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Analysis of nitrogen and phosphorus nutrients in lake sediment

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Analysis of Nitrogen and Phosphorus Nutrients in Lake Sediment

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Abstract

Analytical methods for the determination of nitrogen and phosphorus nutrients (NO_3-N, NH_4-N and PO_4-P) in sediment were studied with the goal of developing extraction steps compatible with analysis by ion chromatography (IC). Research focused on extractant solution composition, Dionex OnGuard® sample pretreatment cartridges for salt removal, and chromatographic resolution. Aqueous test samples, lake sediment samples and spiked lake sediment samples were analyzed. Dionex Ag, Ag/H, and H cartridges were studied for the pretreatment step. Silver (Ag) cartridges were found effective in removing >99% of interfering chloride ion to allow NO_3-N determination by anion IC when 2 M KCl was used for sediment extraction. Ag cartridges were found to react and remove NH_4-N, so an alternative extraction solution of 0.02 M $SrCl_2$ was studied. Extraction by 0.02 M $SrCl_2$ enabled anion IC analysis of NO_3-N and cation IC analysis of NH_4-N without further sample treatment, but this extraction method gave significantly lower values of nutrient ($p < 0.05$) than 2 M KCl extraction. Alternative chromatographic parameters utilizing increased eluent concentration were employed for the detection of NO_3-N in sediment with interfering sulfate ion due to improved resolution of nitrate and sulfate peaks. Extraction with 0.02 M $SrCl_2$ coupled to cation IC and phenate colorimetric methods gave similar results for NH_4-N analysis in some sediments ($p > 0.05$), which demonstrated that the extraction step was the determining factor in nutrient analysis. Analysis of total phosphorus in the form of PO_4-P was precluded by high sulfate and nitrate concentrations required for acid digestion of extracted sediment. Additional research is needed to develop IC methodology for NO_3-N, NH_4-N and PO_4-P.

1. Introduction

There are over 82,000 reservoirs in the United States that have been constructed by damming streams for water storage, irrigation, flood control and recreational purposes (USACE, 2011). Soon after formation, reservoirs take on characteristics of natural lakes, including a life cycle with periods of growth and decline. The stage of a given reservoir in its life cycle depends on its biological productivity, which is a measure of the rate of production of biomass from sources such as algae. As a reservoir accumulates biomass as a result of high productivity, it progresses through a series of trophic states (Figure 1). The first stage in this life cycle is marked by clear water, plentiful oxygen concentrations and limited biological productivity, known as the oligotrophic state (Holdren, Jones, & Taggart, 2001).

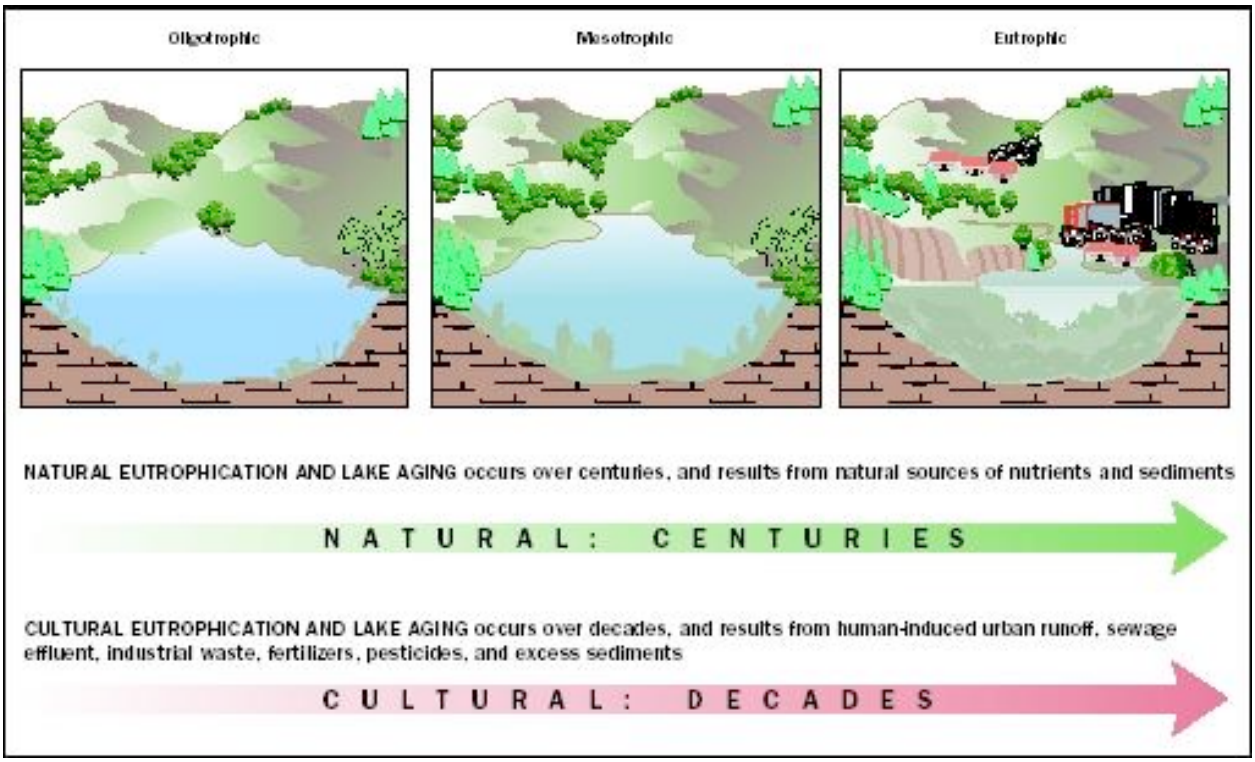

Figure 1. Trophic states of a lake or reservoir (Water Encyclopedia, n.d.). The oligotrophic state is characterized by clear water, abundant DO concentrations and little plant growth. The mesotrophic state is characterized by an increase in plant growth, depletion of DO at low depths and less clear water. The eutrophic state is described by superfluous plant growth, poor water transparency and low DO concentrations. This process, known as eutrophication, occurs naturally over time and can be greatly sped up due to anthropogenic contributions.

As a reservoir ages feeder streams carry eroded particles, dissolved substances and other materials from the watershed and atmosphere to the reservoir. The velocity of flowing water keeps small particulate matter suspended in streams, but as the flow decreases when the water reaches the reservoir, solids settle to the bottom. The solid inorganic and organic material that can be moved by erosive processes and deposited is collectively known as sediment. The sediment composition of any particular lake or reservoir depends on the geography, land cover and soil type of the upstream watershed. The accumulation of these solid particles into layers of sediment over time reduces lake volume and can be harmful for lake utility and wildlife health.

Influent streams also transport nutrients to the reservoir as soluble, bioavailable forms or insoluble and otherwise unavailable forms, bound up in organic compounds or adsorbed to sediment particles. Nutrients are chemical species required for the growth and development of plants and animals that are used in various biological processes or as sources of energy. These chemicals are made available for use by aquatic organisms through the water column or other processes that release nutrients into the water, such as the decomposition of organic material. The influx of nutrients into a body of water is a natural process achieved through leeching from soils and rocks or the decay of organic matter. Human activity is also a large contributor to many of the compounds found in streams and lakes. Some of these sources include sewage treatment plants, household detergents and fertilizers (Water Encyclopedia, n.d.).

Nitrogen (N) and phosphorus (P) nutrient compounds are essential for the growth of algae in lakes and streams. Nitrate, ammonium and phosphate are the most important of these nutrients because they are the preferred forms for plant growth. The concentrations of N and P nutrients directly correlate to the biological productivity of the reservoir, as plant growth and production is dependent on the availability of these compounds. Over time, the oligotrophic

reservoir accumulates sediment and nutrients and progresses into the mesotrophic stage. Mesotrophy is characterized by moderate plant productivity, moderately clear water and possible lack of oxygen at low depths during the summer (Holdren, Jones, & Taggart, 2001).

As the reservoir acquires an excess of nutrients, it enters a state of eutrophy characterized by poor water transparency and algal blooms (Holdren, Jones, & Taggart, 2001). Eutrophication can eventually result in health problems for the aquatic ecosystem, including odor and taste problems, a decrease in available dissolved oxygen, and consequently, disease and death of fish and other organisms. Accordingly, evaluation of nitrogen and phosphorus nutrients in lakes and reservoirs can provide information on the health of the water body and provide a basis for management decisions. Water analyses give information about the current state of the reservoir; sediment analysis can provide a look into the future state of the reservoir. Sediment can be viewed as a sink for nutrients, pollutants and metals in aquatic ecosystems due to the association of these compounds with particulate material (IAEA, 2003). Sediment is also considered a source for these compounds due to processes that release nutrients back into the water.

The key nitrogen and phosphorus elements can be measured in several forms. Phosphorus can be measured either as total phosphorus or biologically available phosphorus, known as soluble reactive phosphorus or phosphate (Michaud, 1991). Nitrogen can be measured in a variety of ways including total nitrogen, nitrate-nitrogen, nitrite-nitrogen and ammonium-nitrogen, with the latter three comprising the biologically available nitrogen forms. One chemical form of a nutrient can be converted to another based on various environmental and chemical properties of the surroundings.

Currently there are several accepted methods for the analysis of nitrogen and phosphorus species in soils and sediments. Three main species of interest include nitrate-nitrogen (NO_3-N), ammonium-nitrogen (NH_4-N) and phosphate-phosphorus (PO_4-P). Common to these procedures is an extraction step in which fine soil particles are treated with an extractant to free the analytes from sites on the soil particles into solution. The process of extraction is dependent on the principle of ion exchange in which nutrient bound to the soil is removed by high concentrations of desorbing ion. This process takes the form Soil-X + A → Soil-A + X, where high concentrations of desorbing ion A drive the reaction forward and freeing nutrient X according to Le Châtelier's principle. Different nutrients are best extracted by certain extractants; nitrate and ammonium are most commonly extracted with potassium chloride (2 M) while phosphate is generally extracted with sodium bicarbonate (0.5 M, pH adjusted to 8.5). Following the extraction step, most methods utilize colorimetric analysis to quantify the nutrient of interest.

