Quality Assurance Project Plan

Groundwater, Soil, and Crop Nitrogen at a Field Where Dairy Waste is Used as Fertilizer in Whatcom County

by
Barbara M. Carey, L.G., L.HG.

Washington State Department of Ecology
Environmental Assessment Program
Olympia, Washington 98504-7710

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Groundwater, Soil, and Crop Nitrogen at a Field Where Dairy Waste is Used as Fertilizer in Whatcom County

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Approvals

Approved by:	November 2004
Andrew Craig, Bellingham Field Office	Date
Approved by:	November 2004
Richard Grout, Section Manager, Bellingham Field Office	Date
Approved by:	October 13, 2004
Barbara Carey, Principal Investigator, Watershed Ecology Section	Date
Approved by:	October 14, 2004
Dale Norton, Unit Supervisor, Nonpoint and Toxics Studies Units	Date
Approved by:	October 19, 2004
Will Kendra, Section Manager, Watershed Ecology Section	Date
Approved by:	October 25, 2004
Stuart Magoon, Director, Manchester Environmental Laboratory	Date
Approved by:	October 21, 2004
Cliff Kirchmer, Ecology Quality Assurance Officer	Date
Approved by:	November 3, 2004
George Boggs, District Manager, Whatcom Conservation District	Date
Approved by:	November 8, 2004
Chris Clark, Whatcom Conservation District	Date
Approved by:	October 21, 2004
Dr. Joe Harrison, WSU-Puyallup	Date

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Abstract

Dairy manure is often applied as a fertilizer on grass fields in Western Washington. This study will evaluate the effectiveness of recently adopted Dairy Nutrient Management Plans in protecting the quality of the Sumas-Blaine Aquifer by documenting the sequence of changes in nitrogen that can be readily measured at a typical grass field. Manure, soil, grass, and groundwater will be sampled over 2-1/2 years at a 22-acre grass field where manure is applied near Lynden, Washington. Seven monitoring wells will be installed in the field where monthly to every six weeks ammonia N, nitrate+nitrite-N, total N, total and ortho phosphorus, chloride, total organic carbon, and total dissolved solids will be sampled as well as depth to water. Soil, manure, and crop samples will be collected and analyzed by the Washington State University Nutrient Management Program. Soil samples will be collected weekly during the fall and monthly during the rest of the year for nitrate and once annually for phosphorus and potassium. Samples of manure will be collected and analyzed for ammonia N and total Kjeldahl N each time manure is applied, and the volume recorded. Grass samples will also be collected and analyzed for dry weight and nitrogen content. Precipitation data will be recorded and used to observe the influence of rainfall on the movement of nitrate from soil to groundwater in the fall. The NLOS (NLEAP on Stella) model will be used to compare observed to predicted concentrations of nitrogen in the soil.

Background

The Sumas-Blaine Aquifer is a shallow, unconfined aquifer covering about 150 square miles of Whatcom County in northwest Washington as shown in Figure 1. The aquifer extends about an equal area into British Columbia, Canada, and is composed mainly of sand and gravel of glacial outwash origin. Alluvial deposits from the Nooksack and Sumas Rivers are also present and composed of mixed gravel, sand, silt, and clay. The flat topography and shallow depth to water over much of the aquifer offer little protection from overlying land uses. In winter, the water level in many areas is at the land surface requiring an extensive artificial drainage system to prevent flooding.

Nitrate-N concentrations in the Sumas-Blaine Aquifer often exceed the Maximum Contaminant Level for drinking water, 10 mg/L as N, as well as the Washington State Water Quality Standards for Ground Waters (Cox and Kahle, 1999; Erickson and Matthews, 2002; Erickson, 2000; Mitchell, et al., 2003; Erickson, 1998; Garland and Erickson, 1994; and Erickson and Norton, 1990). Elevated nitrate in the aquifer has been attributed to storage and application of dairy waste, plough-down of senescing grass and corn crops, and inorganic fertilizers typically applied to corn, raspberries, and potatoes.

The Dairy Waste Nutrient Management Act (Chapter 90.64 RCW) passed in 1998 required that all dairies develop Dairy Nutrient Management Plans (DNMPs). These plans were submitted to the local conservation district for review and approval. DNMPs were required to be approved by July 1, 2002, and implemented with final certification by December 31, 2003.

