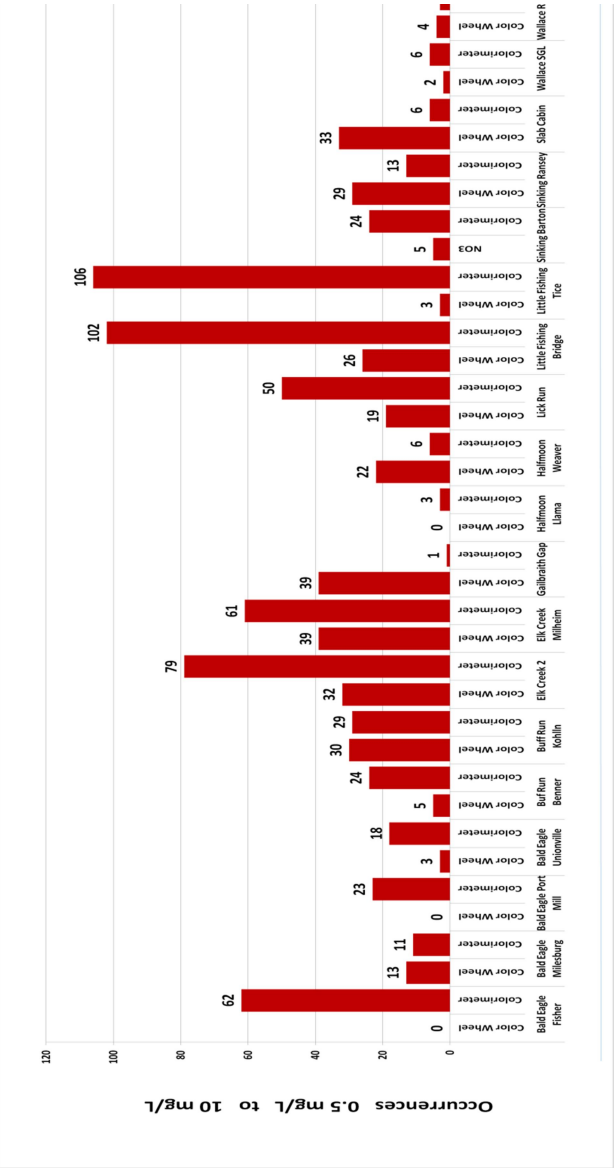


Our goal is to not exceed the red line

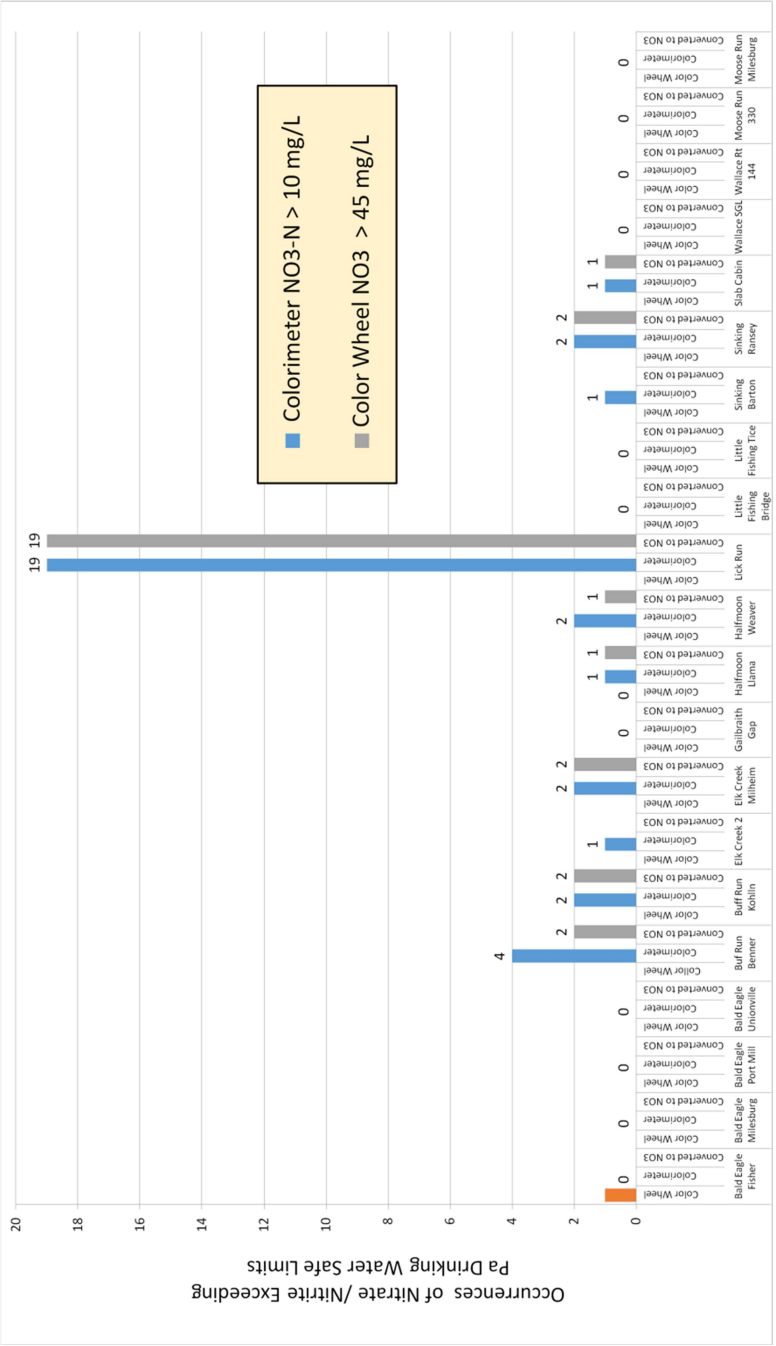
Nitrate results

Our Nitrate RPD results are well in excess of the Nature Abounds goal to be less that 20%. We investigated the probable causes by comparing our previous history of data collected with the color wheel method to that collected using the HACH DR-850 colorimeters (corrected for NO_3) that we began using in 2010 (pages 3 & 4).

The comparison of our historical Nitrate data for the range of 0.05mg/L to 10mg/L taken with the HACH color wheel (NO_3) to that determined with the colorimeter (converted to NO_3) imply the colorimeter measurements tend to be greater.



We feel our Nitrate data is representative with respect to Pennsylvania's drinking water limits for NO_3-N (colorimeter 10mg/L) and the NO_3 (color wheel 45 mg/L). This chart shows the number of occurrences our historical Nitrate data exceeded those limits.