As a part of the most frequently employed method of nitrate determination, the post-extraction solution is passed through a cadmium reduction column that reduces the nitrate present to nitrite (NO_2^-). The nitrite is combined with sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride to form a dye that is quantified colorimetrically (Clescerl, Greenberg, & Eaton, 1999). This method as described gives the total nitrate and nitrite in the sample. To find the concentration of nitrate only, a correction must be made for any NO_2^- present by analyzing the sample without the reduction step. This method is most applicable for nitrate concentrations in the range of 0.01 to 1.0 mg/L NO_3-N, especially for concentrations less that 0.1 mg/L where other methods fail. However, there are interferences and limitations to the cadmium reduction method that can result in issues of accuracy. Samples high in chloride may oxidize the cadmium column and impair its efficiency. Residual compounds that absorb around 540 nm will

interfere in the colorimetric analysis. Sample is subject to contamination due to numerous operational steps and re-oxidation by air back to nitrate, leading to erroneous results. Previous work in our lab has revealed that there is a learning curve associated with preparing, maintaining and operating the cadmium column (Wickham, 2010). This method is time- and labor-consuming, but is recognized as a standard method of nitrate determination in aqueous samples.

In the phenate colorimetric (PC) method of ammonium determination, the extracted sample is treated with phenol to form a blue colored solution. Sodium hypochlorite and sodium nitroprusside are used as an oxidant and catalyst, respectively (Maynard & Kalra, 1993). After incubation, the colored solution is measured colorimetrically at 630 nm. The range for this method is 0.01 to 10.00 mg/L NH_4-N. This method is a well-established approach to ammonium determination in aqueous samples and soil extracts. However, some of the reagents used are toxic and costly and the analysis is time- and labor-intensive. Additionally, glassware and chemical reagents may be easily contaminated by ammonia in the surroundings.

The ascorbic acid method of phosphate determination is performed as a colorimetric technique for the analysis of total phosphorus in aqueous samples. Extracted sample is first acid digested to convert all forms of phosphorus to orthophosphate. The digested sample is neutralized and treated with a combined reagent containing sulfuric acid, potassium antimonyl tartrate, ammonium molybdate and ascorbic acid, giving a blue-colored complex of orthophosphate. The absorbance of the colored solution is measured spectrophotometrically at 880 nm. This method is most applicable in the range of 0.01 to 6.00 mg/L PO_4-P (Pierzynski, 2000).

In an effective analytical method there is a focus on precision, accuracy, ease of execution, and attainment of reproducible results. The method must have the sensitivity to detect analytes at their commonly observed concentrations. Additionally the method must be reliable and demonstrate reproducibility in the results. Desirable analytical methods also reduce the time and labor input of the analyst, giving good results with minimal effort or sample preparation. This thesis seeks to develop an improved analytical method for N and P nutrient analysis that will address these requirements.

Ion chromatography (IC) is an analytical tool that is used for common, inorganic anion and cation analyses of aqueous samples. Multiple analytes can be determined in a single run, including both cations and anions simultaneously in dual channel instruments. In these instruments, sample is delivered to two analytical systems equally to allow for complete, separate analyses. In each system, sample is pumped through a column that separates the analytes based on their affinity for the mobile or stationary phase (Figure 2). This separation mechanism is based on ionic interactions between the analyte ions and the ionic functional groups of the stationary phase. Analytes that interact more with or are more strongly retained by the stationary phase have longer retention times. An isocratic elution keeps the eluent at a fixed concentration over the course of a run whereas a gradient elution consists of varying the eluent concentration throughout a single run. A gradient elution can result in changes to the retention factors of analytes and can therefore alter retention times, allowing for better separation of analyte peaks depending on the parameter settings (Smith, 1988). Before detection, the sample and eluent is passed through a suppressor that reduces the background conductivity of the eluent and improves detection sensitivity. Detection is often accomplished using a conductivity detector. An ion chromatograph can be configured with an automatic sampler to process

numerous samples automatically. Many modern instruments also have automated eluent generation from deionized (DI) water and self-regenerating suppression for convenience.

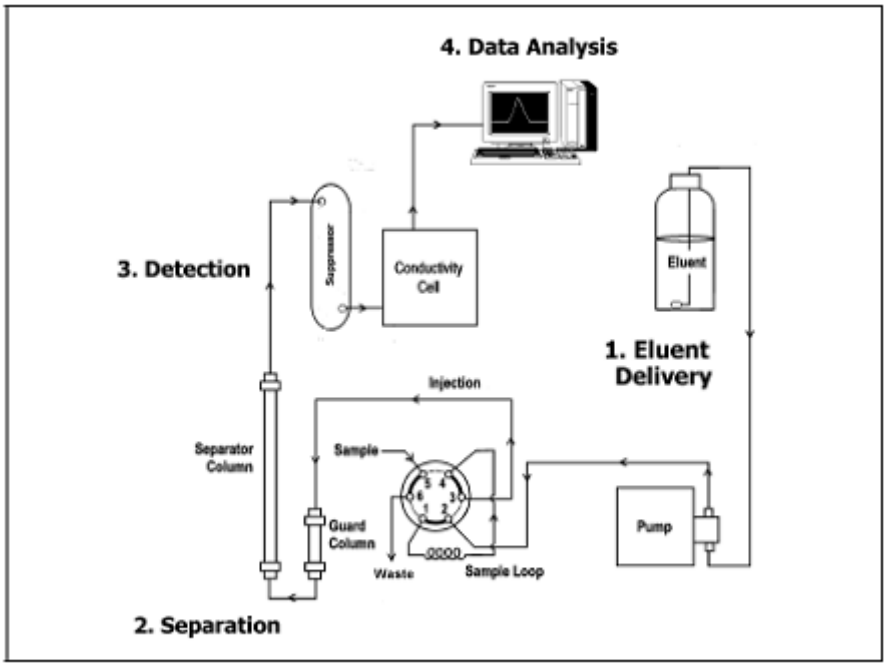

Figure 2. Schematic of single column ion chromatography (IGCAS, 2015). The eluent (mobile phase) is generated and carries the sample through the guard column followed by the separator column. Analytes interact with the stationary phase in the column in equilibrium and ion exchange processes, resulting in separation. The suppressor reduces the signal of the background by removing mobile phase ions via reactions that give uncharged compounds (i.e. water). Analytes are then detected by conductivity and processed for quantitation.

Ion chromatography has not been utilized for nitrate-nitrogen or ammonium-nitrogen determination in sediments due to compatibility issues with extraction solutions. The high salt concentrations required for extraction saturate the columns and detectors, making detection and quantification impossible. On the anion side, excess chloride ion precludes the analysis of nitrate while on the cation side, residual potassium ion prevents ammonium analysis. In order to use IC for the purpose of N and P nutrient analysis, we must employ a fast and simple method to remove the interfering matrices.

Dionex's line of OnGuard® sample pretreatment cartridges was developed for matrix elimination and analyte solid phase extraction (SPE) methods. The OnGuard® products are

packed with a variety of resins appropriate for various experiments. The OnGuard® II Ag cartridge used in this experiment contains a silver-form, high capacity, sulfonic acid cation exchange resin designed to remove halides and other silver-precipitating ions from solution (Thermo Fisher Scientific, 2013). Concerns with using the Ag cartridge as a pretreatment of the extracted soil samples for analysis by IC included: loss of nitrate- or ammonium-nitrogen in the chloride precipitate, reduction of nitrate to nitrite in the cartridge, and interference by cation exchange resin decomposition and wash-off. In previous research, it was found that nearly 100% of nitrate-nitrogen is recovered with no substantial amount of nitrate-nitrogen lost ($p < 0.001$) to precipitation or reduction (Wickham, 2010). The OnGuard® II H cartridge is a high capacity sulfonic acid cation exchange resin with the ability to remove alkaline earth and transition metals from sample matrices (Thermo Fisher Scientific, 2013). These cartridges are well equipped to remove dissolved silver and are therefore effective in protecting the IC column from silver accumulation when used following the OnGuard® II Ag cartridge. The OnGuard® II Ag/H cartridge is essentially a combination of the OnGuard® II Ag cartridge and the OnGuard® II H cartridge in the form of a singular two-layer cartridge.

In this study, a variety of approaches were explored to achieve the desired results. Topics of study include use of Dionex OnGuard® cartridges for sample pretreatment, variation of extraction solution and alteration of instrumental parameters for improved resolution of analytes. Various analytical methods were carried out on aqueous test samples, blank lake sediment samples and spiked lake sediment samples. Proposed methodology includes analysis of NO_3-N, NH_4-N and PO_4-P by IC, executed in parallel with a comparative phenate colorimetric method for NH_4-N determination.

2. Materials and Methods

2.1. Reagents and standards

Glassware was acid-washed with 10% trace metal grade HNO_3 (Fisher Scientific) followed by multiple aliquots of DI water (18 MΩ) to avoid contamination. Extraction solutions were prepared as 2 M KCl (Fisher Scientific, certified ACS) and 0.02 M $SrCl_2$ (Fisher Scientific, certified ACS).

Nitrate-nitrogen

Chemicals used for nitrate analyses include 1000 mg/L NO_3-N stock standard solution (KNO_3, Fisher Scientific, certified ACS). Standards for IC analysis were prepared with concentrations of 0.50 to 4.00 mg/L NO_3-N.

Ammonium-nitrogen

Chemicals used for ammonium analyses include 0.5% sodium nitroprusside (Fisher Scientific, certified ACS), alkaline citrate (trisodium citrate dehydrate, Fisher Scientific, granular certified), 8.25% NaOCl Clorox bleach, liquefied phenol solution in 95% EtOH (Sigma Aldrish, ACS reagent, crystals), 1000 mg/L NH_4-N stock standard solution (NH_4Cl, Fisher Scientific, USP/FCC/EP). Standard solutions for the phenate method of ammonium analysis were prepared fresh at concentrations of 0 to 0.500 mg/L. Standards for IC analysis were prepared with concentrations of 0.2 to 1.2 mg/L NH_4-N.

Phosphate

Chemicals used for phosphate analyses include 1 M NaOH (Fisher Scientific, certified ACS), phenolphthalein indicator (Baker and Adamson), 30% H_2SO_4 (Fisher Scientific), solid

potassium persulfate (Fisher Scientific, certified ACS), concentrated H_2SO_4 (Fisher Scientific, certified ACS plus), concentrated HNO_3 (Fisher Scientific, trace metal grade), 50 mg/L PO_4-P stock standard solution (KH_2PO_4, Aldrich, ACS reagent). Test phosphate standards were made with concentration ranges of 10 to 200 ppb and 1 to 5 ppm in an effort to develop an IC method of detection for phosphate.

