**Quality Assurance Project Plan (QAPP)**

**for Vadose Zone Agricultural Monitoring**

Project Name: Project Name

Location: Project Location Description

Prepared by: Dan Snow, PhD, Lacey Bodnar, & Other Author(s)

University of Nebraska Water Sciences Laboratory & Other Author Affiliation(s)

Date (Month Year)

On behalf of: Funding Agency

# A1. Title and Approval Sheet

Project Title: Vadose Zone Nitrate – City, State

Revision Number: 1.0

|  |  |
| --- | --- |
| Reviewer Signature | Date Signed |
| Program/Project Director Name |  |
| Program/Project Director |  |
| QA/Project Manager Name |  |
| QA/Project Manager |  |
| Field Staff Name |  |
| Field Staff |  |
| Program/Project Specialist Name |  |
| Program/Project Specialist |  |
| NDEQ QA Manager Name |  |
| Department of Environmental Quality QA Manager |  |
| NDEQ QA Manager Name |  |
| Department of Environmental Quality Project Manager |  |

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# A3. Distribution List

A copy of the approved Quality Assurance Project Plan (QAPP) and subsequent revisions will be kept on file at the Daugherty Water for Food Institute at the University of Nebraskain both electronic and hardcopy formats for easy access and review. In addition, an original hardcopy will be maintained in the Nebraska Department of Environmental Quality (NDEQ) Quality Assurance (QA) file. Copies and revisions, either electronic or hard copy, will be provided to the funding agency, Nebraska Department of Environmental Quality and the Nebraska Water Sciences Laboratory by QA/Project Manager.

|  |  |  |
| --- | --- | --- |
| Name | Organization | Email Address |
| Funding Agency Manager (from Cover Page) | Funding Organization | Funding Agency Manager Email |
| Sam Radford  Wellhead Protection Program Coordinator | Nebraska Department of Environmental Quality (NDEQ) | sam.radford@nebraska.gov |
| Laura Johnson  Environmental Quality Program Specialist II | NDEQ | laura.r.johnson@nebraska.gov |
| Dr. Tania Biswas  Laboratory Manager | Nebraska Water Sciences Laboratory (WSL) | [sbiswas8@unl.edu](mailto:sbiswas8@unl.edu) |

# A4. Project/Task Organization

Key individuals involved in all major aspects of the project, including contractors, are identified in the organizational chart below (**Figure 1**). The gray lines indicate lines of authority, with the Project Director having the highest authority. Reporting responsibilities proceed from bottom to top, with each tier of the hierarchy reporting to the person(s) in the tier above.

Individuals and organizations participating in vadose zone monitoring projects typically include:

* Municipality or natural resources district staff who provide the scope of work,
* Scientists and consultants who lead the sampling efforts on behalf of a client,
  + Drillers and field personnel who collect vadose zone samples,
  + Laboratory staff who conduct the laboratory testing methods, and
* A quality assurance officer who will be responsible for monitoring data quality.

Figure 1. Project Organizational Chart

*Acronyms: Nebraska Water Center (NWC), Water Sciences Laboratory (WSL), Daugherty Water for Food Global Institute (DWFI), Nebraska Department of Environmental Quality (NEDQ)*

The project director or lead investigator, Dr. Dan Snow, will be the responsible official for the project, overseeing project tasks including QAPP development, laboratory coordination, field operations, data management and report preparation. He may designate some of these tasks to other project personnel, and that circumstance will be included in this section.

The QA/Project manager, Lacey Bodnar, will be responsible for developing the QAPP, ensuring that all QA elements are accounted for and are consistent with other QA documents (Quality Assurance Manuals and SOPs). She will provide technical input on proposed sampling design, analytical methodologies, and data review. She is responsible for maintaining the official, approved QA Project Plan. Whenever possible, the project quality assurance (QA) manager must be independent of staff collecting samples and generating data.

The QAPP Approver, Sam Radford, at the Nebraska Department of Environmental Quality (NDEQ) will be responsible for reviewing and approving the QAPP, and coordinating any QA concerns with the QA/Project manager.

The Field Technician, Matt Marxsen, will serve as the driller and sampling crew involved in core collection and handling. He is responsible for reviewing and following sample methods, sample handling and custody procedures.

Project Specialists, Jordan Shields and Kobi Benao, will act as laboratory technicians and staff involved in the sample processing, analysis and data generation. Project Specialists are responsible for reviewing and following sample handling and custody procedures; analytical methods; quality control; instrument/equipment testing, inspection, and maintenance; and instrument/equipment calibration.

The QAPP Technical Reviewer, Joe Francis at NDEQ, will review the QAPP for adequacy and compliance with a technical and scientific perspective, and provide comments to the QAPP Approver and QA/Project Manager.

# A5. Problem Definition/Background

Vadose zone agrichemical monitoring is undertaken to evaluate the occurrence, mass, and transport or transformation rate(s) of specific contaminants introduced by surface activities having the potential to reach the water table. The vadose zone is defined here as the region of unsaturated sediments and soil beneath the crop root zone and above the local water table.

## Expected Decisions, Actions, or Outcomes

Nitrate and pesticides, in particular, are contaminants often measured in the vadose zone. Other contaminants and measurements commonly included in vadose zone monitoring are geogenic trace contaminants, such as arsenic and uranium; other forms of nitrogen such as ammonia; moisture content; sediment composition and texture; and properties that control permeability and water movement. Detailed textural descriptions are generally compared to measurements of nitrate-N, ammonia-N, pH, moisture and lithology at specific depths within a core profile. Pairing soil, chemical, and hydrological data creates valuable knowledge outcomes. All of these activities will be conducted to generate data of measurable quality to ensure the information collected meets the requirements for intended use.

Vadose zone agrichemical monitoring projects are generally designed to answer questions related to the occurrence and movement of nitrate-N and other agrichemicals below the crop root zone and above the water table. Questions will include: 1) How much nitrate-N and other potentially mobile contaminants are stored in the vadose zone at a specific location? 2) How rapidly are these contaminants moving and approximately when will they intercept the water table? 3) Are there any changes in concentrations with depth below the surface, and can these changes be associated with changing nitrogen loading and leaching below the root zone? 4) What are baseline concentration levels at this location? 5) Will concentrations of nitrate-N or other contaminant in the groundwater beneath this area increase, decrease or stay the same?

Decisions informed with this information include: 1) How will changes in land management (adoption of alternative fertilizer application methods, timing and rates change) affect nitrate/agrichemical leaching to the vadose zone and water table? 2) What are the consequences to groundwater if there are no changes in management practices at the surface?

INSERT PROJECT-SPECIFIC INFORMATION about why the client initiated this project, including location-specific information and background.

“The client needs to better understand…” “This study will provide a better understanding of…”

This task includes conducting an investigation of the vadose (unsaturated) zone of locations identified for characterization of nitrate and agrichemical contaminant occurrence and transport at the location. (**Figure 2**). Test holes will be drilled to collect and characterize soil types and physical properties, and chemical analysis will be conducted on selected core samples.

INSERT FIGURE

**Figure 2. Location Map with Borehole Sites Marked**

DELETE IF NOT PART OF PROJECT SCOPE. Stable isotope analysis of nitrate from either the vadose zone or wells in the area can be used to characterize nitrate sources and transport. Determination of water retention properties and hydraulic conductivity from undisturbed core samples helps estimate rate of travel of nitrate pulse to ground water. Repeated coring at specific locations permits correlation of nitrate concentration profiles and potentially provides in situ estimates of transport and attenuation rates. Calibration of vadose zone transport calculations at these locations can permit more accurate estimates of transport rates at new sites.

DELETE IF NOT PART OF PROJECT SCOPE. Finally, accurate assessment of the occurrence and potential leaching rates beneath specific land uses help land and water resource managers identify areas where the most effort will be placed on managing fertilizer application and irrigation practices. Standardized protocol for collecting and analyzing vadose zone cores will help provide comparable data between locations and over time help estimate nitrate occurrence and transport rates to the water table. This information will assist local and state government with management actions, including: regulatory compliance; planning, design, and construction of water treatment facilities for communities relying on groundwater for their water supply; and design, monitoring, and evaluation of best management practices to reduce nitrate and other chemical loading in the vadose zone.

## Site Background & Historical Context

INSERT PROJECT-SPECIFIC INFORMATION about geology, aquifer use, previous sampling, demographics, regulation, groundwater contamination, etc.

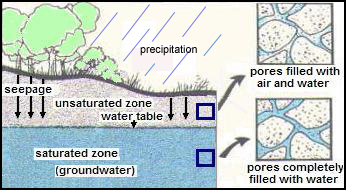
CONSIDER REPLACING THE FOLLOWING WITH PROJECT-SPECIFIC INFORMATION. Nonpoint source contamination of groundwater has been well documented for years, and nitrate-nitrogen (nitrate-N or NO3-N) is the most common contaminant affecting aquifers worldwide [1-3]. Nebraska has some of the most extensive groundwater quality records from across the county, and this rich dataset is a useful source of information on land use practices that lead to a reduction in groundwater nitrate-N concentrations.

Vadose zone monitoring has been conducted in many areas throughout Nebraska to help assess the changing amount of nitrate-N stored in the unsaturated zone, transport rates, and potential for impacting groundwater NO3N concentrations. The vadose zone is the portion of the geologic profile (Figure 3) beneath the earth’s surface and above the water table [4].

A primary reason for continued monitoring of this variably saturated and unsaturated region between the crop root zone and the water table is to assess whether and how changing nutrient and irrigation practices affect nitrate loading to the water table. Repeated sampling over several years can help estimate the rate of travel and predict when and where nitrate stored in the vadose zone will intercept the water table, as well as provide insight to general concentrations of that nitrate in groundwater when it reaches the water table.

Depending on the characteristics of sediments and locations, sampling the entire vadose zone in agricultural areas can be quite challenging due to weather conditions, depth to water, and the additional need to schedule sampling after harvest and before planting. Advanced planning will help ensure that the quality of data collected will meet the intended purposes.

**Figure 3: Diagram of the Vadose Zone (Source: NYSDEC)**



**Vadose Zone**

## Regulatory Information

To protect public health, the Environmental Protection Agency regulates certain contaminants, including nitrate, through the [National Primary Drinking Water Regulations](https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations). If contaminants are found in public water systems in excess of legally enforceable Maximum Contaminant Levels, a utility must either treat the water or find an alternate supply. Thus, natural resources managers, city planners, treatment plant operators, regulators, researchers, and others have an interest in monitoring the vadose zone to anticipate if and when contaminants will reach the groundwater supply, and in what amount.

Well installation must follow Nebraska Department of Health and Human Services guidelines. All boreholes will be decommissioned as a temporary well in accordance with Nebraska Title 178.

# A6. Project/Task Description

## Work Summary

Work activities are composed of several phase, including preparation and review of QAPP, reconnaissance, obtaining permission and land access, drilling/coring, sample processing and analysis, data reduction and plotting, interpretation and reporting.