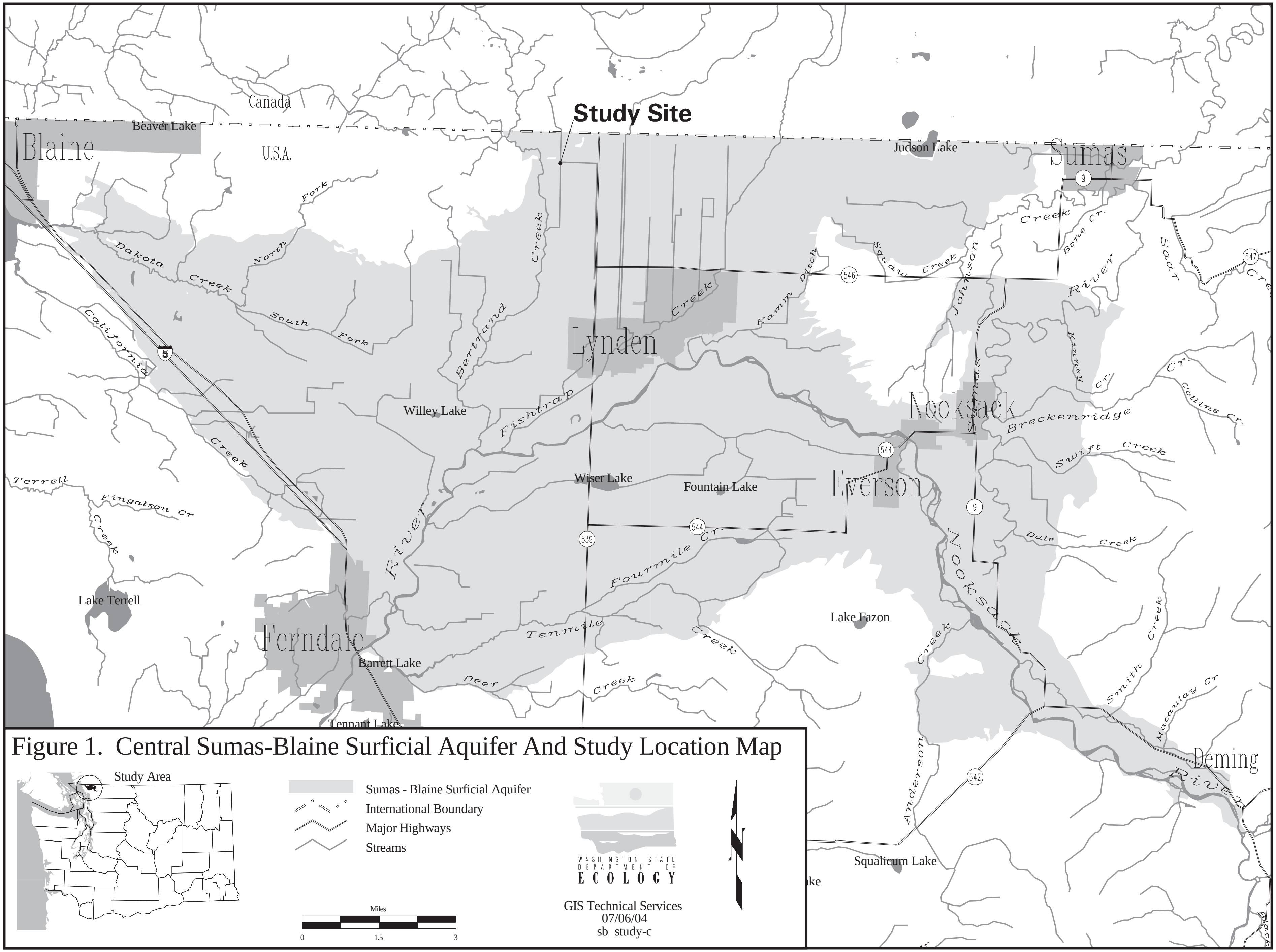

Figure 1. Central Sumas-Blaine Surficial Aquifer And Study Location Map

Much effort has been expended by dairy farmers and state agencies to meet the requirements of the new law; the objective of which is to ensure protection of surface and groundwater quality.

Dairy Nutrient Management Plans include a requirement for fall soil nitrate analysis at each field receiving dairy waste as a tool for evaluating nitrogen application rates relative to uptake by the crop. Timing of soil nitrate sampling can affect the results because nitrate, which is very soluble, leaches readily from the soil during precipitation events (Paul and Zebarth, 1997 and Kowalenko, 1987) and entering underlying groundwater. Likewise, organic nitrogen from manure continues to mineralize during the fall adding to the nitrate pool in the soil after plant uptake has slowed or the crop is harvested. Both of these factors can affect observed soil nitrate values.

The Ecology Bellingham Field Office (BFO) of the Water Quality Program requested that the Environmental Assessment (EA) Program design and conduct a study to evaluate the effectiveness of the DNMPs in protecting the quality of the Sumas-Blaine Aquifer. The purpose of this study is to track the major nitrogen compartments of a field receiving dairy waste: soil, groundwater, and crop removal of nitrogen. (Nitrogen gas lost to denitrification and soil pore-water will not be measured.) The amount of nitrogen applied in manure and inorganic fertilizer will also be measured. Correlations between nitrogen applied in manure and nitrogen in soil, crop, and groundwater, especially in the fall and winter for soil and groundwater, will be evaluated. Nitrogen measurements in the crop will also be compared with that in the soil and groundwater.

Project Description

The principal questions addressed in this study are:

- How much nitrogen in a field receiving dairy waste is taken up by the crop?
- How much nitrate is in the soil when winter rains begin?
- How much nitrate leaches to groundwater?
- How do nitrogen concentrations in the major components of the nitrogen cycle vary seasonally and from year to year?

The answers to these questions will help farm plan managers to tailor manure and fertilizer application plans to minimize leaching of nitrate to groundwater to improve water quality protection. Nitrogen inputs to and losses from the study field will be quantified. Inputs of nitrogen include manure, inorganic fertilizer, irrigation water, decomposing organic material from manure and plant remains, and upgradient groundwater. Nitrogen transformations, uses, and losses include crop uptake, volatilization, denitrification, soil storage, and leaching to groundwater. Volatilization, denitrification, and leaching losses will be estimated based on the conditions during the study.

Generally, about 55% of the nitrogen in liquid manure is in the form of ammonia. The remaining 45% is mostly in the organic N form. Most of the ammonia mineralizes to nitrate in the soil through bacterial processes where it is either taken up by the crop or stored in the soil. A portion of the organic N fraction mineralizes to ammonia and then to nitrate each year and is available for plant uptake or storage in the soil. Nitrate-N remaining in the soil after the growing season is usually assumed to leach to groundwater with heavy fall and winter precipitation (Paul and Zebarth, 1997).

The objectives of the study are to document the sequence of changes in nitrogen that can be readily measured over 2-1/2 years from application as manure or inorganic fertilizer to soil, grass crop, and groundwater. The influences of precipitation and temperature on this sequence are of particular interest.

A groundwater monitoring network of seven wells will be installed at a representative grass field in the Sumas-Blaine Aquifer where dairy waste is applied. Soil, crop, and manure sampling and analysis will be conducted by WSU. A grass field northwest of Lynden was chosen for the study because the dairy has an approved DNMP, the silt/loam soils and seasonal high water table are typical for the area, and the dairyman is willing to allow the study to be conducted.

A summary of the samples and costs is shown in Table 1. Groundwater samples will be collected monthly, via monitoring wells, during the fall and winter and every six weeks during the spring and summer. Groundwater samples will include ammonia-N, nitrate+nitrite-N, total N, ortho- and total phosphorus, total organic carbon, chloride, total dissolved solids, and iron.

Soil nitrate samples will be collected weekly from August to November and monthly during the rest of the year. Crop nitrogen samples will be collected about six times per year, each time the

Table 1. Estimated Laboratory Costs for Each Media to be Sampled.