Silver

Chemicals used for silver analyses include 100 mg/L Ag^+ ($AgNO_3$, Fisher Scientific, certified ACS) in 1% HNO_3. Standard solutions of silver were prepared for AA analysis of Ag in SPE effluent with concentrations ranging 0 to 5 mg/L.

2.2. Sampling sites and procedures

Sediment samples were collected from three sites in the vicinity of Harrisonburg, VA. These sites include Strasburg Reservoir, Lake Shenandoah and Slate Lick Lake. A top layer of sediment from each location was collected and transported to the lab according to protocols established in a Description and Sampling of Contaminated Soils (EPA, 1991). Authentic sediment samples were used to evaluate the proposed methods under realistic conditions. These sites were used because of their proximity to JMU and variety of watershed and environmental properties. Evaluation of sediments with differing characteristics can provide information regarding the robustness of the methodology.

Strasburg Reservoir is a flood control/water supply dam located in the George Washington National Forest near Signal Knob on Massanutten Mountain (Reeser, 2003). Currently the reservoir is no longer utilized for water supply and has been opened up for fishing. Access to the reservoir is via forest roads and hiking trails. Sediment in Strasburg Reservoir is

comprised mostly of sand, and is isolated from urban and agricultural sources. Due to these properties, it is expected that the reservoir does not have high nutrient concentrations and will therefore serve as a good control suitable for spiking. Strasburg Reservoir was sampled by the 2014 Environmental Field Camp in the Department of Chemistry & Biochemistry at JMU.

Lake Shenandoah is a 36-acre reservoir in Rockingham County owned by the Department of Game and Inland Fisheries (VADGIF, 2015). The majority of the lake is shallow at a depth of less than 3 feet, with the maximum depth being 25 feet. Due to its proximity to a golf course and urban development, the lake has received a surplus of nutrients and sediment, resulting in algal blooms. Lake Shenandoah was sampled in August 2014 around the periphery of the reservoir.

Slate Lick Lake is a 10-acre reservoir located in George Washington and Jefferson National forests in Rockingham County. There is lake access via a 0.8 mile trail from Forest Road 230 (VADGIF, 2015). It is inhabited by fish including brook trout, catfish, largemouth bass and sunfish. A management project was implemented in February 2014 to drain the reservoir down, allowing for necessary reparations. Slate Lick Lake was sampled in August 2014 when the lake was drawn down and much of the surface area was exposed, allowing for the sampling of lake bottom sediment in the middle of the lake.

Field-collected sediment samples were air-dried and ground with mortar and pestle to pass through a 90-μm sieve. Approximately 10 g of each type of sediment was placed in an oven at 110°C for 24 hours to determine percent weight water loss. The pH of each sediment was measured by mixing 10 g of fine sediment with 25-mL DI water and stirring the suspension at room temperature (20°C) for 30 minutes. The suspension was allowed to settle out and the pH measurement of the supernatant was recorded.

Aqueous test samples, blank field samples and spiked field samples were evaluated by a number of procedures including IC for NO_3-N, NH_4-N and PO_4-P analysis, phenate colorimetric method for NH_4-N analysis and AA for silver analysis of post-SPE effluent.

2.3. Apparatus and instrumental parameters

A Thermo Scientific™ Orion™ 8102BNUWP ROSS Ultra™ pH electrode in combination with an Oakton pH/mV/ION/°C/°F meter with RS-232 and recorder output was used to determine the pH of sediments. A visible wavelength range spectrophotometer (BL Spectronic 20) was used for the quantification of indophenol in the phenate method of NH_4-N analysis. Percent transmittance of the samples was measured at 640 nm with a 1.00 cm cell and converted to absorbance. A Flame Atomic Absorption Spectrometer (AA, Varian SpectrAA 220 FS) coupled to a SPS 5 Sample Preparation System was used for the analysis of silver in solutions passed through the Dionex OnGuard cartridges. Two dual channel Ion Chromatographs (Dionex ICS-3000 and ICS-5000) with conductivity detection were used in the proposed methods of NO_3-N, NH_4-N and PO_4-P analyses. Dionex IonPac AS18 analytical columns with AG18 guard columns and Dionex IonPac CS12A analytical columns with CG12A guard columns were used for anion and cation separations, respectively. Columns were kept at a constant temperature of 30°C. Both Ion Chromatographs were coupled to AS autosamplers, allowing for processing of up to 49 samples at a time including standards and blanks. Conditions for IC anion analyses are as follows: The flow rate of the eluent (23 mM NaOH) was set at 1.0 mL/min for isocratic runs. The current of the anion suppresser was set at 65 mA. Alternative anion instrument methods were explored for the purpose of optimal phosphate analysis. An alternative isocratic method included a set of chromatographic conditions recommended by Dionex for phosphate analysis. Under these conditions, the flow rate of the eluent was 0.9 mL/min (33 mM NaOH) and the

anion suppresser was set at 82 mA on the ICS-3000. A gradient elution method was employed on the ICS-5000 in which the eluent concentration increased from 12 to 44 mM in the first 5 minutes, remained at 44 mM for 3 minutes, and then increased to 52 mM in 2 minutes. Conditions for IC cation analyses are as follows: The flow rate of the eluent (20 mM MSA) was set at 1.0 mL/min. The current of the cation suppresser was set at 70 mA. Samples were filtered using Fisherbrand 0.2 μm PTFE syringe filters into clean IC vials and placed onto the sample rack with anion and cation standards.

2.4. Extraction procedures

All samples were extracted with 2 M KCl or 0.02 M $SrCl_2$ (Li et al., 2006) for 60 minutes using a magnetic stir bar on high for agitation. A 75-mL aliquot of extraction solution was pipetted into an Erlenmeyer flask containing approximately 7.5 ± 0.5 g of sample (known to the nearest 0.0001 g). The resulting solution was filtered using a vacuum filtration apparatus and the filtrate was collected in a 125-mL Erlenmeyer flask, parafilmed and stored at 4°C until analysis.

2.5. Solid phase extraction by Dionex OnGuard® cartridges

Following extraction by KCl or $SrCl_2$, filtrate was passed through Dionex OnGuard® II Ag cartridges to remove halide ions (Cl^-) for NO_3-N analysis by IC. Filtrate from the 2 M KCl extraction was diluted 1:10 prior to cartridge treatment to put the concentration of NO_3-N within detectable range while placing chloride ion at a concentration removable by one Ag cartridge. Cartridges were purchased from Dionex in the 2.5 cc size with a capacity of 5-5.5 meq/cartridge. The cartridges were prepared according to the Thermo Scientific Dionex OnGuard® II Cartridges Product Manual, including flushing the cartridge with 15-mL of DI water before use with a flow rate not exceeding 2 mL/min and discarding the first 6-mL of sample passed through. BD 5-mL

syringes were used to provide the necessary pressure on the cartridges. At this point, sample effluent was captured in clean IC vials in volume increments of 2- to 5-mL depending on the experiment. Sample was filtered using 0.2 μm PTFE syringe filters into clean IC vials and placed in the sample rack. Post-SPE effluent was tested for silver using AA, collected in three increments of 8-mL each. Dionex OnGuard® II Ag/H and H cartridges were also studied for removal of soluble silver.

2.6. Acid digestion for phosphate determination by IC

Two acid digestion methods were explored to test whether digested samples could be injected on an IC for phosphate analysis. Following the 4500-P B. Sample Preparation method (Clescerl, Greenberg, & Eaton, 1999), aqueous test samples containing 1 ppm PO_4-P were digested by persulfate and sulfuric acid-nitric acid digestions. In the persulfate digestion, samples were treated with 1-mL of 30% sulfuric acid and 0.5 g of potassium persulfate and boiled. Phenolphthalein indicator was added and 1 M NaOH was added until the solution turned a faint pink color. In the sulfuric acid-nitric acid digestion, 1-mL each of concentrated sulfuric and nitric acids were added to the samples. The solutions were boiled and titrated with 1 M NaOH until a faint pink color was observed.

2.7. Determination of ammonium by comparative phenate method

Following the 4500-NH_3 F. Phenate method for the determination of NH_4-N, the diluted extracted solution was treated with 1-mL of phenol, 1-mL of sodium nitroprusside and 2.5-mL of oxidizing solution (Clescerl, Greenberg, & Eaton, 1999). The solution was incubated in a BOD oven at 25°C and the absorbance was measured spectrophotometrically at 640 nm.

3. Results and Discussion

3.1. Site pH and properties

The sediment properties of each site were quite varied. Strasburg Reservoir sediment was sandy in nature, which means that it has poor cation exchange capacity (CEC). This is because the sand particles have no charge and therefore no sites for cations to be retained. The pH of Strasburg Reservoir sediment was 4.35 ± 0.06 (n=3). This finding is consistent with previous observations of acidic lake conditions, which have resulted in a liming project of Little Passage Creek, the stream entering the reservoir (Reeser, 2003). In comparison, the pH of Lake Shenandoah sediment was 7.74 ± 0.02 (n=3). Lake Shenandoah sediment contained more clay and organic matter, which is correlated with a high CEC. Slate Lick Lake sediment also consisted of more clay particles than sandy particles. The pH of Slate Lick Lake sediment was 3.50 ± 0.04 (n=3). The measured pH of Strasburg Reservoir and Slate Lick Lake sediment was very low, and may be artificial values due to sample processing such as air drying and grinding in addition to using DI in the pH measurement. An electrolyte solution, such as 0.02 M $CaCl_2$, would give a more accurate pH reading because it mimics the ionic strength observed in nature and provides ions that can repopulate the sites on the sediment particles. In the future, it would be effective to measure CEC and acid neutralizing capacity (ANC) in addition to pH to give more information about the sediment characteristics.

3.2. SPE of aqueous test solutions

Preliminary and previous research studied the passing of aqueous test solutions through Ag, H, and Ag/H cartridges. In analyzing NO_3-N and NH_4-N test samples with KCl in equivalent amounts used in extraction by IC, it was observed that the high concentration of chloride ion

saturated anion IC, while potassium ion saturated cation IC (Figure 3). Use of the Ag cartridges removed >99% of chloride ion with a starting concentration of 7090 ppm to allow for NO_3-N determination (Table I).