Project work can be grouped by:

* *Field activities*: Conduct reconnaissance, identify and flag coring locations, drill and collect cores with a direct push or hollow stem auger-drilling rig, seal/abandon borehole, transport and store core sections, and document field work. Soil and sediment samples are generally collected within labelled clear plastic core liners.
* *Processing and analysis*: Process sediment, including, at a minimum, a detailed visual and textural description of the composition and color of intact core samples, quantitative determination of moisture content and bulk density (intact core), followed by air drying and measurement of a composite interval (up to 2.5 foot, variable based on what is seen during coring) for sediment pH, nitrate and ammonia-N by standard soil testing methods. Additional measurements will include herbicide concentrations, acid leachable elements (arsenic, selenium and uranium), stable isotopes of water and nitrate (for source discrimination and evidence of denitrification), chloride (loading rate), sediment particle size and soluble organic carbon (denitrification), as available or appropriate. Intact sediment cores will also be collected and tested for saturated and unsaturated hydraulic conductivity, as appropriate.
* *Data analysis*: Graph variation in concentrations, measurements and sediment properties versus depth for each core. Dry weight sediment concentrations of nitrate-N will be converted to a pore water equivalent using the gravimetric moisture content and also graphed versus depth for comparison to groundwater nitrate-N. Compare and correlate profiles and concentration maximums over time to estimate transport rates. Comparison of graphical profiles with sediment composition and texture will be useful in helping to explain changes in concentrations versus depth. Average all composite measurements and provide in tabular form. Bulk nitrate-nitrogen will be estimated using bulk density for each composite interval. Total bulk nitrate-N will also be used for evaluating spatial differences between locations and over time.
* *Products/reports*: Include graphs and tables of averages, any background information specific to the location, trends apparent in previous cores, land use information, fertilizer and irrigation water application rates, estimates of nitrate transport rates, and interpret results in the context for affecting local groundwater quality.

## Work Schedule

A targeted schedule for activities will include schedule for coring and sample collection, expected processing time for laboratory work and turnaround time for analytical results, followed by preparation of tables, graphs and reports. The schedule for work activities will conform to the schedule requirements in the funded proposal from Funding Agency, as well as two proposals for statewide work on vadose zone monitoring, funded by the Nebraska Environmental Trust (NET) and NDEQ. The Funding Agency proposal is included in **Attachment 1**. Changes to agree-upon milestones and due dates will be requested in writing by the Project Director (Dr. Dan Snow), and approved in writing by Program/Project Manager at Funding Agency.

Sample collection for the Location project is scheduled to occur on Date Range. If these dates do not work for any reason, Alternate Dates, will be used as alternate dates. Samples will be delivered to the WSL within 3 days of collection.

## Study Locations

INSERT PROJECT-SPECIFIC LOCATION DESCRIPTION. “The project will include vadose zone coring at # to # sites within the Location. The Location is shown in **Figure x** below.”

## Resources & Time Constraints

Work activities must be carried out within the scope of work, budget, and schedule constraints agreed-upon in the final funded proposal authorizing the collection of vadose zone data. The project-specific proposal/funding agreement is provided in **Attachment 1**. The timeline for the budgeted activities is one year.

# A7. Quality Objectives and Criteria

## Performance & Acceptance Criteria

Refer to **Attachment 2** for detailed methodologies of each test described below.

|  |  |  |
| --- | --- | --- |
| Activity/Test | Method Detection Limit | Acceptable Ranges |
| Soil Core Processing | A method detection limit is not applicable for this procedure. A method detection limit for nitrate and ammonia on the Lachat can be found on the Lachat SOP (13\_02\_02). Attachment 2.2 | Ranges are not applicable for this procedure. Acceptable ranges for nitrate and ammonia Lachat analysis can be found in the Lachat SOP. |
| Lachat QuikChem 8500 | Detection limits vary by analyte and are determined by the method’s specific instrument detection limit (IDL) (See specific Quikchem method Scope and Application section). A full list of method details have been published by Hach (Lachat Instruments, 2012). Attachment 2.3 | Ranges vary by analyte and are determined by the method’s specific instrument detection limit (IDL) (See specific Quikchem method Scope and Application section, Attachment 2.3). The method detection limits are reported at 0.005 mg/L for nitrate-N and 0.003 mg/L for ammonia in KCl extracts. Acceptable ranges are from 0.002 to 0.010 mg/L in KCl. |
| Microwave Assisted Acid Digestion for Elemental Analysis by ICP-MS | New Method [Detection Limit](https://en.wikipedia.org/wiki/Detection_limit)s (MDLs) will be derived for every run to account for variations in method. Attachment 2.5 | MDLs for determination of trace elements in soils and sediments by microwave digestion and ICP-MS range from 0.0002 to 0.002 µg/g. |
| Analysis of Dissolved Trace Elements in Aqueous Solutions by ICP-MS | New MDLs will be derived for every run to account for variations in method. Attachment 2.6 | Acceptable method detection limits for trace element analysis of aqueous samples range from 0.080 to 0.001 using ICP-MS μg/L. |

Analytical data quality objectives for environmental research projects define the confidence level required, and determine the level of reliability, precision, accuracy, detection limits, and validation methods. Although the level of reliability, precision, and accuracy required for most analyses varies according to the method and analyte, data quality is to be kept as high as practical on a day-to-day basis.

## Precision

Relative precision determined from the relative percent difference (RPD) from laboratory duplicates for measurements at concentrations above the method detection limit is generally within an acceptable range at ±20% or less.

## Bias, Representativeness & Completeness

Method bias is determined by analysis of laboratory control samples, performance evaluation samples, and analysis of reference materials by the same or similar methods. Bias is considered acceptable for most purposes if the measure value of the control sample is within 80-120% of the known, certified or previously reported value. Representativeness is the degree to which the measured data can be used to characterize a population or group of measurements, and is ensured by using standardized and validated methods as well as routinely checking for bias. Completeness is the number of measurements within the quality control limits or precision and bias and generally indicated as acceptable when 90% of all measurements are within tolerances.

## Comparability

Comparability the level of confidence that each set of data produced can be statistically compared to another by ensuring that all methods used are comparable, as well as bias and precision within stated tolerances.

## Method Sensitivity

Method sensitivity is demonstrated with a statistically determined instrument and method detection limit. Instrument detection limits (IDL) are specific to the device and the analyte and defined as the smallest signal above background noise that an instrument can detect reliably. Operationally, the IDL is equivalent to the lower limit of detection, and determined by repeated measurement of the lowest calibration standard generally at a concentration approximately five times the signal-noise-ratio, calculating the standard deviation of the replicate injections and multiplying by three. Method detection limits (MDL) are also determined statistically using matrices (water, soil, sediment, etc.) similar to actual samples fortified at 5-10 times the instrument detection limit. The calculation of the MDL is described in a later section.

# A8. Special Training/Certifications

All Field Staff conducting soil coring shall be trained on how to keep a field notebook. Field Staff and Project Specialists engaged in soil core processing will receive 3-4 full days training on the procedure. Any Project Specialists and Nebraska Water Sciences Laboratory staff/students performing laboratory analysis for the Vadose Zone program shall complete the Standardized Laboratory Training Plan (See **Attachment 3**).

Once basic training is complete, the trainee can then proceed with training on an analytical method. This will be followed by a proficiency test, where users will be tested by independently analyzing unknown laboratory-prepared samples. The results of these eight test samples will be used to demonstrate proficiency, documented in the WSL Laboratory Information Management System (LIMS), and reported to the supervisor.

It is expected that users will complete their proficiency tests within two months of their training, thereby showing competence on the instrument, before they are permitted to independently analyze their own samples at the WSL. If the user is unable to analyze their samples within two months of their proficiency test, they will have to perform another refresher proficiency test (at no extra cost) before analyzing their own samples. If the user fails this test, they will have the opportunity to repeat the training again, at the same price as before.

## Trained Personnel

The Field Staff and Project Specialists identified in the organizational chart in Figure 1 have all completed the Standardized Laboratory Training Plan. This includes Matt Marxsen, JordanShields, Kobi Benao. The project manager, Lacey Bodnar, is a certified Project Management Professional (PMP) by the Project Management Institute.

## Training Opportunities

The Nebraska Water Sciences Laboratory accepts new trainees into their Standardized Laboratory Training Plan on a rolling basis. New trainees will contact the Laboratory Manager, Dr. Tania Biswas at [sbiswas8@unl.edu](mailto:sbiswas8@unl.edu) or 402-472-8213 to schedule training.

## Responsibility

The WSL Manager, Dr. Tania Biswas, will oversee the Field Staff and Project Specialist training and ensure that all requirements are met.

## Documentation

Results of trainee proficiency tests and training records will be maintained on the WSL Network Drive. To request copies of the information, contact Dr. Biswas.

# A.9 Documentation and Records

## Report Format

The project final report, and any intermediate progress updates, will report on the scope of work as described in the funded proposal (see **Attachment 1**). The following general headings are suggested:

* Introduction
* Overview of Previous Work
* Statement of Current Objectives & Tasks
* Methodology, by project task
  + Field Sampling, Laboratory Analysis, Soil Particle Analysis, Pesticide Analysis, Acid Leachable, Isotope Analysis, Hydraulic Conductivity & Water Retention
* Results, by project task and analysis
  + Summary table of cores obtained, including water table depth and bulk density
  + Summary table of nitrate, ammonia, chloride, pesticides, stable isotopes, and groundwater ages per core; also includes:
    - Pore water content, Gravimetric moisture content for composited samples below the crop rooting zone, Particle size, Organic carbon content, pH
    - Selected samples with elevated nitrate levels will be measurement of 15N-NO3. 18O-NO3 will be analyzed on water extracts following the methods of Green et al 2008 with isotope analysis using conversion to silver nitrate (Chang et al 1999).
  + Uranium & arsenic results, where available
  + DOC: Leachable organic carbon
  + Soil water retention curves and saturated hydraulic conductivity for selected cores
  + Summary table of stable isotope characterization of nitrate
* Discussion
  + Include discussion of potential for denitrification of nitrate during transport. Discuss how this information can influence or client operation, such as groundwater pumping strategies.
* Conclusions
* References
* Appendix: Detailed Results by Core Sample Interval
  + Core Sample Depth, Bulk Density, Gravimetric Water Content, pH, Soil NH4-N (μg/g), Soil NO3-N (μg/g), Calculated Pore Water NO3-N (mg/L), Calculated Soil NO3-N (lbs-N/Acre-ft), Lithological Description

## Other Project Documents

Field activities, including drilling and core collection, will result in completed field notebooks.

Laboratory processing and analytical data records are stored in sample submittal forms, laboratory notebooks, batch sheets, and instrument reports.