Groundwater (Ecology: monthly in fall and winter, otherwise every 6 weeks)					
Analyte	Number of Samples/Event	Cost/ Sample[1]	Cost/Sampling Event	Number of Sampling Events	Cost/ Analyte
Nutrients-5 (Ammonia-N, Nitrate+Nitrite-N, Total Phosphorus, Ortho-phosphate)	10	64	$640	23	$14,720
Total Persulfate N	10	16	$160	23	$3,680
Chloride	10	12	$120	23	$2,760
Total Dissolved Solids	10	10	$100	23	$2,300
Total Organic Carbon	10	29	$290	23	$6,670
Iron	10	36	$360	9	$3,240
Grain size	1	100	$100	1	$100
Total Cost					*$33,470*

[1]: Costs include 50% "planned" discount for Manchester Lab.

Manure (WSU: 7 times/year)					
Analyte	Number of Samples/Event	Cost/ Sample	Cost/Sampling Event	Number of Sampling Events	Cost/ Analyte
Nutrients-3 (Ammonia-N Total Kjeldahl N, Phosphorus)	2	29	$58	14	$812
Potassium	2	11	$22	2	$44
Total Cost					*$856*

Soil (WSU: weekly Aug-Nov, otherwise montly)					
Analyte	Number of Samples/Event	Cost/ Sample	Cost/Sampling Event	Number of Sampling Events	Cost/ Analyte
Nitrate N	2	7	$14	45	*$630*
Phosphorus and Potassium-- once annually	2	36	$72	2	*$144*

Grass crop (WSU: 6 times/year)					
Analyte	Number of Samples/Event	Cost/ Sample	Cost/Sampling Event	Number of Sampling Events	Cost/ Analyte
Dry weight, crude protein	2	27	$54	12	*$648*

Irrigation water (WSU collects, Ecology analyzes: 4 times/year)					
Analyte	Number of Samples/Event	Cost/ Sample	Cost/Sampling Event	Number of Sampling Events	Cost/ Analyte
Nitrate + nitrite-N	2	12	$24	8	*$192*

grass crop is harvested.   Grass samples will be analyzed for dry weight and crude protein. The quantity and quality of manure will be estimated at the time of application, about seven times per year. Manure samples will be analyzed for ammonia-N, total N, and nitrate+nitrite-N. Irrigation water will also be sampled four times per year and anlyzed for ammonia-N, nitrate+nitrite-N, and total N. If inorganic nitrogen fertilizer is used, the amount will be recorded.

Changes in nitrogen and related constituents will be evaluated seasonally and spatially using Student's T-test, Seasonal Kendall, or equivalent statistical test. This evaluation will be conducted for groundwater, soil, and crop nitrogen.

Organization and Schedule

Project participants and their responsibilities are listed below.

Andrew Craig, Bellingham Field Office, Water Quality Program, is the client. Andrew is responsible for reviewing and approving the Quality Assurance (QA) Project Plan and final report and interacting with interested public (360-676-2217).

Barbara Carey, Environmental Assessment Program, Watershed Ecology Section, is the project lead for the groundwater portion of the study and will have primary responsibility for project planning, data collection and analysis, and preparation of the final project report. She will also have repsonsibility for integrating data analysis for soil, crop, and manure with groundwater (360-407-6769).

Soil, crop, and manure sampling will be conducted by the WSU-Nutrient Management Program under the direction of *Dr. Joe Harrison* as described in Appendix A.   Dr. Harrison will be responsible for ensuring that the provisions in Appendix A are carried out, including the preparation of the final report described therein. Chemical analyses will be conducted by commercial laboratories according to procedures documented in Appendix A of this QA Project Plan.

Dale Norton, Environmental Assessment Program, Watershed Ecology Section, is the unit supervisor responsible for budget planning and internal review of the QA Project Plan and project report (360-407-6453).

Chris Clark, Whatcom Conservation District, is responsible for reviewing and approving the QA Project Plan and for using the data collected to test the NLOS (NLEAP on Stella) soil nitrogen leaching model (360-354-2035).

Cliff Kirchmer, Ecology Quality Assurance Officer, is responsible for review and approval of the QA Project Plan and available for advising on quality assurance and quality control issues during project implementation and assessment.

Pam Covey, Ecology Manchester Environmental Laboratory (MEL), is responsible for coordinating sample requests and providing access to data (360-871-8827).

Karin Feddersen, MEL, is the primary contact for laboratory coordination related to sample management and data quality (360-871-8829).

Stuart Magoon, Director, MEL, is responsible for the laboratory analysis and contracting for the study (360-871-8801).

Project Schedule

Quality Assurance Project Plan Approved	October 2004
Well Drilling and Installation	August 2004
Sampling (Soil, Grass, Manure, Groundwater)	August 2004- November 2006
Draft Report	March 31, 2007
Final Report	May 30, 2007
Data Entry to EIM System	July 2007

Quality Objectives

The main objective of this project is to characterize groundwater, soil, crop, and manure nitrogen and related parameter concentrations over time at a field where manure is applied. For groundwater, annual and seasonal differences between results from three locations in the field will be evaluated (upgradient, mid-field, and downgradient). Because the time of travel is in the range of one foot per day or less, land use activities at the field will influence seasonal groundwater quality changes more than upgradient influences. Therefore, results for the field as a whole will also be examined.

Soil and crop nitrogen characterization does not generally divide the field into separate parts. Samples collected around the field will be composited to represent the whole field.

Standard sample collection procedures will be used to minimize potential changes in groundwater sample chemistry during storage and transport to the Ecology Manchester Environmental Laboratory. Collection procedures for soil, manure, and crop media will be specified in the contact for these samples (Appendix).

Table 2 lists the data quality (measurement) objectives for the project including target accuracy for results, precision, bias, and reporting limit for each analysis.

Table 2. Analytical Measurement Quality Objectives for Groundwater Analytes.

Analyte	**Accuracy**	**Precision**	**Bias**	**Required Reporting**
	(% deviation from true value= (2 x Precision) + Bias)	(% Relative Standard Deviation)	(% Deviation from True Value)	**Limit** (Concentration Units)
Field				
Temperature[1]	± 0.2°C	NA	NA	NA
pH[1]	± 0.15 S.U.	NA	NA	NA
Specific Conductivity[1]	± 10 uS/cm	NA	NA	NA
Dissolved Oxygen[1]	± 0.2 mg/L	NA	NA	0.2 mg/L
Laboratory				
Ammonia-N	<20	7	5	0.010 mg/L
Nitrate+Nitrite-N	<20	7	5	0.010 mg/L
Total Persulfate N	<20	7	5	0.025 mg/L
Ortho Phosphate	<20	7	5	0.010 mg/L
Total Phosphorus	<20	7	5	0.010 mg/L
Chloride	<30	10	10	0.1 mg/L
Total Dissolved Solids	<30	10	10	10 mg/L
Total Organic Carbon	<30	10	10	1 mg/L

[1] Accuracy is specified as units of measurement rather than percentages.

