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USDA LTAR Common Experiment measurement: Total phosphorus (TP) and total dissolved phosphorus (TDP) concentration

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Abstract

Total dissolved P (TDP) includes organic P (e.g., sugars and phospholipids) and orthophosphate. Dissolved orthophosphate (also termed soluble reactive P, dissolved reactive P, dissolved inorganic P, or filterable reactive P) is the form of P most readily available to algae and aquatic plants; however, numerous studies have shown that hydrolysis of other forms of P to the orthophosphate form is possible in natural waters. Therefore, when assessing the long-term potential for accelerated eutrophication of surface water due to P loading, many researchers and watershed managers want to know the total P concentration (regardless of P form) in water samples.

Total dissolved P determination involves digesting filtered water samples to convert organic P species to orthophosphate, followed by colorimetric analysis or analysis by inductively coupled plasma with optical emission spectroscopy (ICP-OES). Determining TP involves the same digestion procedure applied to an unfiltered sample, followed by colorimetric or ICP-OES analysis. The recommended P digestion method is the persulfate oxidation technique, performed using an autoclave or microwave. The colorimetric determination of TDP and TP follows the ascorbic acid “blue” method (USEPA, 1978), whereby an intensely colored blue complex forms from the reaction between P compounds and ascorbic acid. The procedure involves the reaction of ammonium molybdate and potassium antimonyl tartrate with orthophosphate to form an antimony-phospho-molybdate complex. This complex is then reduced to an intensely blue-colored complex by addition of ascorbic acid. The intensity of the blue complex is proportional to the orthophosphate concentration in the sample.

Before start

Appropriate safety, health, and environmental precautions must be followed based on the selected methods, instrumentation, and workflow. Laboratory supervisors are responsible for knowledge of these precautions and their implementation.

Review the *USDA LTAR Common Experiment measurement: Best practices for collection, handling, and analyses of water quality measurements* protocol (Pisani et al., 2024) prior to implementing this protocol.

Sample collection and filtration

1 Return samples to the laboratory On ice and filter them on collection day if possible.

2 To measure TDP, filter samples through a 0.45 µm pore size filter to remove particulates before chemical analysis.

3 If desired, use a 0.22 µm filter to more completely remove the microbial community.

Sample storage and preservation

4 Unless analysis is possible on sample collection day, it is required to store samples at 4 °C for up to 28 days.

Archiving

5 The common practice is to store water samples for TDP or TP analyses until data certification (QA/QC verification).

Sample analysis

6 To determine total P (TP = dissolved P + particulate P), shake an unfiltered sample to suspend the particulate matter before removing a subsample for digestion.

7 Polyphosphates and phosphates bound to organic substances do not react with the molybdate reagent used for colorimetric P analysis, and colorimetric analysis cannot directly measure particulate P.

Therefore, analysis of the total P content of water samples requires that all condensed and organic P compounds, including particulate P, first be converted (hydrolyzed) to orthophosphate to be determined colorimetrically or by ICP-OES (USEPA, 1994).

To accomplish this conversion, samples are digested with persulfate at high temperature and pressure, normally using either an autoclave or microwave (USEPA,1994; Maher and Woo 1998). A laboratory pressure cooker can be used as well to oxidize the organic matter and release P as orthophosphate.

8 After digestion, TDP and TP are determined colorimetrically using the ascorbic acid method (APHA, 2005) or by ICP-OES.

Figure 1. Colorimetric determination of TDP and TP follows the ascorbic acid “blue” method. Photo credit: S. Rahutomo, Iowa State University.