Once the field and laboratory analysis is complete, the data will be included in the Nebraska Vadose Zone public dataset, available on the [Nebraska Vadose website](http://nebraskavadose.unl.edu/). To include soil core information in the dataset, the information must be standardized and entered into a pre-formatted Excel Workbook entitled "Vadose Zone New Sample Format." The workbook, as well as a data formatting tutorial, are available for download at the Nebraska Vadose website [Data Submission](http://nebraskavadose.unl.edu/datasubmission.asp) page.

Once the data is standardized in excel, it will be input into a MATLAB code. MATLAB then creates a unique excel file for each location. These location-specific excel files are what a user of the Nebraska Vadose website will have public access to download when clicking on a core location in the interactive map.

Excel is a useful tool for data processing, but it is not itself a database software. The actual Nebraska Vadose database exists as an Access database. Mark Mesarch, Web/Database Programmer at the University of Nebraska-Lincoln School of Natural Resources ([mmesarch1@unl.edu](mailto:mmesarch1@unl.edu)), maintains this database.

## Information Storage

Project information is stored on UNL Box, a University of Nebraska cloud storage system for 2.5 years. Box is a storage and collaboration service that gives faculty, staff and students the ability to access, store, and share an unlimited amount of content securely — anywhere, anytime, on any device.

## Records Back-Up

All data and records uploaded to Box are immediately backed-up. Box is a contractor of UNL, and is responsible for data protection. Box utilizes multiple servers at various data centers, to ensure that if one server spontaneously fails, client information will not be lost.

Cloud storage systems generally ­rely on hundreds of data servers. Because computers occasionally require maintenance or repair, it is important to store the same information on multiple machines. This is called redundancy. Without redundancy, a cloud storage system could not ensure clients that they could access their information at any given time. Most systems store the same data on [servers](https://computer.howstuffworks.com/web-server.htm) that use different [power supplies](https://computer.howstuffworks.com/power-supply.htm). That way, clients can access their data even if one power supply fails.

Results and supporting documentation will be held indefinitely at the Water Sciences Laboratory, although data older than five years may not be verifiable. Raw results are held in files, notebooks, and other standard forms. Electronic raw results and data are archived in cloud storage. Electronic records are secured through a digital signature. Laboratory staff are assigned unique names and each person choses an individual password. To log into laboratory computers, both the unique name and password are required.

The current proposal is seeking funding from NET and NDEQ to support a post-doctoral researcher to assess the quality of data from various sources and to conduct hydraulic property characterization of the soil cores as well as a database person to design and manage the database for 2.5 years. Active management of the data by the University of Nebraska will be contingent on continued funding. Prior to any funding lapse, the University will provide all relevant data to NDEQ for data retention/storage.

## Current QAPP & Responsibility

The vadose zone QAPP template, and any updated versions, will be emailed by the QA/Project Manager, Lacey Bodnar, to the individuals identified in Section A3. The original QAPP template, version 1, and all subsequent versions, will be saved to the Nebraska Vadose Box account. Versioning and file retention will be the responsibility of Lacey Bodnar.

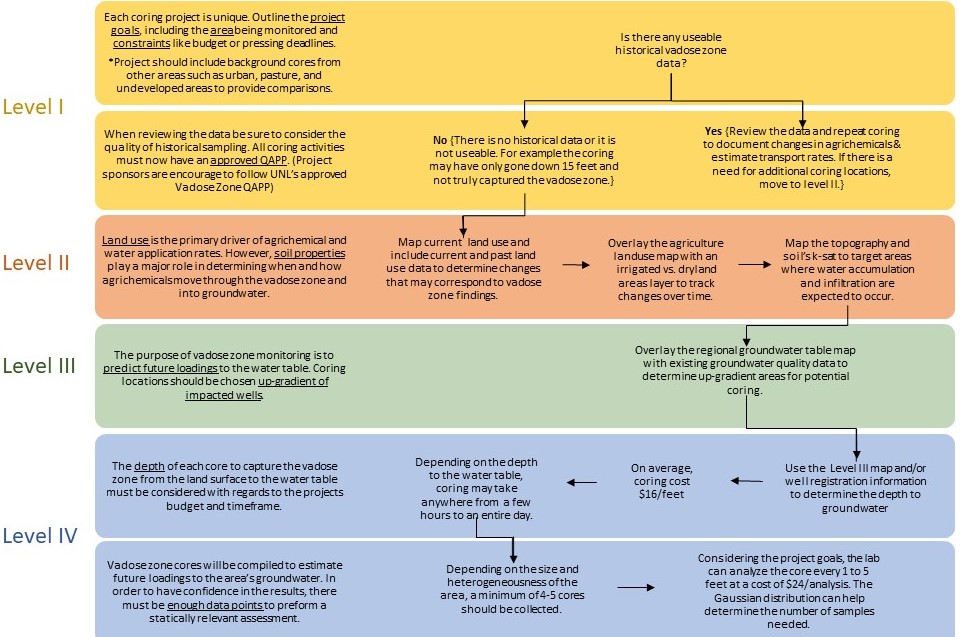
# B1. Sampling Process Design (Experimental Design)

Some general selection criteria can be used in determining the number and locations of deep vadose zone sampling between the root zone and local water table. Spatial variability of leached nitrate-N and other agrichemical in the deep vadose zone is controlled by the spatial variability of sediment framework, spatial and temporal variability of water and fertilizer applications, and variability of nutrient uptake by crops [5-7].

## Design Strategy

INSERT DESCRIPTION OF CRITERIA OR OBJECTIVES WHICH FORMED THE BASIS OF SELECTING SAMPLING SITES. “Sampling sites were selected based on…”.

As with surface soil sampling, collection and analysis of specific locations within a field can also bias results toward whatever processes are controlling residual nitrogen in the unsaturated zone. The following decision tree, shown below, details the high-level selection process used to determine the number and location of vadose zone cores to estimate loading at a field scale for Springfield wellhead protection area characterization of nitrate and other agrichemicals.



perform a

’

**Example decision tree for selection of coring sites to be used in vadose zone monitoring.**

*Level I – Historical Sampling*

If vadose zone samples have been previously collected from an area, and these locations are known to a reasonable level of accuracy (within ~500 feet), then repeated coring offers a way to estimate changes in nitrate-N occurrence and transport rates that can be extended to other areas in the vicinity.

*Level II – Land Use, Surface Soil Physical and Chemical Properties*

Because land use is the primary driver of fertilizer and agrichemical application, the selection process will include a spatial and temporal evaluation of current and previous land use. Irrigated and dryland crops have very different leaching rates. If the purpose of the monitoring is to evaluate the effect of changing irrigation practices, land use will be included in the decision process. Generally, nitrate-N and other agrichemical loading from the surface will follow water application rates (Exner et al 2014; Spalding et al 2001, Spalding et al 2003) and selection of core locations will be directed at areas where irrigation and runoff water would be expected to accumulate and infiltrate. A high-resolution topographic map, overlain with a soil properties map, will offer a reasonable guide for selecting a location based on soil physical and chemical properties as well as infiltration potential.

*Level III – Existing Groundwater Quality and Elevation Information*

Two vadose zone cores were previously collected for the Springfield Wellhead Protection Area. These cores are named “Cemetery Field” (41° 5'45.03"N, 96° 8'11.95"W) and “Bike Trail” (41° 5'59.83"N, 96° 8'11.66"W).

The purpose of vadose zone monitoring is to predict changes in agrichemical loading to the water table. If groundwater quality data is available for the area to be cored, then any spatial and temporal changes in groundwater nitrate/agrichemical concentrations from the area can be reviewed and used to select vadose zone sampling locations. If regional water levels are available, the vadose cores will be located up gradient of wells suspected to be impacted by chemical loading at the water table. This sampling design is similar to those used in point source vadose zone sampling of organic and inorganic contaminants (Nielsen and Johnson, 1991) and is likely valid for characterization of estimating loading within a small area of nonpoint sources.

*Level IV – Number and Frequency of Samples*

The expense of deep vadose zone monitoring, together with spatial and temporal variability of agrichemical loading and transport in the vadose zone likely prevents all-inclusive sampling for contaminant characterization. However, a few statistical tools may help provide justification for the number and frequency of deep coring. The quality and utility of environmental measurements, including vadose monitoring, depends on the validity of sampling design and collection[8]. Vadose zone core samples are typically heterogeneous. If the compositional profile or variability of the concentration is of interest, many samples are analyzed individually, graphed and averaged to determine the spatial variability and overall average concentration. Profiles of nitrate-N versus depth for example, can be compared between locations and over time to determine how much variability has occurred.

Data Review, Verification, and Validation: Criteria

Batch acceptance criteria will be determined for each matrix, analytical group, concentration level, and analyte, if applicable. The criteria will relate to the parameters of precision, accuracy/bias, representativeness, comparability, sensitivity (quantitation limits), and completeness. The parameters indicate the qualitative and quantitative degree of quality associated with measurement data. Reporting of all necessary data and statistics aids in understanding the implications of the results. Without the appropriate accompanying information, inaccurate or incorrect conclusions may be drawn from any set of results. A calibration curve will consist of a blank sample (matrix sample processed without internal standard), a zero sample (matrix sample processed with internal standard), and six to eight non-zero samples covering the expected range, including the Lower Limit of Quantitation (LLOQ). The simplest model that adequately describes the concentration-response relationship will be used. Selection of weighting and use of a complex regression equation will be justified. The following conditions will be met in developing a calibration curve: 1) 20% deviation of the LLOQ from normal concentration, 2) 15% deviation of standards other than LLOQ from nominal concentration, 3) at least four out of six non-zero standards will meet the above criteria, including the LLOQ and the calibration standard at the highest concentration.

Excluding the standards will not change the model used. The correlation coefficient will be no less than 0.99, unless otherwise stated by the validation/method development report. The source, age, storage conditions, and labeling of the standards will be clearly indicated by the specific analytical method. Evaluation of bias is obtained by comparison of the results with those of a known amount of standard reference material in an appropriate matrix. The minimum requirement for ensuring accuracy is one LFB sample per twenty unknowns, or at least 5% of the total samples. Ideally, accuracy will be measured using a minimum of five determinations per concentration, and a minimum of three concentrations in the range of expected concentrations is recommended. The lowest LFB will be approximately three times the LLOQ. The mean value will be within 15% of the actual value, except at LLOQ, where it will not deviate by more than 20%.

## Type & Number of Samples, Tests & Trials

A statistical method for determining the number of samples is possible when the distribution and standard deviation of the population is known or can be assumed to follow a Gaussian distribution[8]. This relationship:

can be used to calculate the required number of samples for a measured, or estimated standard deviation (σ), where Ns is the number of samples, (z) is the value of the normal standard variate based on the desired confidence level (*Students* “T”) and E is the tolerable error, in the form of a confidence level, in the estimate of the mean. The estimated vadose zone distribution can be predicted based on previous coring at that location or from concentration profiles in similar areas.