Sampling Process Design (Experimental Design)

The study will be conducted on a 22-acre grass field in Northern Whatcom County near the Canadian border (Figure 2). The field has been used regularly for dairy manure application from, at least, 1994. The field receives manure during the growing season and has an approved DNMP. During the 2004 crop year, the grass field was plowed and reseeded to grass. The new seeding received two light applications of manure and irrigation water. The decomposition of the old sod may produce elevated nitrate concentrations in the groundwater due to mineralization of organic nitrogen.

The soil at the site is a Hale silt loam which is somewhat poorly drained (SCS, 1992). The depth to water in nearby wells is about ten feet based on drilling logs, and one to four feet deep in the winter based on the SCS (1992) description of Hale silt loam.

The field will receive manure from an injection system that places the liquid manure a few inches below the ground surface or broadcasts the manure with a splash plate system. The manure application rate will be tracked for both application methods. The injection system or tanker will have a mechanism to measure the amount of liquid applied. At least two samples of the applied manure will also be collected during each application.

Groundwater monitoring wells will be used to sample groundwater upgrandient, downgradient and along the groundwater flow path in order to assess the effects of manure and fertilizer (if used) applications on corresponding nitrogen values in the soil, groundwater, and grass crop. Soil, crop, and manure sampling and analyses will be conducted by WSU as described in Appendix A.

Monitoring Wells

The direction of groundwater flow in the area is generally north-south and toward surface water bodies such as rivers and creeks. Bertrund Creek flows north-south and along the west border of the study field. Two monitoring wells will be installed toward the upgradient (north) end of the field. A more precise groundwater flow direction can be determined as the first wells are drilled and depth-to-water measurements are obtained. Two to three monitoring wells will be installed toward the middle of the field, and two wells toward the downgradient end of the field (south). All wells will be located within the area receiving manure.

Because the depth to water will be less than 20 feet and the zone of interest is closest to the top of the water table, the depth to the bottom of the screened interval will be 25 feet or less in all but one of the wells. Exact depths will be determined based on observations of soil and aquifer conditions logged during drilling and on background water level fluctuation information. One downgradient well will be drilled about 50 feet and completed near the bottom of the aquifer. This deep well will be drilled alongside a shallow well. Comparison of water levels in the two wells will allow observation of vertical hydraulic movement in the aquifer.

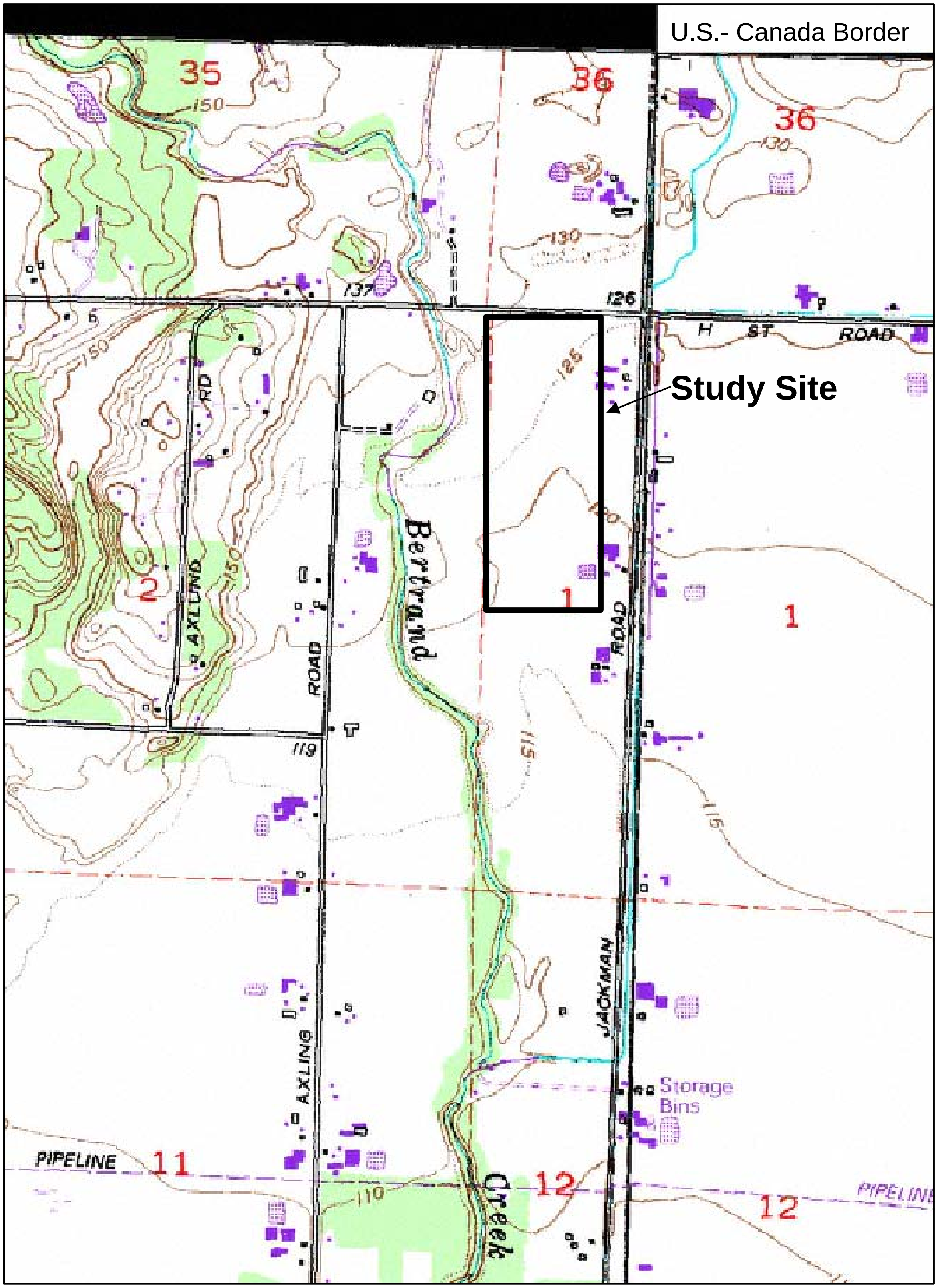

Figure 2. Study site location.