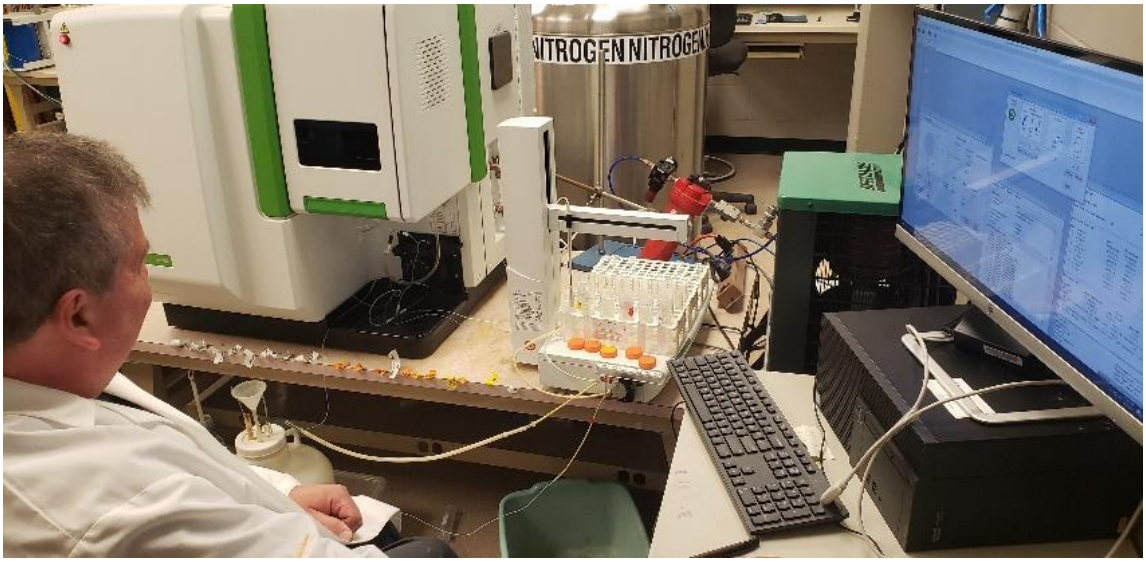

Figure 2. Inductively coupled plasma—optical emission spectrometer (ICP-OES) with an autosampler to determine TP and TDP concentrations in the digestate. Photo credit: A. Morrow, USDA-ARS.

Calculations

9 Prepare a calibration curve by plotting the area of each standard peak against its respective P concentration. Correction of standards and samples for the blank is necessary; assuming virtually P-free deionized or distilled water, the reagents and especially potassium persulfate are usually the source of most of the blank absorbance.

Note

P concentration = unfiltered digested sample
TDP concentration = filtered digested sample

10 Compute the TDP or TP concentration in the sample by comparing the sample peak area to the calibration curve.

Note

Report the concentration as mg P per liter (mg/L).

Covariate metrics to be sampled concurrently

11
- Dissolved NO_3^- concentration
- Dissolved NH_3 concentration
- Total dissolved N (TDN)
- Total N (TN)
- Total suspended solids (TSS)

Recommendations for data collection

12 Table 1. Summary of recommendations for the collection and measurement of TP and TDP concentration.

	A	B	C	D
	Attribute	**Preferred**	**Minimum**	**Comments**
	Spatial scale	Field	Plot	
	Frequency	Event-driven	Event-driven	More frequent (weekly) measurements can be preferential when the flow regime can increase seasonally or

	A	B	C	D
				after precipitation ev ents. Sampling in this protocol should be ev ent-driven to enable c ross-site comparison s
	Covariate metrics	NO3-N, NH3-N, TDN, TSS	NO3-N, NH3-N, TDN	
	Sample preservation and storage TDP	Filtered with a 0.22 or 0.45 µm pore-size filt er on sample collecti on day	To maintain filtered s amples for up to 28 d ays, store them at 4° C	
	Sample preservation and storage TP	Perform the analysis on the same day as c ollection	To maintain samples for up to 28 days, sto re them at 4°C	
	Sample analysis	Persulfate digestion f ollowed by colorimetr ic analysis or ICP		
	Water quantity	Discharge or flow rat e	Discharge or flow rat e	Calculate TP or TDP l oads by linking this metric to the water q uantity metric “flow”

Covariate metrics = other metrics to sample concurrently. NO_3^--N = nitrate-N; NH_3-N = ammonia-N; TDN = total dissolved nitrogen; TSS = total suspended solids

Protocol references

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