Factors that can bias our results

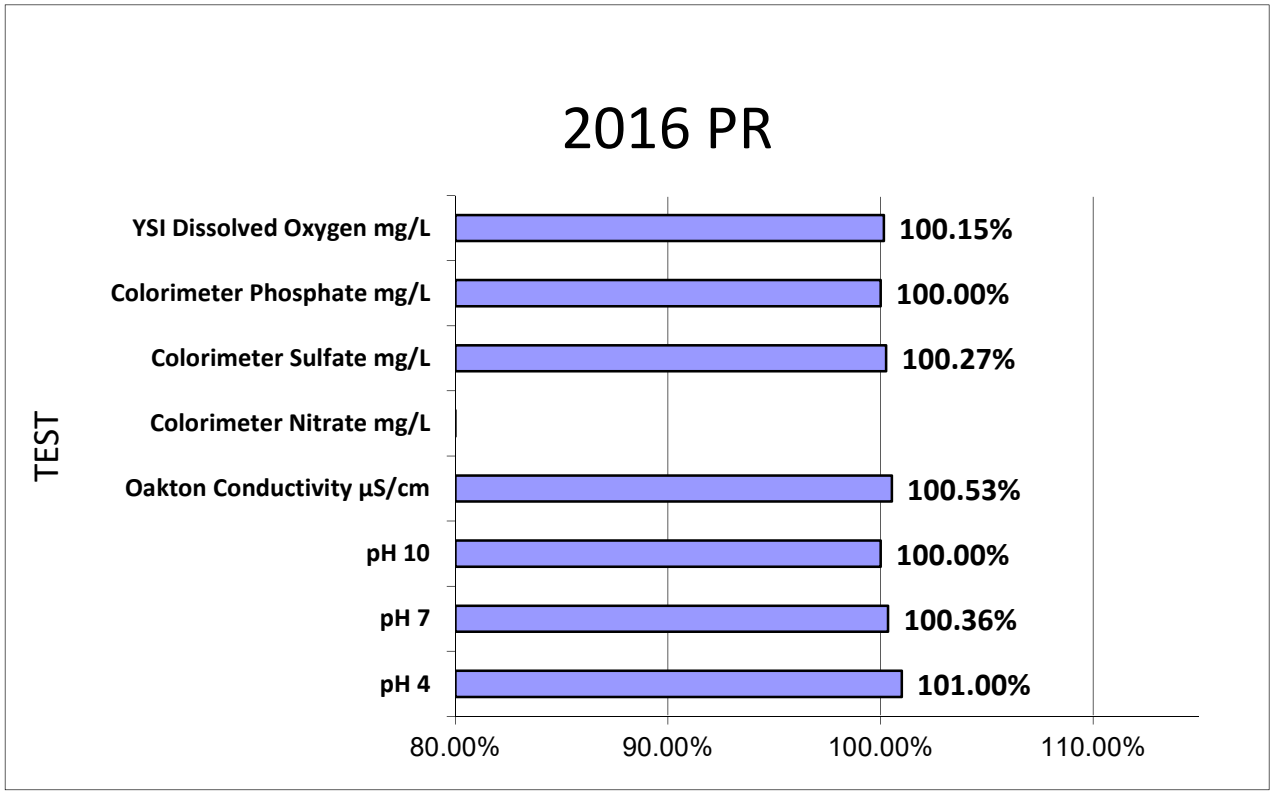
Our teams perform either High or Low Nitrate tests using the DR-850 colorimeters. The comparisons are favorable. Never the less we were concerned about our Nitrate RPD results.

- Our previous experiments with the Sample Cells have demonstrated that their orientation (rotation) with respect to the colorimeter LEDs affect the measurement (***see Appendix 1***). Because both the BASE and Field Sample Cells exhibit this variance, we decided that for consistency, all field team kits dedicate a Sample Cell to each test (Sulfate, Ortho Phosphate, or Nitrate) and we would all align the diamond on the BASE and Field Sample Cells the same way to the colorimeter.
- A comparison of our previous Nitrate data derived using the old HACH color wheel method and our data using our colorimeters have indicated an upward shift that warranted further investigation.
- Our Quality team noticed that it was difficult to completely empty the Nitrate powder packets. Indications of Nitrate Reagent Residue (***see Appendix II***. The amount left behind varied greatly between the field teams and the Quality team. The tests are sensitive to the quantity of reagent. Using less than needed would produce a lower mg/L value and is one likely cause of the disparity in our duplicate tests.
- The Percent Recovery using our Nitrate standard resulted in values much different from the stated value of the standard (The reason is explained on the next page). However, all of the colorimeter PR results for Ortho Phosphate NO_3-N were similar and within a narrow range.
- The law of small numbers describes situations in which we too readily conclude that a pattern we see in a small sample of information also holds for a much larger sample.

Percent Recovery

Percent Recovery (PR) is a measure of the capability of the data measurements of our equipment. Our Quality Control plan calls for testing all of our test equipment each year. The Nature Abounds Quality Plan established PR goal between 90% and 110%.

The tests are performed against standards for pH, Nitrate, Sulfate and Phosphate. We used a common water sample for dissolved oxygen.



The Nitrate PR could not be determined because we were not aware of the need to calculate a correction factor for the Cadmium Reduction method described later in this report. All of the CCPaSEC colorimeters measured the Ortho Nitrate standard range of 7.1 to 8.3 mg/L.

HACH Technical Support

Nitrate Percent Recovery (PR): The HACH Technical service was contacted as to why our equipment tests with the 4.43 Ortho Nitrate standard resulted in results in the mean of 7.86.

