Measurement of Total Phosphorus in AIRMoN Samples by the NADP/CAL

Lee Green and Christopher Lehmann
National Atmospheric Deposition Program
Central Analytical Laboratory (CAL), Illinois State Water Survey
Prairie Research Institute
University of Illinois at Urbana-Champaign
Champaign, IL 61820; leegreen@illinois.edu

Abstract

Phosphorus can be present in water samples in at least three forms: orthophosphate, acid-hydrolysable phosphate and total or organic phosphorus. Organic phosphorus is changed to inorganic by bacterial action. Orthophosphate can be measured directly and the other two forms must be converted to orthophosphate prior to testing.

Total Phosphorus measurements in precipitation samples from the National Atmospheric Deposition Network (NADP) were determined by flow injection analysis from samples received in February 2011 to present. Precipitation samples for this study were collected from the Atmospheric Integrated Monitoring Network (AIRMoN). These samples are collected within a 24 hour precipitation event, are immediately refrigerated, and remain chilled during shipment to the NADP Central Analytical Laboratory (CAL) in Champaign, IL.

These samples were tested by the CAL for Orthophosphate and Total Phosphorus within one week of arrival at the CAL. A second set of samples were collected at Bondville, IL (IL11) site as a special study. These samples were collected side by side with the AIRMoN sample at this site but the sample was collected directly into a refrigerated compartment and never allowed to come to seasonal temperature. Only total phosphorus was analyzed on the special study samples. The total phosphorus method detection limit was determined to be 0.005 mg/L. Total conversion to orthophosphate was determined by using two quality control standards every nine samples during analysis. The recovery for a 0.025 mg/L trimethyl phosphate (TMP) was found to be 96% and a 0.050 mg/L sodium tripolyphosphate (3P) was found to be 100%. Seasonal data from this study will be presented as well as site specific total phosphorus vs. orthophosphate concentrations throughout the year.

Summary of Method

This flow injection analysis is Quick Chem method 10-115-01-3-F. In this method organic phosphorus is converted to orthophosphate by UV catalyzed persulfate digestion and polyphosphates are converted to orthophosphate by sulfuric acid digestion. Orthophosphate ion reacts with ammonium molybdate and antimony potassium tartrate to form a phosphomolybdate complex. This complex is reduced with ascorbic acid to form a blue complex which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

During this study all AIRMoN sites were looked at starting in February 2011 until the present time.

The NADP a is National Research Support Project-3: A Long-Term Monitoring Program in Support of Research on the Effects of Atmospheric Chemical Deposition. More than 240 sponsors support the NADP, including State Agricultural Experiment Stations; universities; private companies and other non-governmental organizations; Canadian government agencies; state, local, and tribal government organizations; and federal agencies, including the U.S. Department of Agriculture-Cooperative State Research, Education, and Extension Service (under agreement no. 2008-39134-19508). Any findings or conclusions in this poster do not reflect the views of the U.S. Department of Agriculture or other NADP sponsors. The Illinois State Water Survey is a division of the Institute of Natural Resource Sustainability at the University of Illinois. The authors thank Pam Bedient for her assistance with the poster layout.