Wells will be constructed with 2-inch diameter PVC, flush-threaded casing, seven- foot long screens in the shallow wells, and a ten-foot long screen in the deep well.   Clean, inert sand pack materials will be placed over the screened interval to two feet above the top of the screen. Bentonite and cement/bentonite seals will be placed along the entire length of the annular space (between the boring and the PVC well) from the top of the gravel pack to the surface. Monitoring wells will be secured with a lock.

The elevations of all wells will be surveyed to a common datum using a surveyor's level and rod. Well elevations will be recorded to 0.01 foot and accurate to 0.05 foot as determined by closure. Wells will be located on topographic maps (1:24,000) and using a Magellan Global Positioning System (GPS). GPS well locations will be recorded as latitude and longitude.

When the study is completed, all wells will be decommissioned in accordance with Chapter 173-160 WAC.

Hydrologic Testing

Aquifer pumping tests will be conducted using the monitoring wells to define the hydraulic properties of the aquifer (ASTM, 1994). These data will be used to estimate the hydraulic conductivity of the aquifer which can be used to estimate the velocity of ground water flow beneath the field.

Sampling Procedures

Groundwater and Manure

Well Installation

A licensed driller under subcontract to Ecology will install the monitoring wells. The wells will meet or exceed the requirements of Minimum Standards for Construction and Maintenance of Wells (Chapter 173-160 WAC). A separate bid document describing the drilling activities is being prepared.

Wells will be constructed with 2-inch diameter PVC, flush-threaded casing, and commercially fabricated seven- or ten-foot long screens.   Clean, inert sand pack materials will be placed over the screened interval to two feet above the top of the screen. Bentonite and cement/bentonite seals will be placed along the entire length of the annular space (between the boring and the PVC well) from the top of the gravel pack to the surface.

Samples will be collected at 5-foot intervals during drilling using a split spoon sampler. Core samples will be placed in labeled plastic zip-lock bags. A portion of the split spoon samples will be analyzed for grain size.

Detailed notes will be taken during the drilling process, and photos will be taken of the drilling site and of representative core samples.

A steel, 6-inch diameter, outer protective casing will be installed over the PVC well. The steel casing will extend to a depth of about two feet below ground. The top of the outer casing will be flush with the ground surface.

After completion, the wells will be developed by the driller until the water removed from the borehole is free of sediment. A state well tag with a unique ID number will be attached to each new well.

Groundwater Sampling

Groundwater samples will be collected over two years: monthly during the fall and winter and every six weeks in the spring and summer. Water levels will be measured at each well before collecting water samples using a clean, calibrated electric probe according to standard U.S. Geological Survey methodology (Stallman, 1983). Measurements will be recorded to 0.01 foot and will be accurate to 0.03 foot.

A peristaltic pump with dedicated polyethylene tubing will be used to purge the wells and to collect samples in the shallow wells. The deep well will be purged and sampled using a submersible pump. Water will be purged from each well for a minimum of 20 minutes and until field parameters (temperature, pH, specific conductivity, and dissolved oxygen) have stabilized to within 10% for consecutive samples spaced at least five minutes apart. Field parameters will be measured using an enclosed flow-through cell to minimize atmospheric effects.

Samples will be placed in bottles obtained from Manchester Laboratory. Bottle materials and preservatives are listed in Table 3. Sample bottles will be placed in coolers on ice and transported to the Ecology Operations Center in Lacey, Washington. Sample coolers will be placed in the walk-in cooler until picked up by the laboratory courier and taken to the Ecology/EPA Manchester Environmental Laboratory in Manchester, Washington.

Table 3. Sample Containers, Preservation, and Holding Time Requirements for Target analytes.

Analyte	Container Type	Container Volume (ml)	Preservation	Holding Time
Ammonia-N	w/m clear Nalgene (pre-acidified)	125	Adjust pH to <2, W/ H_2SO_4 and cool to < 4°C.	28 days
Nitrate +Nitrite-N	w/m clear Nalgene (pre-acidified)	125	Adjust pH to <2, W/ H_2SO_4 and cool to < 4°C.	28 days
Total Persulfate Nitrogen	w/m clear Nalgene (pre-acidified)	125	Adjust pH to <2, W/ H_2SO_4 and cool to < 4°C.	28 days
Total Phosphorus	w/m clear Nalgene (pre-acidified)	125	Adjust pH to <2, W/ H_2SO_4 and cool to < 4°C.	28 days
Ortho-Phosphate	w/m clear Nalgene	125	Cool to < 4°C.	28 days
Chloride	w/m poly	500	Cool to < 4°C.	28 days
Total Dissolved Solids	w/m poly (pre-acidified)	500	Adjust pH to <2,W/H_2SO_4 and cool to < 4°C.	7 days
Total Organic Carbon	s/m poly	60	cool to < 4°C.	28 days

w/m: wide-mouth.
s/m: small-mouth.

Measurement Procedures

The field and laboratory methods that will be used in the study are summarized in Table 4. Standard protocols used in the EA Program will be followed for measuring field parameters and collecting samples. Likewise, standard methods will be used for sample handling, preservation, and storage (WAS, 1993; Ward, 2001).

Table 4. Field and Laboratory Analysis Methods and Expected Range of Results.