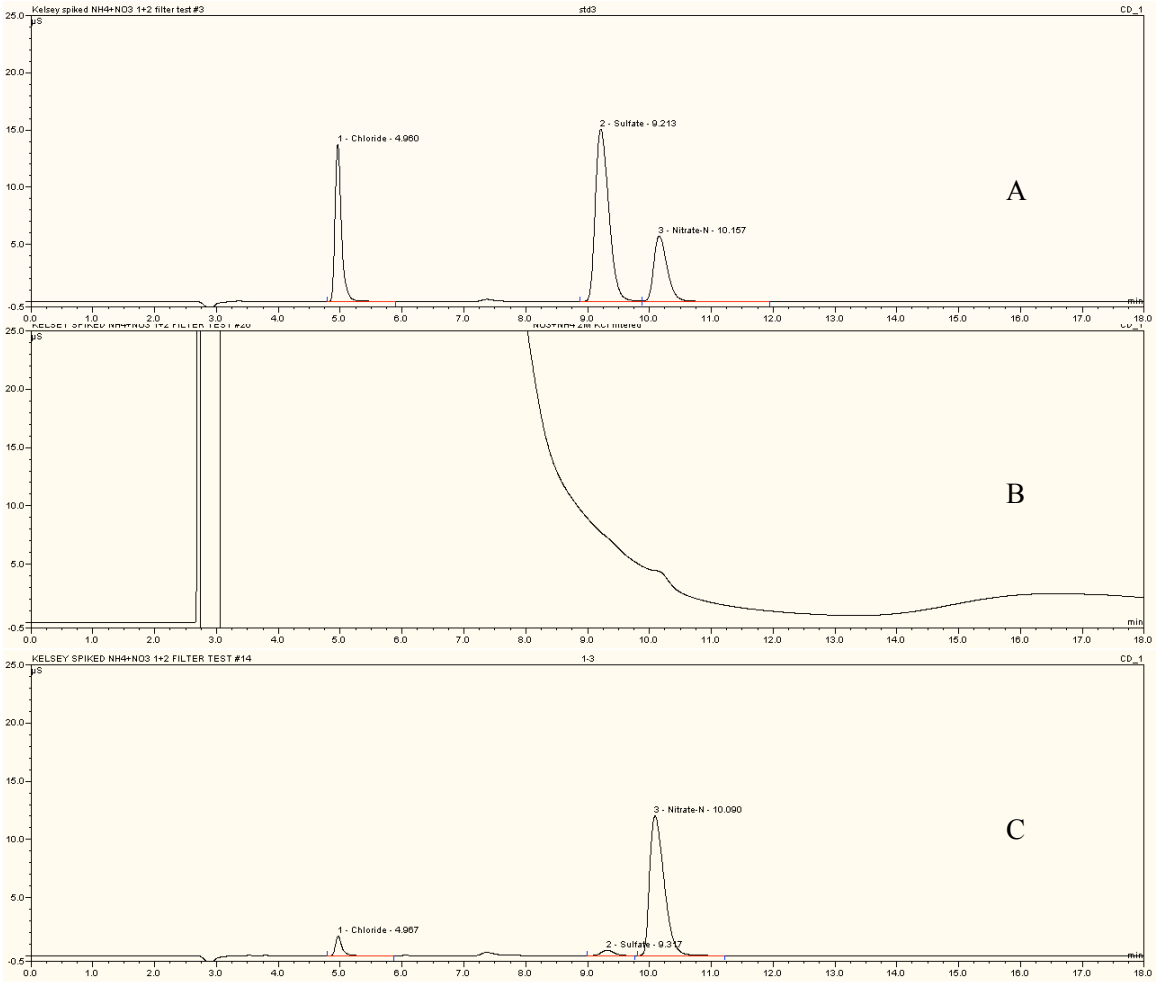

Figure 3. Series of example chromatograms recorded under the same conditions for three different samples: (A) three anion standard containing 1 ppm chloride, 4 ppm sulfate and 2 ppm nitrate-nitrogen in DI water; (B) 1 ppm nitrate in 1:10 diluted 2 M KCl; (C) 1 ppm nitrate in 1:10 diluted 2 M KCl passed through Ag cartridge. Chromatographic conditions for determination: AS18 column, 23 mM KOH eluent, 1.0 mL/min flow rate, retention times for Cl^-: 5.0 min, SO_4^{2-}: 9.2 min, NO_3-N: 10.2 min . Tailing from the high concentration of chloride extractant obscured the nitrate peak in (B). In (C) the Ag cartridge has eliminated the interfering chloride ion and allowed for quantitation of nitrate.

Table I. Analysis results for 2 M KCl spiked with 10.0 ppm each NO_3-N and NH_4-N then diluted 1:10 with DI H_2O. Standard: 1.00 ppm each NO_3-N and NH_4-N in DI H_2O. Trial 1: 4 mL aliquots passed through one Ag cartridge. Trial 2: 4 mL aliquots passed through two Ag cartridges connected in series. For both trials, 6 mL were discarded before collection of samples. Breakthrough is observed between increment 5 and 6 for one Ag cartridge.

Sample	ppm Cl^-	ppm NO_3-N	ppm NH_4-N
Standard	0.00	0.968	1.046
Trial 1-1	0.06	0.982	0.068
Trial 1-2	0.05	0.985	0.063
Trial 1-3	0.70	0.978	0.071
Trial 1-4	0.08	0.982	0.072
Trial 1-5	off scale	0.978	off scale
Trial 1-6	off scale	0.930	off scale
Trial 2-1	0.06	0.974	0.063
Trial 2-2	0.04	0.975	0.034
Trial 2-3	0.03	0.976	0.026
Trial 2-4	0.08	0.978	0.082
Trial 2-5	0.06	0.978	0.062
Trial 2-6	0.06	0.980	0.070

However, use of the cartridges also eliminated potassium and ammonium ion, leaving a single peak in the cation chromatogram thought to be silver ion (Figure 4). It was determined that only one Ag cartridge was necessary to remove the amount of chloride ion contained in spiked 2 M KCl diluted 1:10. The capacity of one cartridge was between 16 and 20 mL of this diluted solution, not including the discarded first 6 mL of sample (Table I). This provided more than enough sample required for IC analysis, and the value of nutrient did not vary substantially between increments. Breakthrough was observed at around 20 mL for one cartridge, at which point ammonium ion was eluted from the cartridge in addition to excess chloride ion.

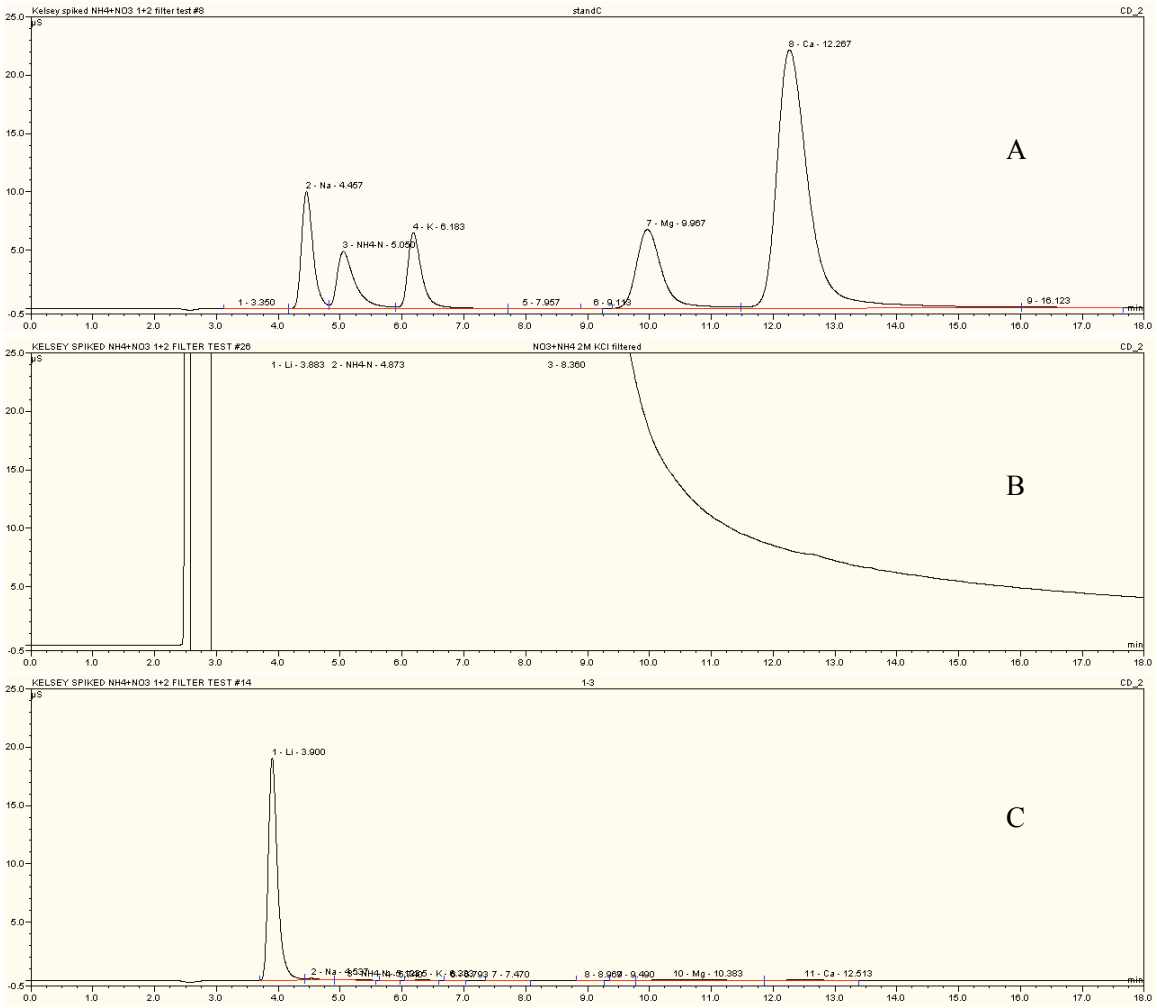

Figure 4. Series of example chromatograms recorded under the same conditions for three different samples: (A) five cation standard containing 0.8 ppm each of sodium, ammonium-nitrogen, potassium, and magnesium and 4.0 ppm calcium in DI water; (B) 1 ppm ammonium in 1:10 diluted 2 M KCl; (C) 1 ppm ammonium in 1:10 diluted 2 M KCl passed through Ag cartridge. Chromatographic conditions for determination: CS14 column, 20 mM MSA, 1.0 mL/min flow rate, retention times for Na: 4.5 min, NH_4-N: 5.0 min, K: 6.2 min, Mg: 10.0 min, Ca: 12.3 min. Tailing from the high concentration of potassium extractant obscured the ammonium peak in (B). In (C) the Ag cartridge has eliminated potassium ion and ammonium ion, eluting a peak thought to be silver.