For example and assuming a Gaussian distribution, if our goal is to characterize 60% (@68% the confidence interval ~1=E) of the total mass of nitrate (or other agrichemicals) in a single core with expected concentrations ranging between 2 and 20 µg/g NO3N (average of 8 and standard deviation of 3 μg/g), then the number of samples to collect is N=((1.96\*3)/1)2 = 35 composite samples spread out over the entire interval. If the expected standard deviation of the concentration is lower, then fewer samples would be needed to characterize the range of concentrations and total mass present.

In practice, most vadose investigations collect and composite samples at fixed intervals (every 1 foot, 2.5’, or 5’) for cores ranging in length from 10 to 120 feet. Analyzing nitrate in every 2.5-foot interval of a 100’ core provides about 40 samples. While some studies composite every 1-foot of core, the improved precision on estimating a mean and delineating the concentration profiles may not be significantly improved. Compositing every 5-feet may be adequate where variability is low (standard deviation is less than 2 µg/g) but coarser sampling may result in missing important layers where nitrate or other contaminants may accumulate. Finally, it is a good idea to increase sampling frequency within a core profile where lithologies change as these zones tend to be where water movement, accumulation and chemical/microbial activities are higher.

Estimating the number of cores per location can also be justified through comparing the predicted “spread” = standard deviation of nitrate or other contaminant concentrations. If the expected variability is low, then the number of cores could be one per field. If variability is high, then more cores and samples would be needed to statistically characterize the mass and extent of contamination.

Finally, the monitoring will include sampling of background or baseline samples from areas where fertilizer and water use inputs are different so that statistical comparisons under different land use and application history can be made. Various land uses may include urban areas, pastures and undeveloped areas for comparison to row crops, and irrigated versus non-irrigated fields.

## Sampling Locations

The project will include vadose zone coring at # to # sites within the Location. The Location is shown in **Figure x** in section A.6.

## Location Accessibility

Most vadose zone monitoring requires access to private land and this access may or may not be granted by the landowner. After selection of ideal locations, landowner willingness to permit access must be used as the final criteria and may override other considerations. The Funding Agency will contact land owners and provide logistical support for sample collection. If a site is not accessible on a specific date or range of dates, such as due to inclement weather, sampling will be rescheduled to a different date. If a site becomes permanently inaccessible, the reason will be documented in the field/coring log, and sampling at that site will cease.

## Sampling Schedule

The sampling schedule will be establish by the Field Staff (refer to organizational hierarchy in Figure 1). Funding Agency will be responsible for coordinating with landowners, via phone or email, to schedule collection dates.

Sample collection for the \_\_\_\_\_\_\_\_\_\_ project will occur on {dates}. Samples will be delivered to the WSL within 3 days of collection.

## Critical Information

When initiating data collection, please refer to the “Vadose Zone New Sample Format” workbook to see the final format that data must take to be included in the Nebraska Vadose database. Workbook fields shaded gray‐blue are required; those that are light orange are optional. Please complete the optional columns if the data is available. While it may be necessary to leave some fields empty, the minimum information required for a core to be included the vadose database is: 1) collection date, 2) a core name, 3) location data, 4) depth of each sample, and 5) nitrate concentrations.

## Variability & Reconciliation

Variability in procedures may result from incomplete or inadequate training or communication. Any deviations from procedures will be documented and additional training provided to ensure conformity. Quality control nonconformity may indicate an analytical problem requiring corrective action. Laboratory corrective action occurs at several levels. The most common and efficient corrective action involves the action of the technician or analyst in charge of analyzing a batch of samples. In most analytical procedures, nonconformity may be signaled by significant deviations in instrument response, variability in replicate analyses of a standard or sample, atypical blank responses, or other unusual characteristics. The technician or analyst then may attempt to locate the cause of the nonconformity and effect correction prior to calibrating and running the samples. Results of QC samples may also signal nonconformity and can also trigger corrective action. Although variations in accuracy and precision reflected in QC samples are typically determined well after a batch of samples has been run, the analyst or technician may also note unusual responses for some blanks, replicates, or reference samples that may immediately be brought to the attention of the Laboratory Director for more immediate corrective action.

# B2. Sampling Methods

## Sampling Standard Operating Procedures (SOPs)

For sampling method SOPs, refer to **Attachment 2** (Field Vadose Zone Coring; version 07\_04\_02.001; by Jordan Shields). This method describes the coring techniques used to plan, obtain, label, document, and store cores for further analyses. This procedure is used when assisting the DPT and hollow stem auger-drilling operator.

For sample processing SOP, refer to **Attachment 2** (Soil Core Processing; version 07\_06\_02.002; by Jordan Shields). This method describes the process of sediment separation, homogenization and extraction for determining moisture content, bulk density, pH, as well as the preparation for ammonia and nitrate analysis.

## Sample Type Collection

These methods and procedures are specific to collection of representative samples for vadose zone monitoring projects, and generally apply to collection of deep (>10’) vadose sediment cores. These guidelines help to maintain sample integrity by preserving the physical form and chemical composition as close as possible to *in situ* conditions. Nebraska soils and unconsolidated vadose zone materials range from dense clay to nearly pure well-sorted sands of the Nebraska Sandhills region. Most soils are a mixture of several particle sizes and aeolian silt (loess) is very common in agricultural areas. Nearly all soil and vadose sediment types can be sampled with either a boring auger-type coring device or direct push tools.

Two cores will be taken every 5 feet. Two 2.5 foot plastic coring tubes are placed inside a 5 foot core barrel each time the drilling operator drills to a new depth. Once the sample is obtained, the core barrel is opened and the cores are removed. Each core is capped, labeled, and recorded in a field notebook before being stored in a labeled Styrofoam container. Cores are stored in a freezer to preserve field conditions (e.g., moisture content, Nitrogen, and VOC’s).

The information and data generated will be stored and evaluated with respect to location, sampling points will be documented for mapping and as to their exact location for purposes of future sampling. Sampling locations and result will be analyzed or modeled in GIS with other spatial data. Accurate sampling locations (NE State Plane Coordinates) will be determined in order to reference the data spatially. Global Positioning System (GPS) receivers will be used for recording sampling points.

All boreholes will be decommissioned as a temporary well in accordance with Nebraska Title 178.

## Instrument Deployment & Operation

Coring Preparation: Ensure that the two 2.5 foot plastic tubes are aligned with the top and bottom of the open steel core encasement once placed inside. Place top shell of the steel core encasement on top of the loaded bottom shell. To avoid cross threading, ensure the two shells are properly aligned with each other before using the pipe wrenches to assist in screwing on the rear steel cap. Screw on the core barrel head assembly and then the shoe after securing the core barrel in place with the pipe vice. 1. Note: An eggshell can be placed inside the front steel cap to prevent sample loss when drilling in sandy sediment.

Core Collection and Labeling: The core barrel will be placed on the core holding rack and secured by the pipe vice. Unscrew the head assembly and the shoe. Clean the thread of any debris with a wet brush. Lift and gently drop one end of the steel core encasement on the holding rack to open it. Note: if both tubes are not fully filled with sediment, inform the drilling operator so adjustments can be made. Insert sediment separator tool in-between the two cores to divide them. Carefully remove the cores and place a rubber tube cap on each side. Label every core with their respective site location found in the coring locations pdf file. If a site has more than one drilling location, add a “-#” to the end to denote the location (i.e., HC1-1, HC1-2, and HC1-3). Label the top cap and highest part of the tube with the depth the sample was taken at. Do the same with the bottom cap and the lowest part of the tube. Place the labeled core into a Styrofoam cooler labeled with the site location, date, and range of depths. Revert to coring preparation.

Hollow-Stem Auger Boring Procedures

Hollow stem auger sampling provides the greatest depth of penetration (up to 150 feet or more below the surface) and, generally offers the most complete method for collection of relatively undisturbed vadose zone cores. Split spoon sampling with a hollow stem auger permits collection of both shallow and deep subsurface soil samples up to 2.5” (or more) in diameter. Split spoon samplers are generally split cylindrical barrels that are threaded on each end. The leading end is held together with a beveled threaded collar that functions as a cutting shoe, and the other end is held together with a threaded collar that serves as the sub used to attach the spoon to the string of drill rod. A 60” continuous sediment core can easily be collected using a split-spoon outfitted with two 30” long by 2.25” O.D. plastic core liners. The spoon containing the liners is advanced inside and slightly ahead of the lead auger bit during hollow stem auger drilling. After the auger flight has been advanced into the sediment column a distance equal to the length of the sampler, it is returned to the surface, where the sampler is removed from inside the hollow stem auger and the threaded collars are removed. The split spoon is then opened for removal of the core samples (**Figure 6**). Plastic liners are labeled to include site name, depth intervals, and orientation (up), capped and then transferred to large coolers for transport and storage.



**Figure 6. Continuous split spoon sampler opened to show the 2.25” O.D. clear acrylic liners containing vadose zone core samples. Orange caps are easily attached to each end of the two 30" core sections recovered from the 5-foot split spoon sampling barrel.**

Direct Push Sampling Procedures

Direct push soil sampling methods are appropriate for collection of shallow and deep subsurface soil samples. It is ideal for shallow (<50’) vadose zone sampling as it has a rapid penetration rate at these depths and low probability of refusal in unconsolidated sediments. Sites that require deeper (>50’) sampling are less desirable for direct push sampling as the penetration rates can be much slower and cost comparable to use of auger rigs. Cores may be smaller diameter (1-1.5”) which may preclude collection of samples for intact (undisturbed) sediment properties such as hydraulic conductivity. Several methods are available for use with either a Geoprobe® or other direct push device outfitted with a hydraulic hammer. All core collection methods are similar to coring with split spoon sampler and involve retrieval of the cores within a thin-walled plastic liner. The following sections describe each of the specific sampling methods that can be accomplished using direct push techniques, along with details specific to each method.

## Instrument Averaging & Storage

Not Applicable – No continuous monitoring will occur.

## Sample Homogenization, Composition, Splitting or Filtering

Soil core processing is a method used to prepare a soil core subsample for instrumental analysis, and includes sediment separation, homogenization and extraction. Prior to chemical analysis of ammonia and nitrate, soil cores must be thawed, divided into smaller subsamples, homogenized and extracted with a 1M potassium chloride solution. Thawed and air-dried samples will be ground and sieved within 24 hours of thawing. After this process is complete, the core subsample will be represented as a liquid, 100 mL potassium chloride solution. Extraction of mineral and exchangeable nitrogen (ammonia and nitrate) requires a KCl salt solution rather than water because the strong activity of the cation in the salt solution will exchange adsorbed NH4+ chloride anion which can help displace weakly exchangeable NO3- on positive adsorption sites.

## Sample Preservation

Collected cores in the field will be capped on both ends and immediately placed in Styrofoam coolers while in the field. Coolers will be transferred to a freezer as soon as possible once returned from the field, to preserve field conditions.

Following soil core processing, the KCl extract will be preserved with 5 drops of sulfuric acid per 100 mL. If the sample will not be run on the Lachat the same day, the sample must be frozen.