Analyte	Matrix[1]	Standard Methods Test Method (APHA, 1998)	Expected Range of Results
Field			
Temperature	G	WTW Field meter	10-17°C
pH	G	WTW Field meter	5.5-7.5 SU
Specific Conductivity	G	WTW Field meter	100-1,000 uS/cm
Dissolved Oxygen	G	WTW Field meter	0.1-10 mg/L
Laboratory			
Ammonia-N	G	4500-NH3 H	0.010- 70 mg/L
Nitrate+Nitrite-N	G	4500-NO3 I	0.010- 70 mg/L
Total Persulfate N	G	4500-NO3 B Modified	0.010- 70 mg/L
Ortho Phosphate P	G	4500-P G	0.010-0.50 mg/L
Total Phosphorus P	G	4500-P I	0.010-0.50 mg/L
Chloride	G	EPA 300	1-40 mg/L
Total Dissolved Solids	G	2540 C	100-500 mg/L
Total Organic Carbon	G	EPA 415.1	1-15 mg/L
Grain size	S	ASTM[2] D422-63	NA

[1] Matrix codes: G=Groundwater, S=Soil.
[2] ASTM (American Society for Testing and Materials) , 1994. ASTM Standards on Ground Water and Vadose Zone Investigations, 2nd Ed., Philadelphia, PA.

Quality Control Procedures

Field Quality Control

At the start of each field day, all field meters will be calibrated according to the manufacturers' instructions. Duplicate field measurements will be collected at one monitoring well on each sampling day to assess overall precision of field parameters after the well has been sampled one time. The pump will be stopped for a few minutes before the well is again purged, field measurements repeated, and water quality samples collected. The laboratory duplicate samples will be used to provide an estimate of the overall accuracy of the sampling and analytical results.

One blind reference sample will also be submitted to the laboratory for nitrate+nitrite-N analysis as part of each sampling event. This sample will help evaluate the analytical accuracy of the results.

Lab Quality Control

Routine laboratory quality control procedures will be used to estimate the accuracy, precision, and bias introduced by laboratory procedures and will be reported to the project lead for data analysis. Manchester Environmental Laboratory's quality control samples and procedures are discussed in detail in the Quality Assurance Manual, Manchester Environmental Laboratory (Ecology, 2001).

Data Management Procedures

Field data will be recorded at the time of sampling in a field notebook using waterproof paper and maintained throughout the project eventually to be archived in project files. Field data will be entered into spreadsheets and, if appropriate, input into the Environmental Information Management (EIM) data repository.

Data generated by MEL will be managed by the Laboratory Information Management System (LIMS) and sent to the project lead in both electronic and hard copy formats. Documentation of lab results should include a discussion of any problems with the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers.

Lab documentation should also include all quality control results associated with the data in order to evaluate the accuracy of the data and to verify that the quality objectives were met. This should include results for all method blanks and check standards included in the sample batch, as well as results for analytical duplicates and matrix spikes prepared from the samples.

After comparison of the analytical data to project measurement quality objectives, the reported results will be input into the EIM system. Data will be entered into spreadsheets for evaluation and presentation in graphical formats.

Audits and Reports

A technical system audit will be conducted for the groundwater component of the study by the project lead in October 2004 and March 2005. The purpose of these audits will be to detect any problems or deviations for the QA Project Plan and to correct them. Less formal audits will occur periodically throughout the study.

The final report for the project will include a quality assurance section describing data quality. The final report will undergo scientific peer reivew by staff, with appropriate expertise, who are not directly connected with the project.

Data Verification and Validation

Data Verification

As part of data review, field notes and data from MEL and any contract laboratories will be reviewed for errors and omissions and to ensure that data are correct, complete, and consistent. Other items that will be reviewed include:

- Results for quality control samples described in Quality Control section of this document accompany sample results.
- Quality control results indicate that acceptance criteria were met.
- Data qualifiers are properly assigned where necessary.
- Data specified in the Sampling Design section above were obtained.
- Methods and protocols specified in this QA Project Plan were followed.

Analytical data generated by MEL will be reviewed and verified by comparison with acceptance criteria according to the data review procedures outlined in the Lab User's Manual (Ecology, 2002). Results that do not meet quality assurance requirements will be labeled with appropriate qualifiers, and an explanation will be described in a quality assurance memorandum attached to the data package.

After receiving the data package, the project lead will verify that the results have met the measurement quality objectives for bias, precision, and accuracy. Precision will be estimated by calculating the RPD for the field duplicate results. Analytical bias is assumed to be within acceptable limits if laboratory quality control limits are met for blanks, matrix spikes, and check standards. Overall accuracy will be assessed by comparing the measured result with the true value of the blind reference sample. If appropriate, sampling procedures, quality control steps, or analytical procedures will be modified to address identified problems.

Data Validation

The complete data package will be reviewed by the project lead with assistance from staff at MEL and the QA Officer. They will evaluate whether the procedures and methods specified in this QA Project Plan were followed and adjustments made as needed in subsequent work.

The soil nitrate model, NLOS (NLEAP On Stella) (Bittman, 2001) will be run using data produced in order to compare soil nitrate results with model predictions.

Data Quality (Usability) Assessment

If measurement quality objectives have been met for all sampling episodes, the data will be considered acceptable for use except as qualified during the data review and validation process. A paired t-test will be used to evaluated differences between upgradient and downgradient water quality at the 95% confidence level. If the data are not normally distributed, they will be transformed.

Results from this study should be comparable to results from previous Ecology, U.S. Geological Survey, Washington State University, and Western Washington University studies conducted in the Sumas-Blaine Aquifer area. The test methods and sampling procedures prescribed in this study are the same as those used in previous Ecology studies and are comparable to the U.S. Geological Survey methods. Routine test methods will be adequate for this study.

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Appendix A

Soil, Crop, and Manure Sampling and Analysis

Soil, Crop, and Manure Sampling and Analysis

Washington State University (WSU), under the direction of Dr. Joe Harrison, will conduct soil, grass crop, and liquid manure sampling and analysis for the two-year study. In addition, WSU will collect samples of irrigation water for analysis by Ecology's Manchester Environmental Laboratory (MEL).

All soil samples will be analyzed for nitrate. Annual soil samples will also be analyzed for phosphorus and potassium. Grass samples will be analyzed for dry matter and crude protein percentage. Manure samples will be analyzed for ammonia, total Kjeldahl nitrogen, phosphorus, and potassium.

Results will be used to estimate the amount of nitrogen applied to the study field each year, the amount removed as crop biomass each year, and the amount remaining in the soil.

WSU will maintain communication with the Ecology Project Lead, Whatcom Conservation District, the Natural Resources Conservation Service, and the dairy producer whose field will be used for the study.

Quality Objectives

Table 1A lists the data quality objectives for the project including target accuracy for results, precision, bias, and reporting limit for each analysis.