The Support Tech's answer: "When testing the standard, you can get higher results on DR-850s using the Cadmium Reduction method." The HACH Tech said the powder pillows contain reagents for cadmium reduction that influence our data. These pillows *assume* a *concentration of cadmium* in the sample that may not be in the general range of our field sample. Many of our Centre County streams have very low levels of Nitrate. The cadmium reduction method may account for some of the apparent increase in Nitrate as measured with the colorimeter shown in (*see pages 3&4*).

The HACH engineer suggested using a correction factor or switching to the Chromotropic (NO3-N) Acid Method 10020 for a less technique-sensitive method. ***However, our DR850 Colorimeters are not programmed for that test method*.** He recommends using a correction factor with our standards (or upgrading our colorimeters to the newer 900 series. The 900 series is listed at $1,341).

The HACH recommended correction method (*see appendix III*) implies that our colorimeter Nitrate data may be skewed high. Our equipment check measurement mean was 7.86 mg/L for the 4.4 mg/L Standard.

If we assume the "*Concentration of the Reagent Blank (B)" for our lot of powder pillows was 0.0,* The HACH NO3-N correction factor would be 0.56. This indicates that all of our Colorimeter Nitrate data may be as much as 1.8 times the actual values.

Our comparison of previous Color Wheel NO3 results correct for with our Colorimeter NO3-N results supports this conclusion (*see pages 3&4*).

We suspect all PaSEC users of the DR-800 series colorimeter will have the same issue.

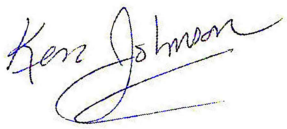
Conclusion and Recommendations:

- We do not recommend any changes in our test procedures. Nature Abounds recognizes the capability of the equipment they have provided us. By maintaining our procedures our published data is consistent and can be compared over time. Our report provides users a measure of the quality of the data. If there is a sudden or profound change in a stream we can notify the proper authorities. Nature Abounds encourage of and approve using the diamond marker for placement of the Sample Cells in the colorimeter.

- It is evident our RPD will exceed Nature Abounds' goals, especially for Nitrate. I believe much of it is inherent in the Sample Cells, the Cadmium Reduction method and not our sampling techniques. I believe our duplicate testing method using a different set of sample cells from the field team include these differences between the sample cells and therefore exacerbate the resulting RPD (for all our colorimeter RPD tests: Nitrate, Sulfate & Phosphate).

- We have no control over the Sample Cells. We should see an improvement in our RPD if the Quality Team performs the duplicate tests with the teams' Sample Cells. The results should be more representative of the team's RPD performance. This will extend the onsite time but we would only need to do this once or twice a year.

- We can improve our RPD results by assuring we completely empty the powder pillows (***see appendix II***). To assure all the reagent is used we should carefully tear open the pillow packs and empty any residue into the sample cells.