## Equipment Cleaning & Decontamination

When collecting cores, use clean liners and caps to prevent cross contamination. Before core collection, clean the core barrel thread of any debris with a wet brush.

When processing soil cores for NO3/NH4 & pH, to minimize cross contamination, clean out the mill between samples by removing all soil particles using a flat-head screwdriver, brushes and the shop vacuum located in the soil lab. The Dispensette® will be cleaned at the end of each day it is used as the KCl dries and degrades the pump over time. To clean the pump, remove it from the container of KCl and pump at least 200 mL of DDI water through it. Make sure that all of the water is out of the pump before placing it back onto the container of KCl.

When finished processing soil cores for pH, clean the electrode thoroughly, using care to remove any sediment from the reference junction, put the cap back on and soak in electrode soaking solution.

## Corrective Action & Responsibility

Perched water tables can interfere with perceived aquifer depths. If unusually shallow saturated sediments are recovered in the core barrel, the Field Staff will drill 5 more feet and attempt to push through the perched table. If sediments are still saturated, reassess the situation. If refusal occurs, the field staff will mark the depth of refusal and discontinue drilling operations.

# B3. Sample Handling and Custody

## Maximum Holding Times

Core samples may be held at room temperature for several hours but will be transferred to frozen storage within 24 hours of collection. Holding times are calculated from the collection and preparation dates. Field samples are typically stored until results are verified and reported and may be held for four weeks after the results have been released and delivered to ensure that reanalysis will not be required. Results for samples prepared and analyzed after the maximum holding times have expired will be flagged.

## Handling, Transportation & Retrieval

Collected cores in the field will be capped on both ends and immediately placed in Styrofoam coolers while in the field. Coolers will be transferred to a freezer in the Filley Hall as soon as possible once returned from the field, to preserve field conditions. Freezing will slow microbial conversions of nitrogen, but depending on the containers used, can lead to contamination from atmospheric sources. Sealed plastic core liners are essentially impermeable to ammonia and freezing in sealed liners is currently the best available method for vadose zone cores. Holding times will vary depending on the soil type, but frozen core samples may be held for several months and will be processed within 3-6 months of collection for nitrate, ammonia, pH and moisture content. Sediment samples for acid leachable metal are generally quite stable and can be held frozen for 12 months or more. Pesticides are the most perishable parameters and will be held frozen and analyzed within 3 months of collection.

## Handling & Custody Documentation

The Field Staff (see organizational chart in Figure 1) is responsible for documenting relevant site information in a field notebook. The Field Staff is responsible for transporting the sample in a cooler to the WSL. Sealed core intervals and samples will be delivered within 48 hours of collection and held chilled or frozen prior to delivery. While deep freezing is the accepted practice for long-term storage of soil and sediment samples, multiple freeze-thaw cycles has been shown to alter inorganic nitrogen concentrations in soils [10-12]. The Field Staff will hand-off the samples to the WSL Laboratory Manager or a Project Specialist. The Project Specialist performing the laboratory analysis assumes responsibility for proper handling of the samples.

## Sample Identification

During core collection, label every core with their respective site location found in the coring locations pdf file. If a site has more than one drilling location, add a “-#” to the end to denote the location (i.e., HC1-1, HC1-2, and HC1-3). Label the top cap and highest part of the tube with the depth the sample was collected. Do the same with the bottom cap and the lowest part of the tube. Place the labeled core into a Styrofoam cooler labeled with the site location, date, and range of depths.

During core extrusion, ensure the beaker is labeled to properly identify which sample it contains. When processing soil cores for NO3/NH4 & pH, after weighing out 30 mg, put the remaining ground soil in a Ziploc bag, labeled with the date and soil sample I.D. and store in the freezer. After filtering the samples into clean Erlenmeyer vacuum flasks, transfer the filtrate into a clean, labeled, 125 mL polyethylene bottle, acidify with 5 drops of sulfuric acid, and store in the freezer. Samples may be stored for 2-3 months. Labels on the bottle will include project name, core number, foot interval and date.

## Chain-of-Custody Procedures

If chain of custody procedures are a project requirement, proper forms shall be filled out and remain with the samples until custody is relinquished to the analytical laboratory.

# B4. Analytical Methods

The table below summarizes the laboratory measurements and references the method generally followed for each method. Example standard operating procedures for each parameter are included in **Attachment 2**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Parameter | Units | Typical Sample size | Detection Limit | Expected range | Method Reference |
| Textural description | NA | Core section | NA | NA | Attachment 2.1: Soil Core Processing  WSL SOP07\_06\_02.002 |
| Gravimetric water content | gm/gm solid | 100 grams | 0.005 | 0-0.35 | Attachment 2.1: Soil Core Processing |
| Bulk Density | gm/cm3 | 50-70 cm3 | NA | 1-3.0 | Attachment 2.1: Soil Core Processing |
| Soil pH | pH | 5 grams | NA | 5-8 | Attachment 2.1: Soil Core Processing |
| Soil NO3N and NH4N | µg/g | 10 grams | 0.005 | 0.0-100 | Attachment 2.3: Lachat QuikChem 8500  WSL SOP13\_02\_02\_001 |
| Acid leachable metals | ng/g | 10 grams | 0.05 to 0.1 | 0.0-500 | Attachment 2.3: Lachat QuikChem 8500 |
| Herbicides | ng/g | 10 grams | 0.05 to 0.1 | 0.0-10 | Attachment 2.7: Analysis of herbicides in solid samples by MASE and GC/MS  WSL SOP06\_01\_02 |
| Particle size (sand/silt/clay) | (%) | 15 grams | NA | 0-100 | Attachment 2.8 Soil Particle Size Analysis |

## Analytical Standard Operating Procedures (SOPs)

|  |  |  |
| --- | --- | --- |
| Analytical Method | SOP by Numbers | Dates Active |
| Plan, obtain, label, document, and store cores for further analyses | 1: Field Soil Coring |  |
| Prepare a soil core subsample for instrumental analysis | 2: Soil Core Processing | 7/10/2018 – present |
| Core Extrusion | 2: Soil Core Processing | 7/10/2018 – present |
| NO3/NH4 & PH Processing | 2: Soil Core Processing | 7/10/2018 – present |
| PH | 2: Soil Core Processing | 7/10/2018 – present |
| Flow injection analysis | 3: Lachat QuikChem 8500 |  |
| Particle size analysis | 4: Particle Fractionation and Particle-Size Analysis | 3/15/2018 – present |
| Inductively coupled plasma-mass spectrometry (ICP-MS) for analysis of element concentration | 5: Microwave Assisted Acid Digestion for Elemental Analysis by ICP-MS | 3/2/2018 – present |
| Inductively coupled plasma-mass spectrometry (ICP-MS) for elemental analysis | 6: Analysis of Dissolved Trace Elements in Aqueous Solutions by ICP-MS | 3/14/2018 – present |
| Microwave-assisted solvent extraction (MASE) and gas chromatography mass spectrometry (GC/MS) for analysis of herbicides in solid samples (i.e. soils, manure, etc) | 7: Analysis of herbicides in solid samples by MASE and GC/MS | 02/2017 – present |
| Soil texture analysis | 8: Soil Particle Size Analysis |  |

## Analytical Equipment & Instrumentation

|  |  |
| --- | --- |
| SOP | Equipment and Materials |
| 1: Field Soil Coring | * Computer with google earth or GIS * 2.5 foot plastic tubes * Rubber tube caps * Styrofoam coolers * Water resistant field notebook * Work gloves * Thick sharpies * Tools and supplies provided by drilling operator: * Drill Rig * Hollow-stem augers * Core barrels * Water level indicator * Egg shell stoppers * Core holding rack * Pipe vice * Pipe wrenches * Sediment separator * Brushes * Water bucket * Bentonite bore-hole plug * GPS unit |
| 2: Soil Core Processing | * Aluminum Foil * Knife * Beakers, 250 mL * Top Loader Scale * Drying Oven * Liter Carboy * Graduated Cylinder * Thomas-Wiley Mill * Whirl-Pak Bags * Erlenmeyer Flasks, 250 mL * Wrist-Action Shaker * Buchner Filters * Whatman #42 filter paper, 7cm * Erlenmeyer Vacuum Flasks * Polyethylene Bottles, 150 mL * Pipette * pH Electrode * EC Electrode * Reagent Grade 1 N KCl * DDI Water * pH Buffer Solutions of pH= 4.00 and pH=7.00 * Potassium Chloride (7447-40-7) * Sulfuric Acid (7664-93-9) |
| 3: Lachat QuikChem 8500 | * Cetac ASX-520 Autosampler * Reagent Pump * System Unit * Windows compatible computer with Omnion FIA software (Seibold, 2010) |
| 4: Particle Fractionation and Particle-Size Analysis | * Siphon * Suction filtration apparatus * Sieve, 47, 300-mesh phosphor bronze wire cloth, 0.0015-in wire, in a 5-inch or 8-inch frame * Pipette sampling apparatus * Brass plunger * Sedimentation cabinet or constant-temperature room. * Shaker, horizontal reciprocating type, 2 ½-inch stroke, 120 strokes per minute. * Sieve shaker, ½-inch vertical and lateral movements, 500 strokes per minute, with automatic timer. * Sieves, set of 6, 3-inch diameter frame, with cover and pan * Hydrogen peroxide, 30% (H2O2) * Calgon (Water softener product) |
| 5: Microwave Assisted Acid Digestion for Elemental Analysis by ICP-MS | * MARS Xpress Microwave 4.1.2. MARS Xpress 50 mL Teflon Vessels and Caps * MARS Xpress Vessel Vent Plugs * MARS Xpress Manual Torque Wrench * Distilled De-Ionized (DDI) Water * 50 mL centrifuge tubes * Nitric Acid (HNO3) (7697-037-2) * Hydrochloric Acid (HCl) (7647-01-0) * Hydrogen Peroxide (7722-84-1) |
| 6: Analysis of Dissolved Trace Elements in Aqueous Solutions by ICP-MS | * 50 mL Centrifuge Tubes * Pipettes (varying sizes) * Autosampler Tubes (14 mL 16mm x 100mm) #SP5178B * Nitric Acid (HNO3) (7697-37-2) * Hydrochloric Acid (HCl) (7647-01-0) * Thermo Scientific™ iCAP™ RQ Inductively coupled plasma mass spectrometer (ICP-MS) * CETAC ASX-560 Autosampler |
| 7: Analysis of herbicides in solid samples by MASE and GC/MS | Consumables   * Disposable filter device, 25 mm 0.2 μm PTFE GD/X filter (Cat 6874-2502) * Laboratory gloves * Kimwipe tissues * Auto-sampler vials with crimp cap (National Scientific #C4012-1 & C4011-1A or equivalent) * Conical vial inserts with spring-type bottom (National Scientific #C4010-S630 or equivalent) * Disposable Pasteur pipette, 225 mm (Fisher Scientific, 13-678-20D) * Disposable glass culture tube, 10 x 75mm (Fisher Scientific, 14-961-25) * Disposable glass culture tube, 15 x 85mm (Fisher Scientific, 14-961-28) * Compressed nitrogen gas * Sodium sulfate (Anhydrous, Fisher Scientific) * Disposable liners for Visiprep DL (Supelco, 57059)   Equipment   * Rapid Vap (LabConco) * Rapid Vap tubes, 120 mL (LabConco) * Centrifuge (Beckman Cp) * 10cc plastic syringes. * Microwave extraction Teflon vessels, 10 ml (CEM Microwave Technology) * Microwave solvent extraction apparatus, MARS-Xpress system (CEM Microwave Technology) * Top-loading analytical balance, precision to 1x10-2 g (Mettler PJ360 or equivalent) * Stainless steel spatula * Adjustable micro-pipettes with reference tips, 10 mL and 100 μL (Eppendorf) * Plastic syringe, 20cc (Norm-Ject all-polypropylene design) * Vortex mixer * Vacuum elution manifold (Supelco Visiprep, or equivalent) with drying attachment   Reagent Solutions   * Methanol (Optima, Fisher Scientific) * Acetonitrile (Optima, Fisher Scientific) * Ethyl acetate (Optima, Fisher Scientific) * Distilled deionized water (DDW)   For required standard solutions, see Attachment 2. |
| 8: Soil Particle Size Analysis | * 50mL centrifuge tubes * 3% by weight solution of Sodium Hexametaphosphate (HMP) * 600-800mL beakers * Soil splitter * Aluminum weighing tins * Wrist action shaker * Oven * 53 micron (#270) sieve * Squirt bottle with DI water * Burette stand with a clamp * Plastic funnel * Soil Textural Class Triangle Hydrogen Peroxide (7722-84-1) |
|  |  |