Table 1A. Measurement Quality Objectives for Soil, Manure, and Grass Samples.

Analyte ***Soil and Manure***	**Accuracy** (% deviation from true value= (2 x Precision) +Bias)	**Precision** (% Relative Standard Deviation)	**Bias** (% Deviation from True Value)	**Required Reporting Limit** (Concentration Units)
Ammonia-N	<20	7	5	0.010 mg/L
Nitrate-N	<20	7	5	0.010 mg/L
Total Kjeldahl N	<20	7	5	0.010 mg/L
Phosphorus	<20	7	5	0.010 mg/L
Potassium	<30	10	10	0.1 mg/L
Grass				
Wet Weight	<20	10	10	0.1 g
Dry Matter	<20	10	10	0.10%
Crude Protein	<20	10	10	0.10%

Field and Laboratory Methods

The field and laboratory methods to be used for soil, grass, and manure samples that will be used in the study are summarized in Table 2A.

Table 2A. Field and Laboratory Analysis Methods and Expected Range of Results for Soil, Manure, and Grass Sampling.

Analyte	Matrix[1]	Standard Test Method	Expected Range of Results
Ammonia-N	S,M	AOAC[2]--954.01	2-17 lb/1000 gallons
Nitrate	S	Galvak, et al (2003)-S-3.30	1-250 mg/kg
Total Kjeldahl N	M	AOAC[2]--955.04	2-48 lb/1000 gallons
Phosphorus (soil)	S	Galvak, et al (2003)-S-4.20	7-350 mg/kg
Phosphorus (manure)	M	AOAC[2] --985.01	1-9 lb/1000 gallons
Potassium (soil)	S	Galvak, et al (2003)-S-5.10	1-250 mg/kg
Potassium (manure)	M	AOAC[2] --985.01	3-30 lb/1000 gallons
Dry Matter	G	Goering, et al (1970)	5-55%
Crude protein	G	AOAC[2] --990.03	10-30%

[1] Matrix codes: S=Soil, M=Manure, G=Grass.
[2] AOAC, Association of Official Analytical Chemists, 2000, 17th edition.

Sampling Process Design (Experimental Design)

Soil, grass, and manure samples will be collected to estimate the amount of nitrogen applied to the field in the form of manure, the amount taken up by the grass crop, and the amount available in the soil over the period of study. The volume and concentration of manure applied will be tracked as well as the mass of nitrogen removed in the grass crop. If inorganic fertilizer is applied, the application rate will be included in the estimate of total N applied to the field.

Results from this study should be comparable to results from previous Ecology, U.S. Geological Survey, Washington State University, and Western Washington University studies conducted in the Sumas-Blaine Aquifer area. The test methods and sampling procedures prescribed in this study are the same as those used in previous WSU soil, manure, and grass studies. Routine test methods will be adequate for this study.

Sampling Procedures

Soil Sampling

Soil samples will be collected from August 2004 through July 2006. Samples will be collected weekly from August through November (or until WSU, Ecology, and the Whatcom Conservation District agree that sufficient precipitation has occurred to make weekly sampling unnecessary), and monthly December through July. Field procedures are described below and are based on Sullivan and Cogger (2003).

Each sample will consist of a composite of 15 subsamples. A one-inch diameter hand-held coring device will be used to collect the one-foot deep soil core subsamples at random locations around the field. Each location of each core will be measured using a Global Positioning System (GPS) and recorded. The loose crop or manure residue at the top of each core will be discarded. The remaining cores will be composited in a 5-gallon bucket and mixed thoroughly by hand. The mixed composite sample will be divided into subsamples and placed into clean plastic bags, one for analysis at the contract lab, one for archival at WSU-Puyallup, and once annually a second sample will be sent to the contract lab as a replicate. Soil samples will be placed in a freezer within one hour of sampling. Frozen samples will be placed in a cooler and shipped overnight via FedEx.

A duplicate set of cores will be taken at a different randomly selected 15-20 locations in the field each sampling day. The duplicate sample will be treated in the same way as the first sample.

Soil cores will be collected within a few feet of the same 30 locations each time samples are collected per recommended protocols.

Manure Sampling

Samples of liquid manure applied to the field will be collected from the applicator (injector, big gun, or truck-mounted dispenser when manure is being applied). Manure will be sampled each time it is applied it to the field (presumably seven times per year for two years). Subsamples will be collected at two times during each application in 5-gallon buckets pre-cleaned with non-phosphate detergent and water. Timing of sample collection relative to the application load will be recorded (i.e., first one-quarter of the load, last quarter of the load, etc.)

Each bucket will be filled roughly half-way, then the two subsamples will be thoroughly mixed together in one bucket. The ladle will be used to scoop the mixture into two pre-cleaned Nalgene containers.

Sample containers will be placed on ice and frozen within two hours. Sample containers will be shipped on ice via FedEx--one to the contract lab; the other to WSU-Puyallup.

The volume of manure applied will also be measured and recorded by the dairyman. WSU will obtain manure application records from the dairyman as well as fertilizer application rates if used.

Grass Sampling

Grass samples will be collected just before the field is harvested for two years, typically six times per year. Five 2-foot square subsamples will be combined to make up each sample. Sampling locations will be selected by tossing a 2-foot square PVC pipe in a randomly selected area in the field. The grass inside the square will be hand-clipped to about one inch above the ground with hand clippers and placed in a plastic garbage bag. Areas of the field that are not representative of the majority of the acreage will be avoided when sampling, (i.e., low grass yield areas, high weed areas, margins of the field). Grass sampling locations will be recorded using GPS.

Grass subsamples will be transported in a cooler with ice packs. The grass samples will be frozen about one hour after sampling. Frozen grass subsamples will be shipped overnight via Fed Ex to WSU-Puyallup and to the contract laboratory. Subsamples will be composited in the laboratory after wet weight and dry weight analyses have been performed. Crude protein analysis will be performed on the composited ground dry sample.

A duplicate sample will be collected and composited from a different randomly selected five locations in the field each sampling day. The duplicate sample will be treated in the same way as the first sample. All future sample locations will also be randomly selected.