One concern with using the Ag cartridges was the potential for leaching of dissolved silver ion into the sample effluent. This would be a problem because silver ion is not good for the IC columns in that it builds up and alters the separating ability of the column. The H and Ag/H cartridges are manufactured to remove dissolved silver ion from solution and here were employed to test the effectiveness of silver ion removal and evaluate any differences in NO_3-N determination. It was found that there was a significant difference ($p = 0.039$) between the NO_3-

N concentration observed using Ag + H cartridges and Ag/H combination cartridges (Table II). Using AA, it was determined that use of either the H cartridge in tandem with the Ag cartridge or the Ag/H combination cartridge resulted in a significant reduction (>80%) in the amount of silver ion in the sample effluent (Table III).

Table II. Analysis results for 2 M KCl spiked with 10.0 ppm NO_3-N then diluted 1:10 with DI H_2O. Three mL aliquots of sample were passed through Ag + H cartridges in series or Ag/H combination cartridges. For both trials, 6 mL were discarded before collection of samples.

Cartridge	Average ppm NO_3-N	p-value
Ag + H	0.987 ± 0.005	0.039
Ag/H	0.994 ± 0.005	

Table III. Analysis results for Ag in cartridge effluent by AA. Sample passed through cartridges was 2 M KCl spiked with 10.0 ppm each NO_3-N and NH_4-N diluted 1:10 with DI H_2O. Trials included effluent from two Ag cartridges in series, one Ag cartridge, one Ag cartridge in series with one H cartridge, and a Ag/H combination cartridge. Percent removal of Ag was calculated used the average ppm in the effluent of the single Ag cartridge as the initial amount.

Cartridge	Average ppm Ag	% Removal
2 Ag	2.15 ± 0.18	
Ag	1.60 ± 1.00	
Ag + H	0.247 ± 0.188	84.6
Ag/H	0.290 ± 0.135	81.9

Once it was determined that use of the Ag cartridges results in loss of ammonium, an alternative extraction method was explored using 0.02 M $SrCl_2$. The Dionex OnGuard® II cartridges are expensive and sample treatment can be lengthy if many samples are to be analyzed. An alternative extraction solution that can extract all three analytes of interest and does not require further sample pretreatment would significantly increase the ease of analysis execution. In analyzing NO_3-N and NH_4-N spiked $SrCl_2$ by IC, it was found that the considerably lower salt concentration does not swamp the column, allowing for both nitrate and ammonium analysis. In the anion chromatogram, a large chloride peak can be seen yet nitrate can still be resolved and quantified (Figure 5). On the cation side, strontium ion elutes much later

in the chromatogram and therefore ammonium can be resolved and determined. Treatment of the spiked $SrCl_2$ extractant with Ag cartridges removed chloride ion and positive ions such as potassium and ammonium from solution. Therefore, $SrCl_2$ may be an acceptable alternative extractant to the common KCl extractant with the advantage of being compatible with IC analysis without requiring the use of SPE if the extraction abilities prove comparable.

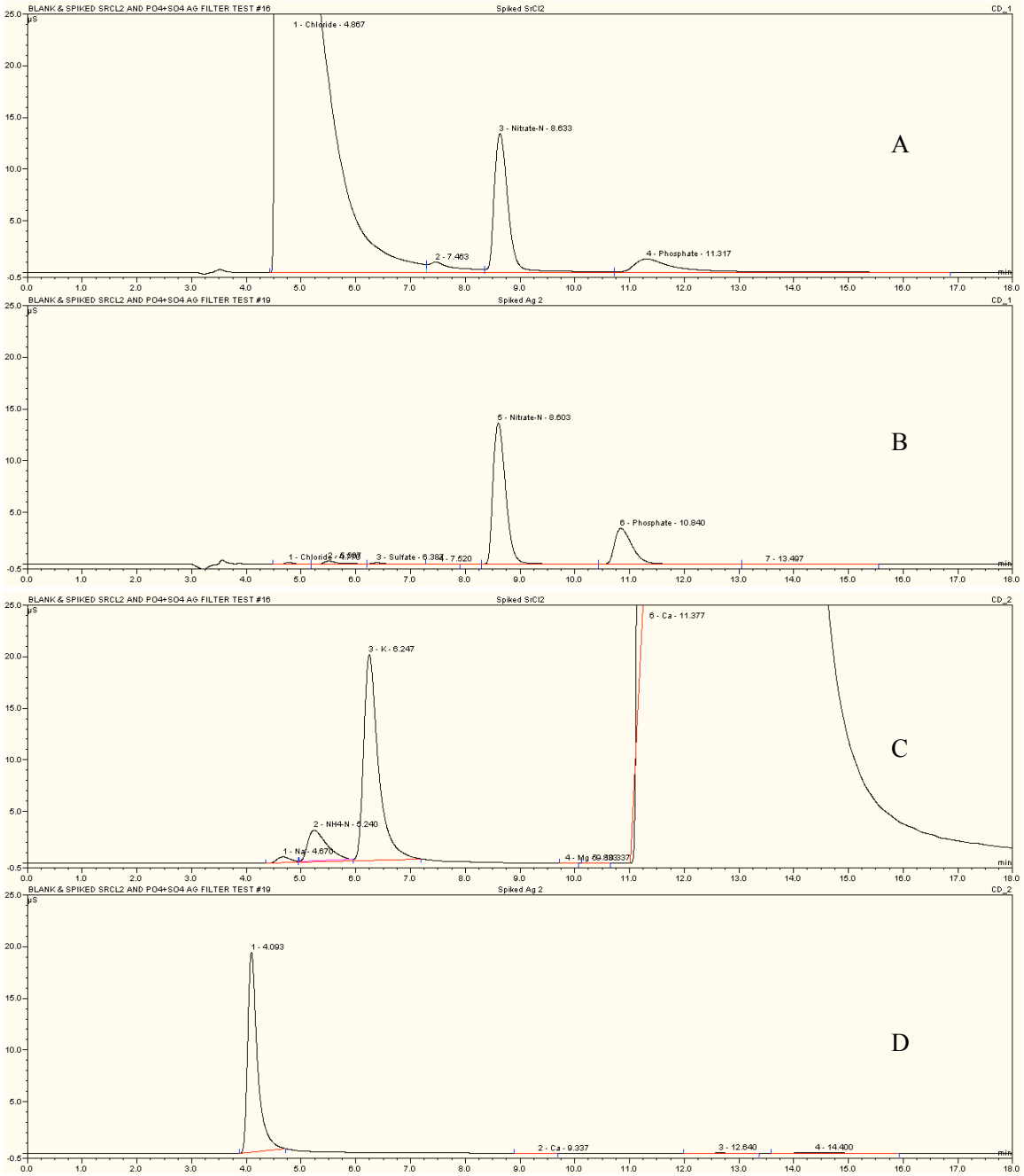

Figure 5. Series of example chromatograms recorded under the same conditions for cation analyses and anion analyses: (A) 1 ppm each nitrate and phosphate in 0.02 M $SrCl_2$; (B) 1 ppm each nitrate and phosphate in 0.02 M $SrCl_2$ passed through Ag cartridge; (C) 1 ppm ammonium in 0.02 M $SrCl_2$; (D) 1 ppm ammonium in 0.02 M $SrCl_2$ passed through Ag cartridge. Anion chromatographic conditions: AS18 column, 33 mM KOH, 0.9 mL/min flow rate, retention times for Cl^-: 4.8 min, NO_3-N: 8.6 min, PO_4-P: 10.8 min. Cation chromatographic conditions: CS14 column, 20 mM MSA, 1.0 mL/min flow rate, retention times for Na: 4.6 min, NH_4-N: 5.2 min, K: 6.3 min, Mg: 10.0 min, Ca: 12.2 min. Nitrate in $SrCl_2$ was not interfered with by chloride ion in (A), so use of the Ag cartridges for chloride removal was unnecessary. Strontium ion did not interfere with ammonium determination when $SrCl_2$ was used as the extractant in (C), appearing later in the chromatogram.

3.3. NO_3-N in Strasburg Reservoir, Lake Shenandoah and Slate Lick Lake sediment

Nitrate-nitrogen in Strasburg Reservoir sediment was determined by IC with varying extraction methods. Methods compared included KCl extraction coupled with Ag cartridge SPE, $SrCl_2$ extraction and $SrCl_2$ extraction coupled with Ag cartridge SPE (n=3 for each method). KCl and $SrCl_2$ extraction methods were employed for blank samples and sediment spiked with 1 ppm NO_3-N (10 mg/kg for a 7.5 g sample). For both blank and spiked samples, the value of NO_3-N given by the KCl extraction method was greater than that given by the $SrCl_2$ extraction (Table IV), although in the spiked samples the difference was non-significant ($p > 0.05$) (Table V). This may be because the spiked analyte is much easier to extract than nutrient adsorbed to sediment particles, meaning that nearly all of the spiked analyte is recovered. This observation is supported by the high % recovery of the $SrCl_2$ extraction method (94.8%) (Table VI). The comparatively low % recovery observed of the KCl extraction and SPE method may be accounted to the large variation in results for the unspiked samples (RSD = 72.7%) and therefore a right-skewed expected value due to a high outlier (Table IV). Comparison of mg/kg NO_3-N values obtained from $SrCl_2$ extraction and $SrCl_2$ extraction followed by Ag cartridge SPE determined that any difference is non-significant ($p = 0.56$) (Table V). However, the $SrCl_2$ extraction only gave a higher average concentration of NO_3-N and analyte peaks were resolved without further sample pretreatment or dilution, making this method preferable to the SPE-containing method.