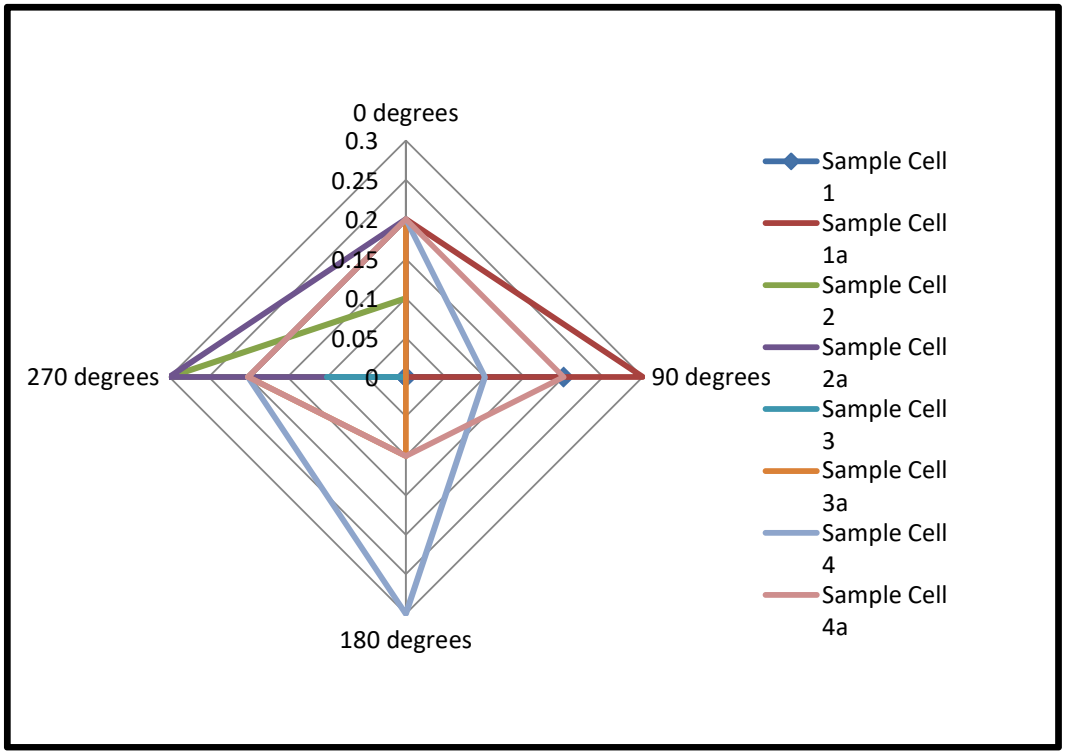
Appendix I

Sample Cell variations and orientation in the colorimeter is another likely factor contributing to the differences in the duplicate tests. The Sample Cells glass walls are uneven and refract the colorimeter light causing a misinterpretation of the light attenuation between the base and water sample. The difference can be substantial.

We compare the orientation of the BASE Sample Cell (0 degrees Diamond) to the Test Sample Cell as rotated through 360 degrees. Two test runs were made with each Sample Cell.

The NO_3-N results range between 0 and 0.3 mg/L.

The diagram illustrates the variance in colorimeter readings due to the orientation of the sample cells in the colorimeter. All sample cells exhibit these variances and are random.



Our field teams orientate the sample cells with the diamond, not as a method to improve accuracy but for consistency of our data over time.

Other test results of the Sample Cells with just distilled water had variations of 0.03. Although the differences seem small, they do affect the actual sample tests. The result of only 0.03 on the low nitrate RPD is shown below:

Original RPD calculation			
Nitrate 0 - 30 mg/L		**Nitrate Delta**	**RPD**
Team	**QC Dup.**		
0.16	0.12	0.04	28.571

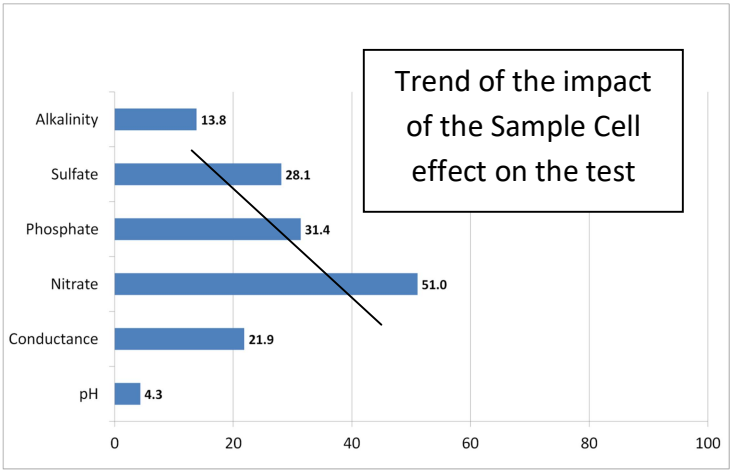
Original RPD calculation			
Phosphate 0 - 50 mg/L		**Phosphate Delta**	**RPD**
Team	**QC Dup.**		
0.34	0.37	0.03	8.451

RPD when you add a 0.03 to the teams result			
Nitrate 0 - 30 mg/L		**Nitrate Delta**	**RPD**
Team	**QC Dup.**		
0.19	0.12	0.07	45.161

RPD when you add a 0.03 to the teams result			
Phosphate 0 - 50 mg/L		**Phosphate Delta**	**RPD**
Team	**QC Dup.**		
0.37	0.37	0.00	0.000

Note: The differences in the Sample Cells between the QC's and Team's can work either way when calculating the RPD.