Irrigation Water Sampling

Irrigation water will be collected from the irrigation water applicator equipment while the field is being irrigated, typically four times per year. Irrigation water samples will be collected into an acid-washed container twice at different times throughout the irrigation water application session. Bottle materials and preservatives are listed in Table 2. The two subsamples will be composited and mixed in an acid-washed container. The sample will be poured into two bottles with preservative and placed in a cooler with ice for shipping via FedEx. One sample will be shipped to the Ecology/EPA Manchester Environmental Laboratory in Manchester, Washington, for analysis, and the other to WSU-Puyallup.

Quality Control Procedures

Field Quality Control

Table 3A summarizes the quality control samples to be collected and analyzed for soil, grass, and manure.

Table 3A. Quality Control Samples, Types, and Frequencies.

Parameter	Media	Field Duplicates	Field Splits	Laboratory
Nitrate	Soil	Each event	1/4 events	Standard procedures for check standards, method blanks, analytical duplicates, and matrix spikes.
Crude protein	Grass	Each event	1/year	
Dry matter	Grass	Each event	1/year	
Ammonia	Manure	Each event	1/year	
Total Kjeldahl N	Manure	Each event	1/year	
Phosphorus	Manure	1/year	1/year	
Potassium	Manure	1/year	1/year	

A blind duplicate soil nitrate sample will be collected each time soil samples are collected. The duplicate will be collected using the same methods as the sample (composite of 15 one-foot cores) but at different randomly selected locations to evaluate field variability. A blind split nitrate sample will be submitted once every four sampling events to evaluate laboratory precision.

A blind duplicate grass sample will be collected each time grass samples are collected and analyzed for dry weight and crude protein. The duplicate will be collected using the same methods as the sample (composite of five subsamples) but at different randomly selected locations to evaluate field variability. Blind split samples for dry matter and crude protein will be submitted once per year to evaluate laboratory precision.

A blind duplicate manure sample will be collected on each date and analyzed for ammonia, total Kjeldahl N, and once annually for phosphorus and potassium. Two times per year blind split samples of manure and irrigation water will be submitted to the laboratory for all constituents analyzed.

Lab Quality Control

Routine laboratory quality control procedures will be used by contract laboratories to estimate the accuracy, precision, and bias introduced by laboratory procedures and will be reported to the project lead for data anlaysis. For irrigation water samples, Manchester Environmental Laboratory's quality control samples and procedures are discussed in detail in the Quality Assurance Manual, Manchester Environmental Laboratory (Ecology, 2001).

Data Management Procedures

Field data will be recorded at the time of sampling in a field notebook and will be maintained throughout the project and eventually archived in project files. Field data will be entered into spreadsheets and sent to the Ecology project lead. If appropriate, field data will be input into the EIM data repository.

Data generated by MEL (irrigation water results) will be managed by the (LIMS) and sent to the project lead in both electronic and hard copy formats. Data generated by WSU will be submitted to Ecology in quarterly reports as they become available. Data will be compared with project data quality objectives, and the reported results will be input into the EIM system. Laboratory data will be entered into spreadsheets for evaluation and presentation in graphical formats.

Any problems with laboratory analyses will be included with the data including corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. All laboratory quality control results associated with each data set will be included with the data in order to evaluate the accuracy of the data and to verify that measurement quality objectives have been met. Quality control data include results for all method blanks and check standards inlcuded in the sample batch, as well as analytical duplicates and matrix spikes prepared from samples for the study.

Washington State University will maintain communication with Ecology, Whatcom Conservation District, Natural Resources Conservation Service, and the dairy producer whose field will be used for the study. WSU will submit quarterly reports describing progress on the study including available results. A technical summary of the data and analysis set forth in this appendix will be prepared and include the following:

- Map showing sampling sites.
- Results of data collected, (i.e., soil nitrate, grass, and manure in units of mg/kg and lb/acre).
- Estimates of nitrogen application rates (manure + fertilizer + irrigation water) for each application event and annual totals.
- Estimates of nitrogen uptake by the grass crop for each cutting and annual totals.
- Analysis of the above information including relationships with weather data to be collected by Ecology, or if not available, the nearest reliable weather station, and implications for leaching of nitrate to groundwater.
- Photos showing soil, grass, and manure sampling.
- CD of all data and the technical summary.

The draft technical write-up will be presented to Ecology by January 10, 2007. Ecology will provide review comments by February 10, 2007. The final technical summary will be presented to Ecology by March 30, 2007.

Audits and Reports

WSU will conduct a Technical System Audit (TSA) which is a qualitative audit of conformance to the QA Project Plan described in this Appendix once per year after the first four weekly soil sampling events. The results of these two audits will be included in the next quarterly report so that corrective actions, if needed, can be implemented early in the project.

WSU will submit quarterly reports describing progress on the study including draft results of field studies described in Appendix A and an evaluation of data acceptability based on a review of quality assurance results. Quarterly reports should be submitted in December, March, June, and September.

Data Verification and Validation

Analytical data will be reviewed for any errors or omissions and verified by comparison with acceptance criteria described in the Quality Objectives section (Table 1A). As part of data review, field notes and data from contract laboratories WSU-Puyallup will be reviewed for errors and omissions and to ensure that data are correct, complete, and consistent. Other items that will be reviewed include:

- Results for quality control samples described in Quality Control section of this document accompany sample results.
- Quality control results indicate that acceptance criteria were met.
- Data qualifiers are properly assigned where necessary.
- Data specified in the Sampling Design section above were obtained.
- Methods and protocols specified in this QA Project Plan were followed.

Results that do not meet quality assurance requirements will be labeled with appropriate qualifiers, and an explanation will be provided in a quality assurance memorandum attached to the data package.

After receiving the data package, the project lead will verify that the results have met the measurement objectives for bias, precision, and accuracy. Precision will be estimated by calculating the RPD for the field duplicate results. Analytical bias is assumed to be within acceptable limits if laboratory quality control limits are met for blanks, matrix spikes, and check standards. If appropriate, sampling procedures, quality control steps, or analytical procedures will be modified to address identified problems.

If data measurement objectives have been met for all sampling episodes, the data will be considered acceptable for use except as qualified during the data review and validation process and the reported results will be input into the Ecology EIM system by the project lead.

Data Quality Assessment

If measurement quality objectives have been met for all sampling episodes, the data will be considered acceptable for use except as qualified during the data review and validation process.

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