Table IV. Analysis results for NO_3-N in unspiked sediment by various methods. Strasburg Reservoir sediment was extracted by 2 M KCl or 0.02 M $SrCl_2$ coupled with Ag SPE as well as 0.02 M $SrCl_2$ extraction alone. Lake Shenandoah and Slate Lick Lake sediment was extracted by 2 M KCl or 0.02 M $SrCl_2$ and analyzed by two different IC methods (standard and alternative). Standard instrumental method refers to conditions of 23 mM NaOH and a flow rate of 1 ml/min, while alternative instrumental method refers to conditions of 33 mM NaOH and a flow rate of 0.9 mL/min.

Site	Extraction & Instrumental Methods	Average mg/kg NO_3-N
Strasburg Reservoir	KCl +Ag SPE	4.60 ± 3.34
	$SrCl_2$	0.957 ± 0.145
	$SrCl_2$ +Ag SPE	0.903 ± 0.023
Lake Shenandoah	KCl +Ag SPE standard	6.35 ± 0.24
	KCl +Ag SPE alternative	4.45 ± 1.28
	$SrCl_2$ standard	5.92 ± 0.03
	$SrCl_2$ alternative	5.18 ± 0.04
Slate Lick Lake	KCl +Ag SPE standard	54.1± 0.8
	KCl +Ag SPE alternative	1.70 ± 0.16
	$SrCl_2$ standard	off scale
	$SrCl_2$ alternative	4.07 ± 0.09

Table V. P-values of NO_3-N method comparisons. For Strasburg Reservoir, methods compared were 0.02 M $SrCl_2$ extraction followed by Ag SPE or 0.02 M $SrCl_2$ extraction only, and 1 ppm spiked sediment samples extracted by 2 M KCl followed by Ag SPE or extraction by 0.02 M $SrCl_2$. For Slate Lick Lake, methods compared were 2 M KCl or 0.02 M $SrCl_2$ extraction followed by analysis via the alternative instrument method.

Site	Methods	p-value
Strasburg Reservoir	$SrCl_2$ + Ag vs. $SrCl_2$	0.56
	KCl + Ag vs. $SrCl_2$ (spiked)	0.11
Slate Lick Lake	Alternative KCl vs. $SrCl_2$	0.000026

Table VI. Analysis results for NO_3-N in 1 ppm spiked Strasburg Reservoir sediment extracted by 2 M KCl with Ag SPE or 0.02 M $SrCl_2$. The expected mg/kg NO_3-N for each method was determined by converting 1 ppm NO_3-N to mg/kg based on the masses of the samples (10 mg/kg for a 7.5 g sample), and adding this value to the average mg/kg NO_3-N for each respective unspiked method.

Method	Average mg/kg NO_3-N	Expected mg/kg NO_3-N	% Recovery
KCl + Ag SPE	11.3 ± 0.6	14.8	76.6
$SrCl_2$	10.5 ± 0.3	11.1	94.8

Nitrate-nitrogen analysis in Lake Shenandoah sediment was performed using IC with two different instrument methods in addition to the two extraction methods. The standard instrumental parameters (23 mM NaOH, 65 mA, 1 mL/min) were used initially and the alternative method (33 mM NaOH, 82 mA, 0.9 mL/min) was implemented for the improved resolution of nitrate peaks, particularly for Slate Lick Lake samples with high concentrations of interfering sulfate ion. The effect of this alternative method on the Slate Lick Lake samples is discussed in the next paragraph. A two-way ANOVA test with replication was performed comparing the extraction and IC methods of Lake Shenandoah sediment (Table VII). There was no significant difference between extraction methods ($F(1,4) = 0.15$, $p = 0.71$). There was a significant effect of instrumental method ($F(1,4) = 12.41$, $p = 0.0078$), with the standard method giving significantly higher values of NO_3-N. There was no significant interaction of extraction method and instrumental method ($F(1,4) = 2.37$, $p = 0.16$).

Table VII. Two-way analysis of variance of NO_3-N in Lake Shenandoah sediment by extraction solution and instrumental conditions. Extraction solutions tested were 2 M KCl and 0.02 M $SrCl_2$. Instrumental conditions tested were the standard (23 mM NaOH, 1 mL/min flow rate) and alternative (33 mM NaOH, 0.9 mL/min flow rate) methods.

Source	SS	d.f.	MS	F	p-value	F crit
Instrument method	5.233	1	5.233	12.412	0.008	5.318
Extraction solution	0.064	1	0.064	0.153	0.706	5.318
IM x Extraction	1.000	1	1.000	2.372	0.162	5.318
Within groups	3.373	8	0.422			
Total	9.670	11	0.879			

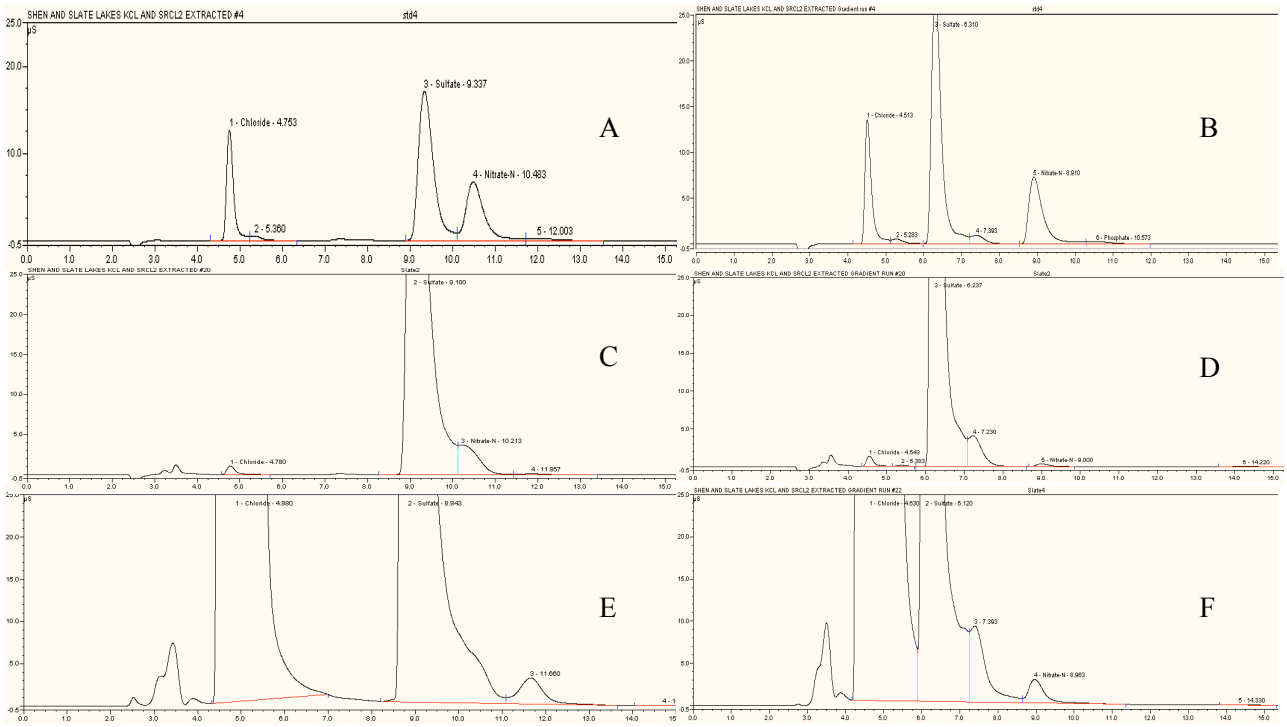

Figure 6. Series of example chromatograms recorded under standard or alternative instrumental conditions: (A) three anion standard under standard instrumental conditions containing 2 ppm Cl^-, 8 ppm SO_4^{2-}, and 4 ppm NO_3-N; (B) three anion standard under alternative instrumental conditions containing 2 ppm Cl^-, 8 ppm SO_4^{2-}, and 4 ppm NO_3-N; (C) nitrate in 2 M KCl extracted Slate Lick Lake sediment diluted 1:10 under standard instrumental conditions; (D) nitrate in 2 M KCl extracted Slate Lick Lake sediment diluted 1:10 under alternative instrumental conditions; (E) nitrate in 0.02 M $SrCl_2$ extracted Slate Lick Lake sediment under standard instrumental conditions; (F) nitrate in 0.02 M $SrCl_2$ extracted Slate Lick Lake sediment under alternative instrumental conditions. Standard chromatographic conditions: AS18 column, 23 mM KOH, 1.0 mL/min flow rate, retention times for Cl^-: 4.8 min, SO_4^{2-}: 9.3, NO_3-N: 10.5 min. Alternative chromatographic conditions: AS18 column, 33 mM NaOH, 0.9 mL/min flow rate, retention times for Cl^-: 4.5 min, SO_4^{2-}: 6.3, NO_3-N: 8.9 min. The chromatograms obtained under standard instrumental conditions (C & E) displayed nitrate peaks (should have appeared around 10.5 min) that were significantly interfered with by sulfate ion. The chromatograms obtained under the alternative instrumental conditions (D & F) exhibited improved resolution between sulfate peaks and nitrate peaks (appeared around 9.0 min), allowing for quantitation.

The same experiments were performed on Slate Lick Lake sediment samples as were executed on the Lake Shenandoah samples. Originally, the standard instrumental method yielded anion chromatograms with large sulfate interferences (Figure 6). The same samples were run using the alternative instrumental method, which was adopted for improved resolution of phosphate. Whereas no measurable NO_3-N could be found in the standard method with $SrCl_2$ extraction, NO_3 could be resolved and quantified using the alternative method. There was also

sulfate interference in the standard instrumental method with KCl extraction, shown by the large value of NO_3-N resulting from the software analyzing part of the sulfate peak as nitrate (Table IV). Use of the alternative instrumental method allowed for the quantitation of N-NO_3 in KCl extracted sediment. Controlling for the alternative instrumental method, the $SrCl_2$ extraction exhibited a significant increase in NO_3-N concentration compared to KCl extraction ($p = 0.000026$) (Table V). The alternative instrumental method proved to be extremely useful in IC analysis of samples with high sulfate concentrations that prevent the determination of NO_3-N.