## Method Performance Criteria

Method performance criteria are described in Section A7.

## Corrective Action & Responsibility

Corrective action is first the responsibility of the technician or analyst performing the measurement. In most analytical procedures, nonconformity may be signaled by significant deviations in instrument response, variability in replicate analyses of a standard or sample, atypical blank responses, or other unusual characteristics. The technician or analyst then may attempt to locate the cause of the nonconformity and effect correction prior to calibrating and running the samples. Results of QC samples may also signal nonconformity and can also trigger corrective action. Although variations in accuracy and precision reflected in QC samples are typically determined well after a batch of samples has been run, the analyst or technician may also note unusual responses for some blanks, replicates, or reference samples that may immediately be brought to the attention of the Laboratory Manager and/or Director for corrective action related to repairs or maintenance.

## Sample Disposal Procedures

Samples are disposed only after results have been released and evaluated by data users. Clients have up to 90 days after receiving data to request reanalysis. Additional time can be provided as a nominal fee.

## Turnaround Times

Turnaround times for most methods are listed on the laboratory website. For client projects, the turnaround required for progress reports and final reports is specified in the contract with the laboratory or university.

## Method Validation & SOPs for Nonstandard Methods

Method development and validation generally requires three steps: 1) Determination of the Method Detection Limit (MDL), 2) Determination of the Recovery by analyzing independently prepared unknown samples and 3) A Holding Time Study. Depending on the constituent or characteristic of interest, the matrix, or the necessary instrumentation, other tests and analyses may be needed. This document does not give guidelines about how to develop the actual steps of the method, but how to validate a method once it has been developed. Methods developed at the Water Sciences Laboratory need to be both robust and accurate. Following this general method validation procedure will assist in ensuring that new methods meet the rigorous standards required at the WSL. The actual steps in the method will be determined by the analyst, and are usually based on previous experience, other similar methods, and peer-reviewed scientific papers. The steps required for method and instrument detection limits are described in the following section.

# B5. Quality Control (QC)

Quality control (QC) includes all procedures followed to ensure the accuracy of the data generated are known to a stated degree of probability. QC encompasses instrument calibration, personnel training, and use of pure reagents and certified standards. QC checks (samples) are used to monitor the performance of the analytical system. All QC samples, whether laboratory or field, are logged into the WSLims database and assigned a unique laboratory ID number and laboratory batch number. Thus, during processing and analysis, QC samples are indistinguishable from other samples.

In general, laboratory policies emphasize the prevention of problems rather than detection and correction of problems after they occur. The laboratory shall use published standardized methods and provide written procedures, including basic QA/QC requirements, to staff for all routine methods and activities influencing data quality. New methods will be verified using suitable test samples or reference materials, and compared to previous validated methods if possible. The laboratory shall retain copies of all supporting documentation, including analytical results, for a period specified by each project. If necessary, results are held indefinitely to verify the actions taken for each sample analyzed at the facility. A comprehensive calibration and maintenance program optimizes instrument performance and data quality. Reagents and supplies shall be of appropriate grade for the procedure, and gravimetric and volumetric apparatus shall be of a suitable class and calibrated as necessary.

Analytical data quality objectives (DQO) for environmental research projects typically define the confidence level required, and determine the level of reliability, precision, accuracy, detection limits, and validation methods. Although the level of reliability, precision, and accuracy required for most analyses varies according to the method and analyte, data quality is to be kept as high as practical on a day-to-day basis.

## QC by Sampling, Analysis & Measurement Technique

Data review and validation may be performed by both a supervising chemist and Laboratory Director and includes calculation of quality control statistics (range and recovery). Data review includes a check of calibration data for linearity, slope and intercept, QC results, completeness of supporting documentation and results, and determination if results are ready for release in the form of a final report. If concentrations are not already in standard units, results are converted to mg/L or µg/L for liquid samples, µg/g or ng/g for solid samples, and µL/L or nL/L for gaseous samples, with method sensitivity determining the appropriate range. Results falling below the most recent reporting limits are converted to “<reporting limit” unless the project or individual requesting the analyses specifies uncensored results. A disclaimer is added to uncensored results indicating that concentrations below reporting limits are indeterminate and cannot be verified.

Checks for laboratory quality control include the following in all routine standard analyses:

Table 9.1: Laboratory Quality Controls

|  |  |  |
| --- | --- | --- |
| Description | Abbreviation | Frequency |
| Laboratory Regent Blank | LRB | at least 5% |
| Laboratory Fortified Blank | LFB | at least 5% |
| Laboratory Duplicate | LD | at least 5% |
| Laboratory Fortified Matrix | LFM | up to 5% |

For trace-level analysis, the following additional checks may be added:

Table 9.2: Additional Checks

|  |  |
| --- | --- |
| Description | Frequency |
| Internal standards | every sample |
| Surrogates | every sample |
| Reference/Certified standard | as available |
| Instrument replicates | at least 5% |
| Batch replicates | at least 5% |
| Solvent replicates | at least 5% |
| Spike check | at least 5% |
| Performance evaluation | as available |

Depending on the project, the Water Sciences Laboratory also analyzes and evaluates field QC samples, including:

Table 9.3: Field QC Samples

|  |  |  |
| --- | --- | --- |
| Description | Abbreviation | Frequency |
| Field Duplicate samples | FD1 | at least 5% |
| Field Reagent Blanks | FRB | at least 5% |
| External Laboratory Duplicates | FDX | up to 5% |
| Field Equipment Blanks | FEQ | up to 5% |

Most analysis involve the generation of multilevel or multi-standard calibration curves immediately prior to sample analysis. The number of calibration levels range from two to ten-point, depending on the protocol, with a higher number of levels used in more critical trace-level analytical work. Samples with analyte concentrations above the calibration curve are normally rerun after adjusting either the sample concentration or the calibration range to produce a response falling within the calibration range. Calibrations are often checked using an externally prepared reference sample or certified standard.

## QC Effectiveness & Documentation

Quality control results falling outside control limits are immediately subjected to corrective action as discussed in the previous section. If corrective action does not resolve the nonconformity, and the source of a problem cannot be identified, the results for the affected sample batch are reported with a footnote describing the quality control issue. If the source of the problem can be identified, but cannot be corrected, the results may be discarded and the sampler or other responsible party will be contacted to determine whether re-sampling or other alternatives can be arranged in order to provide valid results. Issues that affect data quality are included in the cover letter or narrative that is produced with the sample results.

## QC Statistics

Analytical precision and accuracy are monitored through the use of Shewhart statistical parameters (I, R, and P) and quality control charts. Control charts are usually generated to visually monitor duplicate ranges (R), spike recovery (P), and matrix-spike recovery (P).

Upper control limits (UCL) for the range (R) of duplicate analyses is determined by:

“R” values for duplicate analyses are generally calculated, tabulated, and graphed using WSLims or spread-sheet software (Excel, Microsoft Corporation).

Accuracy is monitored using perfect recovery (P) in fortified blanks (LFB; equation 2.4) and matrix spike (LFM; equation 2.5) samples, and may be checked using standard reference materials (SRM) and performance evaluation (PE) samples.

Upper (equation 2.6) and lower control (equation 2.7) limits for recovery are determined by:

Qualitative identification and confirmation of contaminants, or absence thereof, is done by comparison of the results with those of a known amount of standard reference material or by comparison to a second well-characterized method. For assay and impurity tests, specificity is demonstrated by the resolution of the two closest eluting compounds. If impurities are available, it must be demonstrated that the assay is unaffected by the presence of spiked materials (impurities and/or excipients). If impurities are not available, the test results are compared to a second well-characterized procedure. This is further described in the specific analyte SOP.

Method Detection Limit (MDL)

A method detection limit (MDL) is defined as the minimum concentration that can be measured with a 99% confidence that the concentration is greater than zero. MDLs are determined for all routine analytical methods from analysis of a prepared test sample in a matrix similar to typical unknown samples. The procedure used is taken directly from EPA Federal Register (1989) Pt. 136 Appendix B, Definition and procedure for the determination of the method detection limit – Rev. 1.11. All new or revised methods are subjected to MDL tests before use on unknown samples. MDLs for trace-level analyses are repeated annually, or more frequently if necessary, to confirm sensitivity. Reporting limits, or Quantitation Limits (QL), are typically set at 3 to 5 times the concentrations obtained from method detection limit tests to compensate for additional uncertainty when handling unknown samples.

# B6. Instrument/Equipment Testing, Inspection, and Maintenance

## Equipment Maintenance & Schedule

Calibration runs and instrumental maintenance are documented in bound instrument notebooks or through electronic instrument logs. The instrument notebook or operation logs contain all pertinent instrument identification information on the first page, including manufacturer, model and serial numbers, UNLID university property ID numbers, installation date, warranty information, room and building numbers, and any other relevant information. Calibration record entries include the date and time, the sample batch, instrument identification and location, calibration procedure used, the instrument operator and the results of the calibration.

All maintenance work, whether preventative or unscheduled, is documented in the instrument notebook. Maintenance record entries include the date and time, symptoms, maintenance or repair details, date repair completed, parts replaced, name or initials of the person who performed the work, and any other relevant information. The current instrument notebook is to remain stationed with the appropriate instrument for continuous reference and updating. Troubleshooting and repair procedures are performed with an instrument malfunctions. Diagnostic procedures are usually found in the instrument manual, notebook, or may be obtained from the instrument manufacturer. All repairs and maintenance are performed by trained and qualified personnel from the instrument manufacturer, university instrument shops, or the Water Sciences Laboratory.