Quality Control

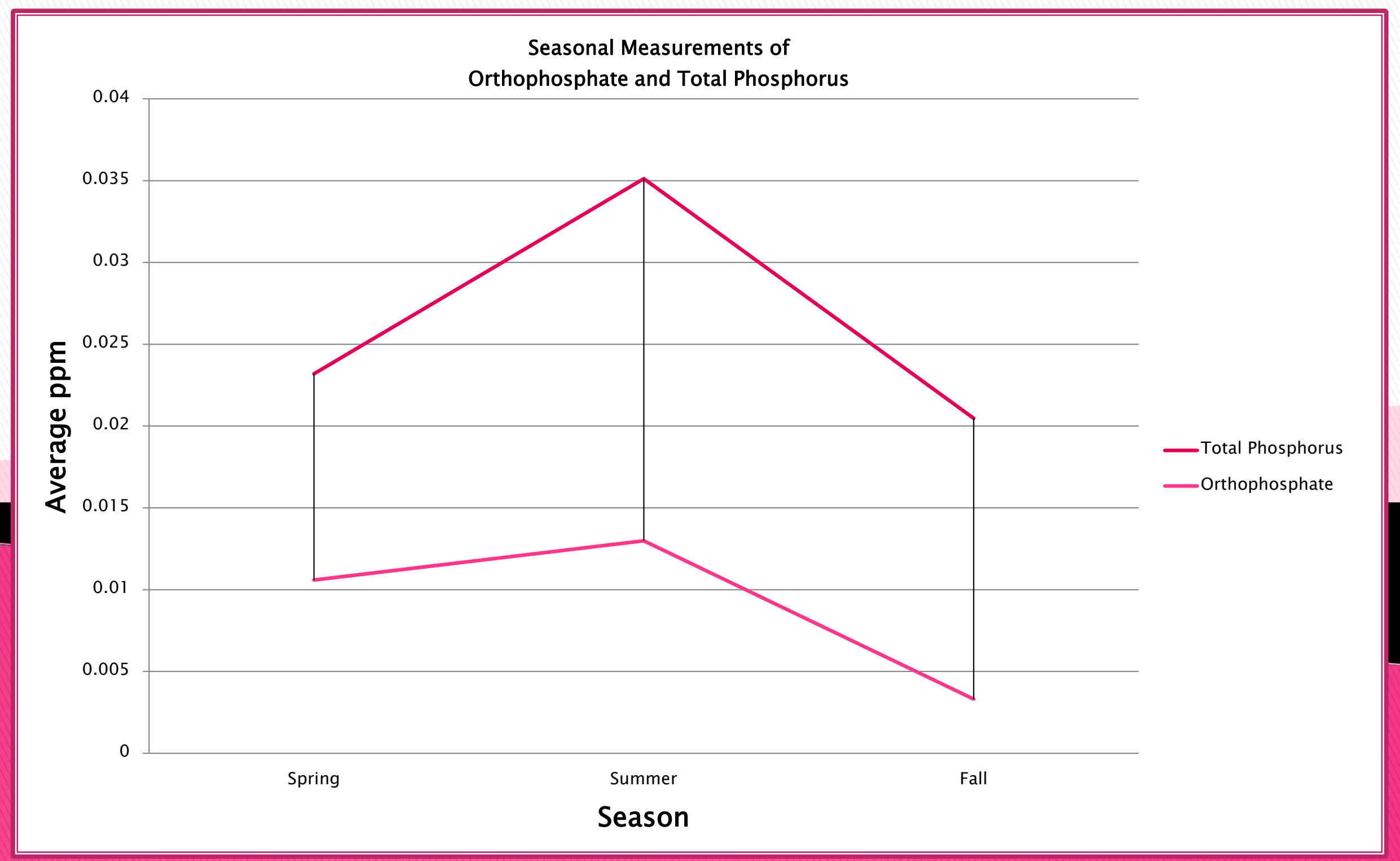
	Linear Range	R²	MDL	IDL
Total Phosphorus	0 – 0.1 ppm	99.9%	0.005 ppm	0.004 ppm

R^2 values are correlation coefficients displayed as a percentage reflecting the agreement of the measured data points to the calibration curve. MDL (Method Detection Limit) was calculated by measuring a 5 ppb Total Phosphorus standard seven times. This method is based on the Environmental Protection Agency (EPA) definition of MDL found in 40CFR 136.2.

Standard	Target Value	Mean ppm	Median Value	Standard Deviation	Number of Measurements
Stock Digest1	0.025	0.026	0.026	0.003	27
Stock Digest 2	0.050	0.050	0.050	0.001	14
Low	0.005	0.005	0.005	0.002	21