3.4. NH_4-N in Strasburg Reservoir, Lake Shenandoah and Slate Lick Lake sediment

Ammonium nitrogen in Strasburg Reservoir sediment was evaluated by three distinct methods: $SrCl_2$ extraction with IC analysis, $SrCl_2$ extraction with PC analysis and KCl extraction with PC analysis. These methods were employed for blank samples and sediment spiked with 10 ppm NH_4-N (100 mg/kg for a 7.5 g sample). The phenate colorimetric method was used as a comparative technique for IC analysis. Data from the method of KCl extraction with IC analysis was not reported due to the loss of ammonium in the Ag cartridges. As observed in the NO_3-N analysis, methods with KCl extraction gave higher concentrations of NH_4-N than those using $SrCl_2$ extraction (Table VIII). The results from each method are statistically significantly different ($p < 0.05$) with the borderline exception of the PC analysis of unspiked samples using KCl and $SrCl_2$ extraction methods ($p = 0.058$) (Table IX). IC analysis consistently gave lower values of NH_4-N even for the same extraction method (Table 8). Percent recovery was also lowest for IC analysis following $SrCl_2$ extraction (71.7%) and highest for the comparative method (>100%) (Table X).

Table VIII. Analysis results for NH_4-N in unspiked sediment by various methods. All three sediments were evaluated by 0.02 M $SrCl_2$ extraction followed by IC or PC analysis and 2 M KCl extraction followed by PC analysis.

Site	Method	Average mg/kg NH_4-N
Strasburg Reservoir	$SrCl_2$ extracted IC	18.6 ± 0.4
	$SrCl_2$ extracted PC	23.3 ± 2.4
	KCl extracted PC	27.0 ± 0.3
Lake Shenandoah	$SrCl_2$ extracted IC	13.2 ± 2.4
	$SrCl_2$ extracted PC	13.8 ± 5.2
	KCl extracted PC	24.2 ± 4.1
Slate Lick Lake	$SrCl_2$ extracted IC	28.5 ± 2.7
	$SrCl_2$ extracted PC	28.3 ± 4.4
	KCl extracted PC	45.1 ± 12.5

Table IX. P-values of NH_4-N method comparisons. For Strasburg Reservoir, method comparisons included 0.02 M $SrCl_2$ extracted sediment (spiked and unspiked) followed by IC or PC analysis, and 2 M KCl or 0.02 M $SrCl_2$ extracted sediment (spiked and unspiked) followed by PC analysis. For Lake Shenandoah and Slate Lick Lake, methods compared were 0.02 M $SrCl_2$ extraction followed by IC or PC analysis, and 2 M KCl or 0.02 M $SrCl_2$ extractions followed by PC analysis.

Site	Method	p-value
Strasburg Reservoir	$SrCl_2$ IC vs. PC (unspiked)	0.027
	$SrCl_2$ IC vs. PC (spiked)	0.0040
	PC KCl vs. $SrCl_2$ (unspiked)	0.058
	PC KCl vs. $SrCl_2$ (spiked)	0.00056
Lake Shenandoah	$SrCl_2$ IC vs. PC	0.86
	PC KCl vs. $SrCl_2$	0.054
Slate Lick Lake	$SrCl_2$ IC vs. PC	0.95
	PC KCl vs. $SrCl_2$	0.093

Table X. Analysis results for NH_4-N in 10 ppm spiked Strasburg Reservoir sediment extracted by 0.02 M $SrCl_2$ with IC and PC analysis or 2 M KCl with PC analysis. The expected mg/kg NH_4-N for each method was determined by converting 10 ppm NH_4-N to mg/kg based on the masses of the samples (100 mg/kg for a 7.5 g sample), and adding this value to the average mg/kg NH_4-N for each respective unspiked method.

Method	Average mg/kg NH_4-N	Expected mg/kg NH_4-N	% Recovery
$SrCl_2$ IC	85.6 ± 4.4	119	71.7
$SrCl_2$ PC	103 ± 3	124	83.0
KCl PC	136 ± 5	132	103

As with Strasburg Reservoir, Lake Shenandoah sediment was analyzed for NH_4-N by three combination methods: $SrCl_2$ extraction with IC analysis, $SrCl_2$ extraction with PC analysis and KCl extraction with PC analysis. The difference between both $SrCl_2$ methods is non-significant ($p = 0.86$) (Table IX). This indicates that both IC and PC methods coupled to $SrCl_2$ extraction yield similar results. The increased NH_4-N concentration obtained by the KCl extraction and PC method is borderline non-significant compared to the corresponding $SrCl_2$ extraction with IC method ($p = 0.054$). In contrast, compared to the $SrCl_2$ extraction with IC method, the KCl extraction with PC method gives significantly higher results (Table VIII). This finding is consistent with previous observations that a method with KCl extraction gives higher values for nutrients than one with $SrCl_2$ extraction.

For NH_4-N determination of Slate Lick Lake sediment, samples were extracted with either KCl or $SrCl_2$ and analyzed by either IC or PC methods. As observed with Lake Shenandoah sediment, there was no significant difference between the two analytical methods of $SrCl_2$ extracted samples ($p = 0.95$) (Table IX). Once again, this indicates that extraction with $SrCl_2$ yields a certain value of nutrient, and both analytical methods agree on this value. The higher concentration of NH_4-N resulting from KCl extraction followed by PC analysis is non-significant compared to PC analysis of $SrCl_2$ extracted sediment ($p = 0.093$). However, it can clearly be seen that the mean nutrient concentration determined by a KCl extraction is considerably higher than that of $SrCl_2$ extractions (Table VIII). In general, the IC methods exhibited smaller RSD values compared to PC methods. Since RSD is an indicator of precision, these results suggest that the IC method was more precise in this case than the PC method for NH_4-N analysis.

3.5. PO_4-P in aqueous test samples

In order to develop IC methodology for PO_4-P, various standards were tested with respect to instrument response. Standards were made within the range of 10 to 200 ppb and evaluated by a gradient elution run on the ICS-5000, with each standard giving an observable conductivity response. Standards with higher concentrations (1, 2.5 and 5 ppm) were evaluated by the alternative instrumental method on the ICS-3000 along with increments of 1 ppm PO_4-P passed through a Ag cartridge. No loss of PO_4-P was observed using the Ag cartridge and consecutive increments gave similar results, with the exception of the first increment (Table XI). This demonstrates that any phosphate extracted by KCl will not be lost during SPE and can be analyzed simultaneously as nitrate. However, phosphate is not usually extracted with KCl and requires acid digestion to convert all forms of P to phosphate in analysis of total P.

Table XI. Analysis results for 1 ppm PO_4-P through Ag cartridges. Trials consisted of consecutive collections of 2-mL increments; 6 mL were discarded before collection of samples.

Sample	ppm PO_4-P
Trial 1	0.609
Trial 2	1.01
Trial 3	1.01
Trial 4	1.01
Trial 5	1.01
Trial 6	1.01
Trial 7	1.02

Two acid digestion methods were tested to determine whether the high acid content would allow for phosphate determination by IC. Blank and phosphate-spiked samples were digested by persulfate and sulfuric acid-nitric acid methods. The digested solutions were neutralized with NaOH and analyzed by IC. The sulfuric acid-nitric acid digestion required a significantly larger volume of NaOH to neutralize the acid because concentrated acid was used. Chromatograms of the sulfuric acid-nitric acid digested samples exhibited sulfate/nitrate peaks

that completely swamped out any phosphate, whereas a peak is visible in the chromatogram of the persulfate digestion (Figure 7). These observations are consistent with the volumes of acid used in each digestion method in that 2 mL of concentrated acids were used in the sulfuric acid-nitric acid digestion whereas only 1 mL of 30% sulfuric acid was used in the persulfate digestion. Phosphate determination of acid digested samples may be possible if interfering sulfate and/or nitrate peaks are removed.