## Testing Criteria, Spare Parts, Inspecting Equipment Before Usage, Responsibility

All instrument usage in the Water Sciences Laboratory is scheduled through a website service called QReserve. Users are able to reserve usage of a piece of equipment during a specified day and time of their choosing. All students, staff, and faculty using the lab must reserve all of their Instrument usage on QReserve. Monthly maintenance for laboratory instruments and housekeeping occurs throughout the month, and laboratory users may be assigned particular

Maintenance tasks. Students and staff will sign and date each task as it is completed on the checklist located on the bulletin board outside Room 204. Consumables and spare parts are stored in the same area as the equipment used or where sample processing occurs. Each WSL staff member is responsible for maintaining specific equipment housed in their area, and the Laboratory Manager is responsible for ensuring that all users are properly trained and follow expected scheduling and reporting.

## Corrective Action & Responsibility

Each user (staff, student or researcher) is responsible for reporting any problems in daily use of equipment to the Laboratory Manager, who then is responsible for scheduling troubleshooting, additional maintenance and/or repairs.

# B7. Instrument/Equipment Calibration and Frequency

## Equipment, Tools & Instruments to Calibrate

Top loading and analytical balances are used for weighing samples, reagents and standards. All balances are checked and serviced annually by a certified balance repair company. Users who are trained in use of each balance check analytical and electronic balances with standard calibration weights. This shall be done at two levels in the range for which the balance is used, typically with 1 and 50 g weights.

## Calibration Procedures & Criteria

Specific calibration procedures for each method is detailed in the respective standard operating procedure. Balance checks and criteria are detailed in the Balances SOP and use the following table for tolerances:

|  |  |  |  |
| --- | --- | --- | --- |
| Balance Sensitivity | 10 mg Limit (± g) | 1 g Limit (± g) | 50 g Limit (± g) |
| 0.1 | - | 0.1 | 0.1 |
| 0.01 | - | 0.02 | 0.02 |
| 0.001 | - | 0.002 | 0.002 |
| 0.0001 | 0.0003 | 0.0003 | 0.0005 |
| 0.00001 | 0.00009 | 0.00009 | - |

pH measurement: Using buffers pH= 4.00 and pH=7.00, calibrate the pH meter before use. Check the calibration buffer every 20 samples.

Lachat QuickChem 8500: Calibrate with standards that bracket the sample concentrations. Review each calibration. Select Calibration Results icon. View graph and r for each analyte. Correlation coefficient will be greater than or equal to 0.990. Delete one or all calibration levels, if necessary. Recalibrate one or all levels, if necessary. Confirm calibration with accuracy and precision controls. Check calibration curve for drift, accuracy and precision with standards and controls every 20 samples.

Microwave Assisted Acid Digestion for Elemental Analysis by ICP-MS Standard Solutions: For metal analysis, blanks and calibration standards will be prepared with 0.5% HNO3 (v/v) in DDI water. For some other samples, DDI water is used instead. Refer to training for specific elements (like anions). Blanks: Two types of blanks are required for analysis. The calibration blank is used in establishing the calibration curve. The rinse blank is used to flush the system between samples and standards. The calibration blank ought to consist of the same stock of 0.5% HNO3 or DDI water used to prepare the final dilutions of the calibration standard solutions. This 50 mL centrifuge tube will be kept as full as possible throughout the standard preparation process to ensure the process is as uniform as possible. The rinse blank consists of either DDI water or 0.5% HNO3 (v/v) in DDI water. There must be a sufficient quantity to flush the system between standards and samples.

Fresh multi-element calibration standards will be prepared every two weeks or as needed. Dilute each of the stock multi-element standard solutions to levels appropriate to the operating range of the instrument using the calibration blank, which is composed of either 0.5% HNO3 or in DDI water. Calibration standards will be prepared at a minimum of 3 concentration levels. All calibration standards, including the calibration blank, ought to be treated with the same protocol as the samples in order to maintain the same matrix.

Analysis of Dissolved Trace Elements in Aqueous Solutions by ICP-MS Standard Solutions:

For metal analysis, blanks and calibration standards will be prepared with 0.5% HNO3 (v/v) in DDI water. For some other samples, DDI water is used instead. Refer to training for specific elements (like anions). Blanks: Two types of blanks are required for analysis. The calibration blank is used in establishing the calibration curve. The rinse blank is used to flush the system between samples and standards. The calibration blank consists of the same stock of 0.5% HNO3 or DDI water used to prepare the final dilutions of the calibration standard solutions. This 50 mL centrifuge tube will be kept as full as possible throughout the standard preparation process to ensure the process is as uniform as possible. The rinse blank consists of either DDI water or 0.5% HNO3 (v/v) in DDI water. There must be a sufficient quantity to flush the system between standards and samples. Fresh multi-element calibration standards will be prepared every two weeks or as needed. Dilute each of the stock multi-element standard solutions to levels appropriate to the operating range of the instrument using the calibration blank, which is composed of either 0.5% HNO3 or in DDI water. Calibration standards will be prepared at a minimum of 3 concentration levels.

## Corrective Action & Documentation

Corrective action occurs during the measurement process, preliminary data review and reduction. Documentation includes noting the issues that occurred during operation of the instrument and what steps were required to correct the problem.

# B8. Inspection/Acceptance for Supplies and Consumables

## Critical Supplies & Consumables

WSL policies emphasize the prevention of problems rather than detection and correction of problems after they occur. The WSL shall use published standardized methods and provide written procedures, including basic QA/QC requirements, to staff for all routine methods and activities influencing data quality. New methods will be validated using suitable test samples or reference materials, and compared to previous validated methods if possible. The WSL shall retain copies of all supporting documentation, including analytical results, for a time period specified by each project. If necessary, results are held indefinitely to verify the actions taken for each sample analyzed at the facility. A comprehensive calibration and maintenance program optimizes instrument performance and data quality. Reagents and supplies shall be of appropriate grade for the procedure, and gravimetric and volumetric apparatus shall be of a suitable class and calibrated as necessary. Purchased equipment, supplies, reagents, standards and other testing materials must be of sufficient quality so as not to adversely affect analytical results. Scientific vendors are regarded as resources or extensions of the analytical laboratory, and thus must adhere to the same standards of quality. The WSL has access to and experience with a wide variety of scientific manufacturers, both directly and indirectly through the University Purchasing Department. The Laboratory also is fortunate in most, if not all, cases to have the final word in choosing a supplier.

## Responsibility

The Laboratory Manager is responsible for ensuring that all users are properly trained and for monitoring equipment use, operation and status. Staff assigned to specific equipment will monitor use and ensure that operation and maintenance procedures are continuously followed.

# B9. Non-direct Measurements

## Data Sources

Non-direct measurements are generally in the form of project final reports, government scientific reports and published journal articles. Data in these sources are primarily produced to quantitively evaluate the occurrent of nitrate in the deep unsaturated (vadose) zone. Whenever possible, raw data (nitrate-N, ammonia-N, metal concentrations, moisture content, pH, texture, etc.) will be used to reproduce calculated values (pore water, etc.). Measurement methods used in existing reports will be reviewed to ensure that data are comparable to currently used methods.

## Intended Use

The intended use of non-direct measurements will be to compare temporal changes at fixed locations with multiple measurements, and to quantify spatial differences due to nitrogen loading, leaching and attenuation rates.

## Acceptance Criteria

Acceptance criteria for use of non-direct measurement include use of comparable sampling and analytical methods, quality controls, and similar project objectives.

## Resources & Support Facilities

Resources and support facilities required for non-direct measurements include personnel trained on evaluating methods and data quality, as well as computational equipment and software that permits digitizing and cross-checking calculated fields. Digitizing previous reports and data tables requires an additional step off reviewing graphs of numerical results to identify outliers and data transcription errors.

## Limits to Validity & Operating Conditions

Final limits to validity of final data tabulation and interpretation will be left to the data users. Operating conditions , data sources and history will be supplied with all released data.

# B10. Data Management

## Data Management Scheme

Working files and files composing the Nebraska Vadose database will be kept on UNL Box. Files which pertain to project contracts, including the final proposal, budget, schedule, annual reports, final reports, etc. will be stored on the UNL Projects website. This is a project management website which is maintained by the University IT Department, and which is backed-up once daily.

The technician or analyst in charge of the analysis is responsible for verifying and tabulating raw data into a form containing the Lab ID#, field identifier, collection date, project, protocol, batch number, analysis date, and results of analysis. The analyst reviews the tabulated results to verify that sample preparation/analysis documentation is correct and complete, the appropriate SOP was followed, QC results are within control limits, and that any special sample preparation/analysis requirements have been met. A standard operating procedure will list general acceptance and reporting procedures. Any problems with sample analysis will be communicated verbally and in writing to the supervisor, together with an explanation of how the problem was resolved. Calculations for data reduction are included in the method’s standard operating procedure. Results are typically entered or transferred electronically to a computer spreadsheet for performing calculations and reporting, although handwritten results are acceptable. The data package is then initialed, dated, and passed on for review.

## Record-Keeping & Tracking

Working files in Box will be marked with the initials of the last person to edit the document and date edited the end of the file name. This will designate which document is the most recent. Within each working folder, a subfolder will be made named “Archive.” Old versions of documents will be continually moved into the Archive folder. Ideally, only the most recent version of a file will be at the highest level of the working folder.

Revisions to documents which require approval will be stored as separate versions. Document versions will be marked in the file name with the label v1, v2, etc. Within the UNL Projects website, files will be assigned a category, including: Draft, Draft: For Review, Final, Final: Executed.

## Data Handling

Access to the UNL Box folder and UNL Projects website will be restricted to staff and students at the University actively working on the Nebraska Vadose program. Within Box, new users must be invited by current users to view folders. Within UNL Projects, users must have a University email address and be invited by the Project site administrator to view files.

Stakeholders outside of the project team may request files and data in writing by contacting the Project Manager, Lacey Bodnar, at [lbodnar@nebraska.edu](mailto:lbodnar@nebraska.edu).

## Responsibility

The Project Manager (refer to organizational chart in Figure 1) is responsible for project file management. The WSL Laboratory Manager is responsible for management of documents and data created at the WSL. The Laboratory Manager will be responsible for ensuring that the most recent versions of all documents are used by laboratory staff.

## Data Archival & Retrieval

Within each working folder on UNL Box, a subfolder will be made named “Archive.” Old versions of documents will be continually moved into the Archive folder. Ideally, only the most recent version of a file will be at the highest level of the working folder.

Any document which is finalized and relates to the project contract will be filed in the UNL Projects website. The Project Manager will be responsible for filing the final version of a document, maintaining the versioning system if updates are needed, and distributing files to those who submit a relevant request via email.