Our current RPD results also indicate the Sample Cells may have impacted the Phosphate & Sulfate results. The effect on the Sulfate RPD is less because of the magnitude of the number. Our RPD for the Alkalinity and pH are excellent – not being determined with the colorimeter.



Appendix II

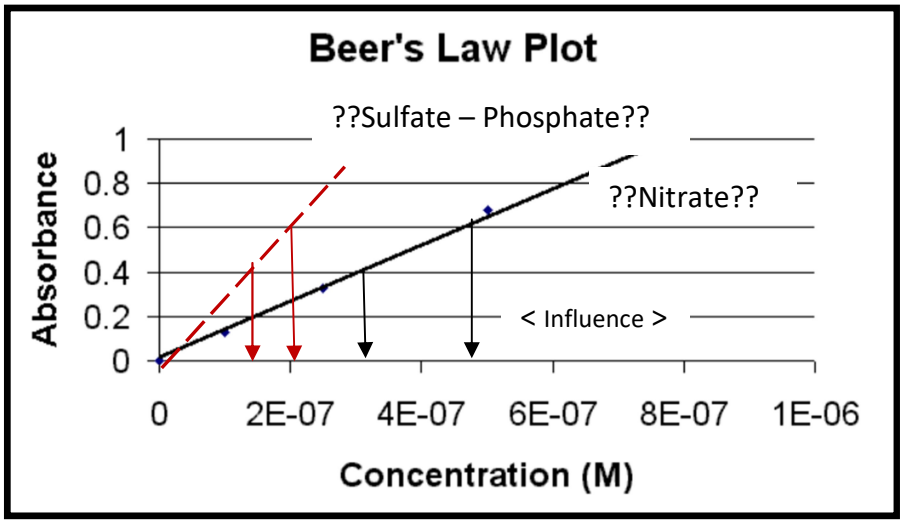
Why it is important that we completely empty the reagent powder packs

Using less reagent will result in a lower colorimeter reading. The influence of reagent residue on our tests for phosphate and sulfate may be less critical than Nitrate if the absorbance line for Nitrate is greater than those chemicals.

Illustration:

If we use less than the prescribed amount of reagent, the field sample will absorb less light.

The slope of the absorbance line is different for each chemical. If the slope for the Nitrate line is less than those for Sulfate or Phosphate; the proportion of reagent used would have a greater affect on the derived concentration.



Indicators of unused reagent:

Please tear open the Pillow Pack and empty the remains into the field test Sample Cell before performing the colorimeter test.

Appendix III

HACH *recommended Formula for Correction of Differences for Cadmium Reduction Method of Nitrate Analysis;*

A=True Concentration of the Sample
B=Concentration of the Reagent Blank (what you get when you run Deionized water as a sample).
C=Observed Concentration of the Sample
D=True Concentration of the standard
E=Observed Concentration of the standard
*A = (C - B) * [D / (E - B)]*
So, when you get your new lot of NitraVer 5 Nitrate Powder pillows, you should run a test on deionized water, to see what color the powder pillows read as. This is your reagent blank (B). If you get a result of .5 mg/L, then B would be equal to .5 mg/L.

When you test your samples, you will also test a standard solution at the same time. Be sure to shake the sample cells all the same. Take a Hach standardized solution of Nitrate and run it through the test. The number you get is your (E) in this equation. Let's presume you got 12 mg/L. on a 10 mg/L standard. Because your standard is supposed to be 10 mg/L (that's what it says on the box), the true concentration of your standard (D) is 10 mg/L. This is your D value.

With all that in mind, run your sample (C). Imagine that you get a result of 15 mg/L. This is your C, or the Observed Concentration of your sample. So,

*A = (15 - .5) * [10 / (12 - .5)]*
*A = (14.5) * [10/11.5]*
*A = 14.5 * .87*
A = 12.6 mg/L

And THAT is the true concentration of the sample that initially read 15 mg/L. If you decide not to determine the reagent blank value, then the formula is simply: A = C × D ÷ E