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USDA LTAR Common Experiment measurement: Dissolved ammonia (NH₃) concentration

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We use this protocol and it's working

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Abstract


Ammonia can form naturally from organic matter mineralization or can enter the aquatic environment via anthropogenic sources such as municipal effluent discharge and agricultural runoff. The presence of ammonia (NH_3) vs. ammonium (NH_4^+) in water depends on water pH and temperature. The un-ionized NH_3 form is toxic to aquatic organisms, and both forms (NH_4^+ and NH_3) can contribute to eutrophication and hypoxia of surface waters. The reported measurement of ammonia in water is typically the total ammonia N ($\text{TAN} = \text{NH}_3 + \text{NH}_4^+$). The recommended techniques for measuring NH_3 in water are the colorimetric salicylate and phenate methods, whereby an indophenol color complex is proportional to the NH_3 concentration of the sample.

Safety warnings

- ⚠ Follow appropriate safety, health, and environmental precautions based on the selected methods, instrumentation, and workflow. Laboratory supervisors are responsible for knowledge of these precautions and their implementation.



Sample collection and filtration

- 1 Return samples to the laboratory  On ice and filter them on collection day if possible.
- 2 Filter samples through a 0.45 micrometer (μm) pore-size filter to minimize interference from particulates before chemical analysis.


Note

- Filters can be either membrane or glass fiber.
- Occasional checks of filter blanks by filtering deionized water with the same equipment are always prudent.
- Ammonia is particularly prone to air contamination outdoors or in a lab.

- 3 As samples collected and stored in an autosampler are vulnerable to ammonia loss by volatilization and nitrification, ideally, pre-acidify the samples to $\text{pH} < 2$ (H_2SO_4) and retrieve from the field within seven days of autosampler collection.

Note

Ammonia concentrations can change if samples are left in ambient conditions too long, regardless of autosampler refrigeration (Burke et al. 2002).

- 4 If pre-acidification is not possible, retrieve the samples as soon as possible and transport them back to the laboratory  On ice .


Sample storage and preservation

1d

- 5 As soon as possible after sample collection, filter the water samples through a 0.45 μm pore-size filter to minimize interference from particulates.
- 6 Analyze samples within 24 hours after collection.





- 7 To store samples not pre-acidified in the field, preserve the samples with sulfuric acid to pH < 2, cool them at  4 °C , and hold them for up to 28 days (US EPA, 1993).
- 8 Preserve the samples that are not acidified by freezing to minimize ammonia loss by volatilization.

Archiving

- 9 Store the water samples for NH₃ analysis until data certification (QA/QC verification).

Note

The storage of preserved water samples should not exceed 28 days.

Sample analysis

- 10 Direct determination of NH₃-N without distillation is possible for water samples with low NH₃-N concentrations.
- 11 Samples with high NH₃-N concentrations (> 5 mg-N/L) may need to be distilled before analysis to minimize interferences and improve precision (APHA, 2005).
- 12 The colorimetric determination of ammonia in water is carried out using the salicylate or phenate method.

Note

Several automated colorimetric procedures are available from the US EPA and USGS National Water Quality Laboratory (NWQL).

- 13 **Salicylate method** : Heat the sample with salicylate and hypochlorite in an alkaline phosphate buffer in the presence of sodium nitroprusside (catalyst). The reaction produces an emerald-green indophenol dye proportional to the NH₃ concentration of the sample.

Note

The salicylate method has become popular primarily because it is much less toxic and less sensitive to changes in pH.

- 14 **Phenate method** : In this method NH_3 reacts with alkaline phenol and sodium hypochlorite in the presence of sodium nitroprusside to enhance sensitivity. The indophenol blue dye is proportional to the NH_3 concentration of the sample.

Note

The EPA accepts the phenate method for regulatory monitoring (USEPA, 1993).

Covariate metrics to be sampled concurrently

- 15 Dissolved NO_3^- concentration, total dissolved N (TDN), total dissolved P (TDP), and total suspended solids (TSS). These metrics are described in the following protocols:
- USDA LTAR Common Experiment measurement: Dissolved nitrate (NO_3^-) concentration
 - USDA LTAR Common Experiment measurement: Total nitrogen (TN) and total dissolved nitrogen (TDN) concentration
 - USDA LTAR Common Experiment measurement: Total phosphorus (TP) and total dissolved phosphorus (TDP) concentration
 - USDA LTAR Common Experiment measurement: Total suspended solids (TSS)

Calculations

- 16 Prepare a calibration curve by plotting the blank-corrected area of each standard peak against its respective $\text{NH}_3\text{-N}$ concentration.
- 17 Compute the $\text{NH}_3\text{-N}$ concentration in the sample by comparing the sample peak area to the calibration curve. Report the concentration as mg $\text{NH}_3\text{-N/L}$.

Recommendations for data collection

18 Table 1. Summary of recommendations for the collection and measurement of dissolved $\text{NH}_3\text{-N}$ 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 after precipitation events. Sampling in this protocol should be event-driven to enable cross-site comparisons.
Covariate metrics	$\text{NO}_3\text{-N}$, TDN, TDP, TSS	$\text{NO}_3\text{-N}$, TDN, TDP	
Sample preservation and storage	Filter with a $0.45\ \mu\text{m}$ pore-size filter (membrane or glass fiber), refrigerate and analyze within 24 hours	Filter with a $0.45\ \mu\text{m}$ pore-size filter (membrane or glass fiber), refrigerate, acidify to $\text{pH} < 2$ as soon as possible, store at 4°C , and analyze within 28 days	Omit sample acidification if dissolved organic matter (DOM) analyses are performed. Alternatively, use a $0.7\ \mu\text{m}$ GF/F. Use a $0.2\ \mu\text{m}$ pore-size filter to exclude bacteria from samples but at much slower flow rates.
Sample analysis	Colorimetric salicylate method	Colorimetric phenate method	
Water quantity	Discharge or flow rate	Discharge or flow rate	Calculate $\text{NH}_3\text{-N}$ loads by linking this metric to the water quantity metric "flow"

Covariate metrics = other metrics to sample concurrently. $\text{NO}_3\text{-N}$ = nitrate-N; TDN = total dissolved N; TDP = total dissolved phosphorus; TSS = total suspended solids



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