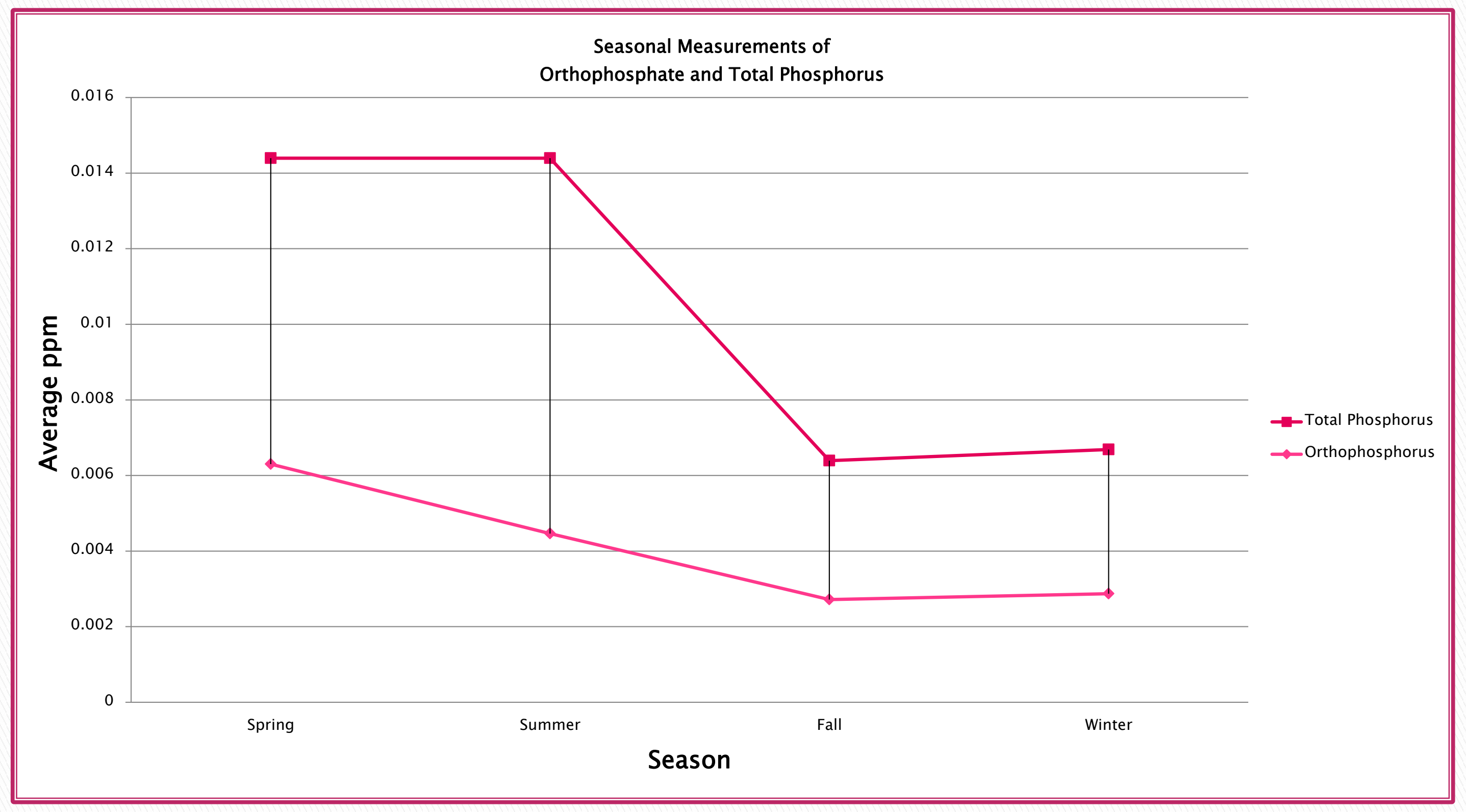
This table shows the controls used while measuring samples for total phosphorus. Stock digest 1 is trimethyl phosphate (TMP) prepared at 25 ppb and stock digest 2 is sodium tripolyphosphate (3P) prepared at 50 ppb. The low standard is from our working calibration standards run as check samples. All values are measured in ppm.

Results



This chart shows the special study samples that were collected and refrigerated for the duration of the study. There were no samples collected during the winter months.

Seasonal differences between orthophosphate and total phosphorus are very minimal although total phosphorus is consistently higher. The combined method detection limit (MDL) between the two methods is 0.008 ppm. So, the differences that we are seeing in this graph could be within the noise of the system.