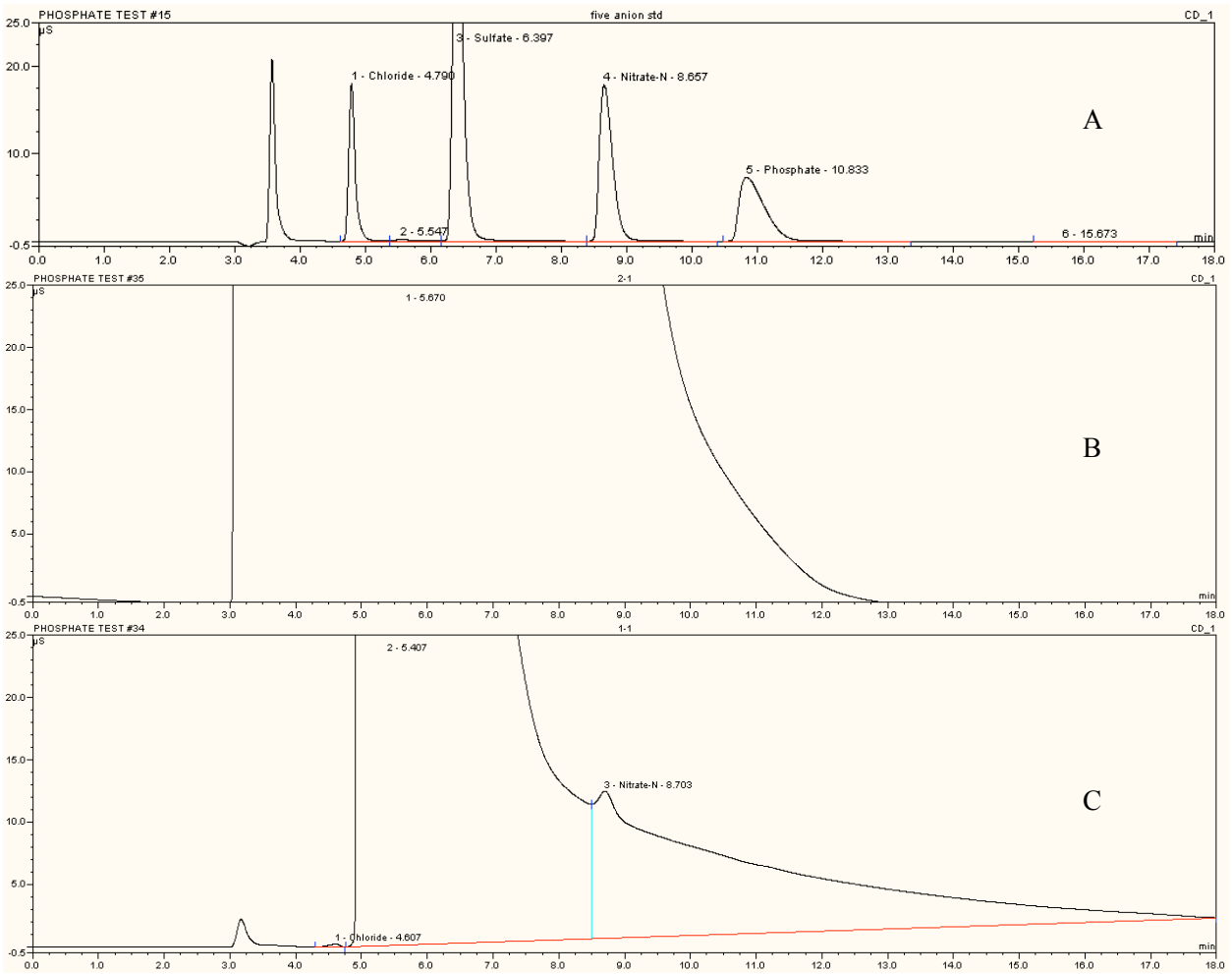

Figure 7. Series of example chromatograms recorded under the same conditions for three different samples: (A) five anion standard containing 1.0 ppm fluoride, 1.5 ppm chloride, 7.5 ppm sulfate, 5.0 ppm nitrate and 7.5 ppm phosphate; (B) 1 ppm phosphate in sulfuric acid-nitric acid digestion; (C) 1 ppm phosphate in persulfate digestion. Chromatographic conditions: AS18 column, 33 mM NaOH, 0.9 mL/min flow rate, retention times for F^-: min, Cl^-: 4.8 min, SO_4^{2-}: 6.4 min, NO_3-N: 8.7 min, PO_4-P: 10.8 min. The sulfuric acid-nitric acid digestion (B) showed a single peak that swamped the entire chromatogram. The persulfate digestion (C) depicted a large peak that interfered with phosphate; however, a small peak was observed on the shoulder of the larger peak.

4. Conclusions

The methodology developed achieved the above goals with mixed results. Residual chloride after removal via silver precipitation did not exceed 3 ppm, which allowed for sufficient quantification of nitrate-nitrogen. Ions washed into solution during cartridge use did not interfere with IC nitrate-nitrogen determination. A loss of ammonium-nitrogen was observed with cartridge use, so alternative extraction solutions were explored. Although the lower concentration of 0.02 M $SrCl_2$ allowed for the use of IC for NH_4-N determination without prior chloride removal, the $SrCl_2$ extractant gave consistently lower values of nutrient than the KCl extractant. Possible ways to overcome this issue include longer extraction time, increasing the concentration of salt, or changing the pH of the extractant. An alternative IC method utilizing increased eluent concentration was found to be effective for nitrate evaluation of samples with interfering sulfate concentrations due to the increased separation between sulfate and nitrate peaks. Compared with the colorimetric method of ammonium determination, the IC method demonstrated increased precision.

Much additional research is needed in each area of nutrient determination. For NO_3-N and PO_4-P analyses, comparative methods must be employed for an evaluation of the results obtained by the IC method. Sediment samples should be extracted by 0.5 M $NaHCO_3$, the most commonly used extractant of phosphorus, for comparison of PO_4-P extraction capabilities with 0.02 M $SrCl_2$. Additionally, Dionex OnGuard® II Ba cartridges should be used to test whether sulfate can be removed from the acid digested sample matrix without loss of PO_4-P for analysis by IC. Experiments for the determination of LODs, LOQs and linear dynamic ranges for each nutrient/method combination should be performed to compare sensitivity and detection limitations of proposed and comparative methods.

5. Summary of Analytical Procedures

Simplified, recommended procedures for analysis of each nutrient in lake sediment studied in this project are described as follows:

I. Analysis of NO_3-N

1. Place approximately 10 g of finely ground sediment onto a watch glass and record the exact mass. Dry the sediment in an oven at 110°C for 24 hours and record the exact mass. Mass lost is due to loss of water.
2. Place 7.5 ± 0.5 g (known to nearest tenth of a milligram) of finely ground sediment into a 125-mL Erlenmeyer flask.
3. Pipet 75-mL 2 M KCl solution into each sample.
4. Stopper each flask and shake for one hour.
5. Allow the sample to settle and filter using a 42.5 mm Buchner funnel and Whatman size 1 filter paper into a clean, dry Erlenmeyer flask.
6. Transfer filtrate into a clean flask and parafilm for short-term storage at 4°C.
7. Flush Dionex OnGuard® II Ag cartridges with 15-mL DI water at a maximum flow rate of 2 mL/min. Use 5-mL syringes and orient the cartridges vertically.
8. Pipet 10-mL of each sample into a clean 100-mL volumetric flask and dilute to volume. Sediment known or predicted to have high concentrations of nitrate may be diluted further.
9. Draw the diluted sample into syringe and flush through one cartridge at a maximum flow rate of 2 mL/min. Discard the first 6-mL of sample.
10. Collect at least 5-mL into a dry, clean sample vial.

11. Draw up filtered sample into a new syringe and filter through 0.2 μm syringe filter into a clean, dry IC vial.
12. Load IC vials into sample tray along with standards and place in the auto sampler for the IC. Set dilution factor to 10 (or whatever is appropriate depending on dilution made).
13. Calculate percent weight water loss in the 24-hour drying experiment and correct recorded masses for water loss.
14. Record ppm NO_3-N from IC results. Convert to mg NO_3-N/kg sediment using the equation: mg NO_3-N/kg sediment = [(mg NO_3-N/L filtrate) * 75 mL / x g sediment corrected for water loss].

II. Analysis of NH_4-N

1. Place approximately 10 g of finely ground sediment onto a watch glass and record the exact mass. Dry the sediment in an oven at 110°C for 24 hours and record the exact mass. Mass lost is due to loss of water.
2. Place 7.5 ± 0.5 g (known to nearest tenth of a milligram) of finely ground sediment into a 125-mL Erlenmeyer flask.
3. Pipet 75-mL 2 M KCl solution into each sample.
4. Stopper each flask and shake for one hour.
5. Allow the sample to settle and filter using a 42.5 mm Buchner funnel and Whatman size 1 filter paper into a clean, dry Erlenmeyer flask.
6. Transfer filtrate into a clean flask and parafilm for short-term storage at 4°C.
7. Prepare NH_4-N standards at concentrations of 0, 0.100, 0.300 and 0.500 mg/L from a stock solution of 1000 mg/L N as NH_4Cl .
8. Pipet 25-mL of standard or sample into a clean, dry 125-mL Erlenmeyer flask.

9. Pipet 1-mL of phenol solution, 1-mL of sodium nitroprusside and 2.5-mL of oxidizing solution into the flask.
10. Parafilm flask and swirl to mix. Place in BOD incubation oven at 25°C for one hour.
11. Measure the absorbance of each standard and solution at 640 nm using a spectrophotometer with a 1.00 cm cell, adjusting with the blank.
15. Prepare a calibration curve and calculate the concentration of NH_4-N in the samples, correcting for any dilutions. Convert to mg NH_4-N/kg sediment using the equation: mg NH_4-N/kg sediment = [(mg NH_4-N/L filtrate) * 75 mL / x g sediment corrected for water loss].

III. Analysis of PO_4-P (Total P)

1. Place approximately 10 g of finely ground sediment onto a watch glass and record the exact mass. Dry the sediment in an oven at 110°C for 24 hours and record the exact mass. Mass lost is due to loss of water.
2. Place 5.0 ± 0.5 g (known to nearest tenth of a milligram) of finely ground sediment into a 250-mL Erlenmeyer flask.
3. Pipet 100-mL 0.5 M $NaHCO_3$ solution into each sample.
4. Stopper each flask and shake for 30 minutes.
5. Allow the sample to settle and filter using a 42.5 mm Buchner funnel and Whatman size 1 filter paper into a clean, dry Erlenmeyer flask.
6. Transfer filtrate into a clean flask and parafilm for short-term storage at 4°C.
7. Prepare PO_4-P standards at concentrations of 0, 10, 25, 50, 100 and 200 μg/L from a stock solution of 50 mg/L P as KH_2PO_4.

8. Pipet 50-mL of standard or sample into a clean, dry 125-mL Erlenmeyer flask and add one drop of phenolphthalein indicator. If a pink color is observed, add small quantities of concentrated acid until the color disappears.
9. Add 1-mL 30% H_2SO_4 and 0.5 g $K_2S_2O_8$ to each standard or sample.
10. Digest samples on a hot plate with boiling for 30-40 minutes, then reduce the volume to 10-mL. Do this in the fume hood and digest multiple samples simultaneously on different hotplates.
11. Cool the flask to near room temperature and add approximately 20-mL of DI water to bring the total volume to 30-mL.
12. Add one drop of phenolphthalein and swirl to mix. Add small drops of NaOH until a faint pink color is observed.
13. Quantitatively transfer solution to a 100-mL volumetric flask and dilute to volume with DI water.
14. Pipet 50 mL of this solution into a clean, dry flask. If solution appears pink or red with the addition of phenolphthalein, add 2.5 M H_2SO_4 until the color disappears. Add 8-mL of the combined reagent (50-mL 2.5 M H_2SO_4, 5-mL potassium antimonyl tartrate, 15-mL ammonium molybdate, 30-mL ascorbic acid) and mix.
15. Measure the absorbance of each standard and sample at 880 nm using a spectrophotometer with a 5.00 cm cell, adjusted with the blank. Solutions should be measured after 10 minutes but before 30 minutes since adding the combined reagent.

16. Prepare a calibration curve and calculate the concentration of PO_4-P in the samples, correcting for any dilutions. Convert to mg PO_4-P/kg sediment using the equation: mg PO_4-P/kg sediment = [(μg PO_4-P/L filtrate) * 50 mL * 0.001 * 2 / x g sediment corrected for water loss].

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