Laboratory results and supporting documentation may be held indefinitely at the WSL, although data older than five years may not be verifiable. Raw results are held in files, notebooks, and other standard forms. Electronic raw results and data are archived in cloud storage. Electronic records are secured through a digital signature. Laboratory staff are assigned unique names and each person choses an individual password. To log into laboratory computers, both the unique name and password are required.

## Hardware & Software Acceptability

Computer controls and automated software is now used for nearly all data acquisition and processing. The acceptability and proper functioning of new hardware and software occurs immediately after acquisition and installation. A baseline verification uses manual calculations to confirm the correctness of software calculations, and ongoing verification takes place during laboratory data review process whenever a reviewer replicates one of the results generated. Raw data for environmental methods comprise standardized calibration and quantitation reports from various instruments, mass spectra, and chromatograms. Laboratory data reduction for these instrumental analytical methods is computerized often where data is imported into a spreadsheet for further reduction and verification of quality controls. The SOP for every analytical method contains a section that details calculations used in the method’s data reduction.

# C1. Assessments and Response Actions

## Assessment Activities & Schedule

Assessment activities will include project meetings, where activities and schedules are evaluated quarterly, semiannually or annually.

## Responsibility

The Project Director will conduct these assessments, and has the authority to issue stop work orders, changes in project schedules, and will inform project specialists as well as any other project participants about the changes in the schedule or assessment process.

## Reporting

The Project Director is responsible for preparing project reports that include any response actions which may be required.

## Corrective Action

Any team members that identify potential issues, will report these issues to both the Project Manager and Project Director via email. The Manager and Director will determine what corrective action is needed, and either make the corrective action or instruct a team member to make the correction.

# C2. Reports to Management

## QA Status Reports

Quality control reports, prepared by queries to WSLims database, are reviewed each time results are released to a project client. Reports of results are generated monthly. An annual progress report will be provided to NET, NDEQ and Funding Agency for each year of funding. A final project report will be provided at the end of the grant period.

## Report Responsibility & Acceptance

The Project Director and Project Manager will prepare progress and final reports, with input from the staff and students supporting the research program.

# D1. Data Review, Verification, and Validation

Data review includes a check of calibration data, QC results, completeness of supporting documentation and results, and determination if results are ready for release in the form of a final report. If concentrations are not already in standard units, results are converted to mg/L or µg/L for liquid samples, µg/g or ng/g for solid samples, and µL/L or nL/L for gaseous samples, with method sensitivity determining the appropriate range. Results falling below the most recent reporting limits are converted to “<reporting limit” unless the project or individual requesting the analyses specifies uncensored results. A disclaimer is added to uncensored results indicating that concentrations below reporting limits are indeterminate and cannot be verified.

## Criteria

Reporting of all necessary data and statistics aids in understanding the implications of the results. Without the appropriate accompanying information, inaccurate or incorrect conclusions may be drawn from any set of results. A calibration curve will consist of a blank sample (matrix sample processed without internal standard), a zero sample (matrix sample processed with internal standard), and six to eight non-zero samples covering the expected range, including the Lower Limit of Quantitation (LLOQ). The simplest model that adequately describes the concentration-response relationship will be used. Selection of weighting and use of a complex regression equation will be justified. The following conditions will be met in developing a calibration curve: 1) 20% deviation of the LLOQ from normal concentration, 2) 15% deviation of standards other than LLOQ from nominal concentration, 3) at least four out of six non-zero standards should meet the above criteria, including the LLOQ and the calibration standard at the highest concentration.

Excluding the standards will not change the model used. The correlation coefficient should be no less than 0.99, unless otherwise stated by the validation/method development report. The source, age, storage conditions, and labeling of the standards will be clearly indicated by the specific analytical method. Evaluation of bias is obtained by comparison of the results with those of a known amount of standard reference material in an appropriate matrix. The minimum requirement for ensuring accuracy is one LFB sample per twenty unknowns, or at least 5% of the total samples. Ideally, accuracy will be measured using a minimum of five determinations per concentration, and a minimum of three concentrations in the range of expected concentrations is recommended. The lowest LFB should be approximately three times the LLOQ. The mean value should be within 15% of the actual value, except at LLOQ, where it should not deviate by more than 20%.

# D2. Verification and Validation Methods

## Verification and Validation Standard Operating Procedures (SOPs)

Method validation is described in the “Method Validation” SOP (**Attachment 2.9**). Method development requires three steps: 1) Determination of the Method Detection Limit (MDL), 2) Determination of the Recovery by analyzing independently prepared unknown samples, and 3) A Holding Time Study. This document does not give guidelines about how to develop the actual steps of the method, but how to validate a method once it has been developed. Methods developed at the Water Sciences Laboratory is both robust and accurate. Following this method validation procedure ensures that new methods meet the rigorous standards required at the WSL.

The most recent versions of the quality assurance manual, standard operating procedures, and other relevant documents are made available to laboratory staff, and a complete set of documents is available at all times either in hardcopy or cloud storage. The Laboratory Manager will be responsible for ensuring that the most recent versions of all documents are used by laboratory staff. The following verification and validation methods will be used on this project.

The Instrument Detection Limit (IDL) is defined as the minimum mass amount (e.g. ng or pg quantities) of a substance that can be measured on the instrument and reported with 99% confidence that the constituent amount is greater than zero. It is determined by analyzing a low-level standard containing the constituents(s) of interest at least 8 times, calculating the standard deviation of the measured concentration, and then multiplying by the appropriate student t value. The injected volume is used to calculate the mass of constituent(s) injected from the known concentration of the standard. Typically, the lowest standard of the instrument calibration curve is used to determine the IDL.

* Analyze eight or more injections of the low calibration standard solution.
* From the determined values, calculate the standard deviation of the eight or more samples. See the Data Reduction section for statistical formulas.
* Multiply the standard deviation of the eight or more samples by the appropriate student t value. See Data Reduction section for the relevant formula. See Student t Values Table for t values. Select the value of t for n – 1 degrees of freedom at the 99% confidence level. If eight replicates have been run, the student t value is 2.998.

Method Detection Limit (MDL)

The Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the constituent concentration is greater than zero. It is determined by taking samples containing the constituent(s) of interest and processing them through the complete proposed analytical method, calculating the standard deviation of the values, and then multiplying by the appropriate student t value.

* Fortify a suitable quantity of matrix (reagent water, sand, etc.) with target compound(s) as to be able to run eight or more samples of known concentration at a level near the estimated MDL. (This can be estimated by consulting the MDL values listed in other similar methods, or by multiplying the blank/noise for the method by three to five.)
* Analyze eight or more portions of this solution by processing it through all the steps of the proposed method over a period of at least three days. (Processing over three or more days ensures the MDL determination is more representative than measurements performed sequentially.)
* From the determined values, calculate the standard deviation of the eight or more samples. See the Data Reduction section for statistical formulas.
* Multiply the standard deviation of the eight or more samples by the appropriate student t value. See Data Reduction section for relevant formulas. See Student t Values Table for t values. Select the value of t for n – 1 degrees of freedom at the 99% confidence level. If eight replicates have been run, the student t value is 2.998.

The recovery of the target compound(s) in a matrix is the measured value obtained in a fortified sample divided by the calculated concentration. Recovery pertains to the extraction efficiency of an analytical method within the limits of variability. Recovery will be consistent, precise, and reproducible. Recovery experiments will be performed by comparing the analytical results for the extracted samples at a concentration representative of the concentration of the unknown samples. Known samples can be prepared in the analysts laboratory using either purchased analytical grade reagents, or standards available from the National Institute of Standards and Technology (NIST).

* Prepare or obtain (i.e. from NIST) a sample(s) containing a known amount of the constituent(s) of interest in the appropriate matrix.
* Process the sample(s) through the proposed method.
* Compare the results with the initial known concentration of the sample by dividing the average of the determined results by the initial known concentration, and multiplying by one-hundred. See Data Reduction section for the formula.

Holding Time Study - Short Term Stability

Three samples of known concentration will be warmed to room temperature and kept at this temperature from 4 to 24 hours (based on the expected duration that samples will be maintained at room temperature in the intended study) and analyzed. The recovery will then be determined as stated in the Recovery section.

Long Term Stability

The storage time in a long-term stability evaluation will exceed the time between the date of first sample collection, and the date of last sample analysis. Long-term stability will be determined by storing at least three samples of known concentration under the same conditions as the study samples. The volume of samples will be sufficient for analysis on three separate occasions. Test the stability of samples on three separate occasions spaced equally apart, for the expected duration of the study. The recovery of the stability samples will then be determined as stated in the Recovery section.

## Verification and Validation Responsibility

Data review and validation may be performed by both a supervising chemist and Laboratory Director and includes calculation of quality control statistics (range and recovery).

## Corrective Action & Responsibility

Any team members that identify potential issues, will report these issues to both the Project Manager and Project Director via email. The Manager and Director will determine what corrective action is needed, and either make the corrective action or instruct a team member to make the correction. If corrective action does not resolve the nonconformity, and the source of a problem cannot be identified, the results for the affected sample batch are reported with a footnote describing the quality control issue. If the source of the problem can be identified, but cannot be corrected, the results may be discarded and the sampler or other responsible party will be contacted to determine whether re-sampling or other alternatives can be arranged in order to provide valid results. Issues that affect data quality are included in the cover letter or narrative that is produced with the sample results.

## Checklists, Forms & Calculations

Other records include, and are not limited to, personnel records, QA corrective action files, laboratory notebooks and worksheets, batch sheets, maintenance logs, standard logs, and laboratory sample log-in files. Sample log-in information is stored electronically. Records are stored in designated file drawers or electronically and are retained for 5 years, or as specified by contract, to allow for access to raw data information. The following blank forms are included in **Attachment 4**: Chain of Custody Record, Sample Submittal Form, Soil Moisture Content calculation sheet, Core Breakdown template.

# D3. Reconciliation with User Requirements

## Evaluating Uncertainty

A data quality assessment, included in the annual and final project report (see Section A.9), summarizes the data collection activities and states whether the data are of the right type, quantity and quality to support the intended use. The narrative includes a short description of the project objectives, intended use and describes project documents used in data collection, and the evaluation procedure with the references to the source and acceptance criteria. Tabulations of qualified data for each intended use are provide with quantitative summaries of uncertainties listing at a minimum, average and standard deviation of recoveries from fortified blanks, concentrations measured in method and field blanks, and results of duplicate analyses. Comparability and completeness for intended use, as well as a statistical evaluation of any uncertainty measured from quality controls.

## Reporting Limitations on Data

Limitations will be summarized based on the uncertainty and comparability of methods and data generated as compared with other studies and laboratories conducting similar work.

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# Attachment 1: Funded Final Proposal(s)

# Attachment 2: Standard Operating Procedures (SOPs)

# Attachment 3: Standard Laboratory Training Plan

# Attachment 4: Checklists, Forms & Calculations