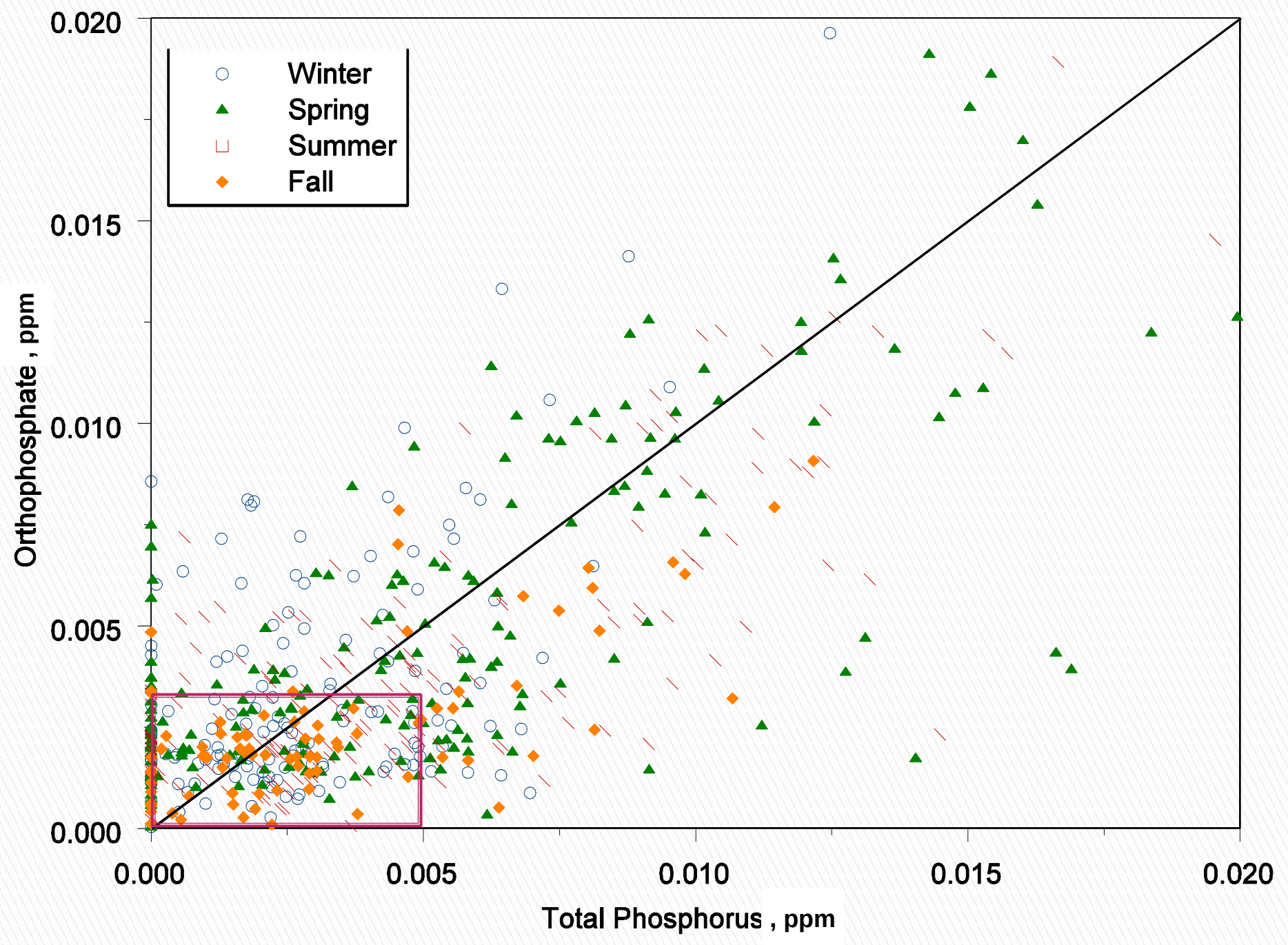


This chart shows all AIRMoN data collected during the testing period.

Seasonal differences between orthophosphate and total phosphorus are very minimal although total phosphorus is consistently higher. The combined method detection limit (MDL) between the two methods is 0.008 ppm. So, the differences that we are seeing in this graph could be within the noise of the system.

This chart contains all AIRMoN data compiled in this study.

Orthophosphate's MDL = 0.003 ppm
Total Phosphorus' MDL = 0.005 ppm



Conclusion

The preliminary data collected for this study shows that we do not see significant differences between orthophosphate and total phosphorus when tested by Flow Injection Analysis.

In 2004, Tracy Dombek, performed a similar experiment on the ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) to measure the sensitivity of the ICP-OES as well as explore possible interferences. The minimum detection limit was found to be 9 ppb and there were no matrix effects present. It was difficult to detect small differences between orthophosphate and total phosphorus due to the fact that orthophosphate has to be converted to phosphorus and it is slightly over three times greater.

In order to detect measurable differences on the ICP-OES and the FIA, samples containing levels greater than the detection limit of orthophosphate need to be analyzed.

The labor involved to prepare reagents and related costs for the total phosphorus method would increase AIRMoN analytical fees by $4,368.00 per site each year. Short term projects are easily accomplished but a long term effort for this project may be impractical, because we see very insignificant differences between the total phosphorus and the orthophosphate methods.

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