QUALITY CONTROL AND QUALITY ASSURANCE (QC/QA) OPERATIONAL MANUAL

TABLE OF CONTENTS

A. SAMPLING & ANALYSIS OF GROUND-WATER AND SURFACE WATER

1. QUALITY ASSURANCE/QUALITY CONTROL OF WATER SAMPLING

Sample collection is often the greatest source of error in water monitoring and a proper Quality Assurance / Quality Control (QA/QC) program should be establish to ensure that data obtained is **accurate** and **representative** of actual water conditions.

Quality Control is a set of procedures followed to measure and, when necessary to correct data quality. **Quality Assurance** is a set of procedures followed to provide documentary assurance of the proper application of quality control and of the resulting data quality. The first step that should be undertaken in a sampling program before any field investigation commence, is the development of **a sampling protocol** - a written description of the detailed sampling procedures that should be followed throughout the program. The protocol should contain the following elements described later in details:

- sampling locations (use a map)
- sample collection method to be used
- equipment used, including calibration, maintenance and decontamination procedures (if necessary)
- number of required field sample
- quality control samples (number and type)
- type, number, and size of sample containers to be used
- sample volumes to be collected
- order of sampling (least contaminated to most)
- preservation instructions (the laboratory should provide the necessary preservatives, if needed)
- documentation requirements for water sampling records and sample log record
- procedures for maintaining chain of custody records
- plans for storage and transportation of samples.

2. QUALITY CONTROL SAMPLES

2.1 Control Site Samples

Control site samples are analyzed to determine background contamination level of groundwater foe comparison with other contaminated wells. Control site samples obtained from at least 1 well, which is installed upstream from the contaminated area provides baseline water quality information for the site. The well should abstract water

from the same aquifer that is contaminated. The control site samples should be taken in the same time as other samples.

2.2 QC Duplicates

A second set of samples should be collected from each sampling location (well piezometer, surface water) during the same sampling event to provide confirmation of contamination levels.

One set of duplicates should be collected for each set of samples, or for large sets, one each for every 20 samples.

For the project purpose, it is recommended that duplicate samples will account 5% of the samples taken for nitrate, phosphate and pesticide residue analyses. The duplicate samples will be spiked upon return to the laboratory for later analysis.

2.3 Blanks

Three types of quality control blanks are used during sampling:

> **Trip Blanks:** are used to verify if sample contamination occurred in the sample containers and/or as a result of sample cross contamination during sample transport and storage.
>
> **Field Blanks:** are used to verify if sample contamination occurred as a result of reagent and/or environmental contamination, such as from contaminated air at the sampling location.
>
> **Equipment Blanks:** these are designed to check for contamination from sampling equipment, such as pumps and bailers. Equipment blanks are useful for evaluating the effectiveness of equipment decontamination procedures.

Blank Preparation:

Use the same sampling containers for blanks as you would to collect water samples. However, the blanks are prepared using contaminant-free (blank) water. For water sampling, an excellent source of blank water is *distilled water*. All laboratories can supply distilled water.

> **Trip Blanks:** prepare by filling sample containers prior going into the field. These blanks are carried with the field samples in the sample cooler, and are not opened in the field.
>
> **Field Blanks:** prepare by pouring blank water from a clean container into a clean sample container in the field at the same time of sample collection.

Equipment Blanks: prepare in the field by pouring blank water into the collecting devices, and are processed as if they were field samples.

Prepare a blank of each type for each sample set, or for large sets one each for every 20 samples.

For the project purpose, blank samples representative of equipment rinses and distilled water pump through the system will be taken at each sampling event. Duplicate samples will be collected from the well and piezometer samples for nitrate, phosphate and pesticide residue analyses. Duplicate samples for bacteria examination will be taken only in specific situations, taking into account the high costs of the analysis. They will not be collected from the automatic samplers because these are continuos sampling equipment.

2.4 Spikes

Spiked samples are prepared in the field at the same time as sample collection to provide a quantitative measure of analyte loss by microbial degradation, volatilization, adsorption of sampling equipment, and other mechanisms. To avoid cross-contamination, spiked samples should not be carried in the same cooler as the field samples.

Samples are prepared by adding a known mass of the target compounds or elements of interest to a known volume of contaminant-free water. The concentration levels of target compounds should be about **10 times** the analytical detection limit. The concentration of target compounds in spiking solutions and their stability must be independently verified.

Both blanks and spikes should be available from the analysis laboratory.

For the project purpose, the duplicate samples will be spiked upon return to the laboratory for later analysis.

2.5 Split Samples

For the project purpose, the split samples will account for 1% of the samples taken for nitrate, phosphate and pesticide residue analyses. A fraction of the split samples are sent to the QA/QC laboratory.

2.6 Identification of Quality Control Samples

Each quality control sample should be assigned a unique number in the same time with the field samples, with the details of each sample recorded on a **Sample Log Record**.

3. RECORD KEEPING AND DOCUMENTATION

Record Keeping is an integral part of the sampling procedure. If the sampling is not adequately documented, the sample results may well be meaningless. The documentation can be grouped into three areas: **sample identification**, **sample log record**, and **chain of custody record**.

3.1 Sample Identification

Each sample should be assigned a unique number in the same sequence as the field samples were taken. The details of each sample should be recorded in a sample log record. To avoid laboratory bias during the analysis, the only information that the laboratory should be provided with is the sample number.

3.2 Sample Log Record

A detailed record should be kept of the sampling procedures and should contain the following:

- Sampling site details (site ID, Magellan GPS coordinates, other available coordinates)
- Sampling date and time
- Water sample (well, piezometer or drainage ditches) identification number (main sample/duplicate unique number)
- Unique sample number
- If the sample is a field sample, a control site, a QA/QC duplicate, a blank, a spike, or a split sample
- Performed field analyses (pH, electrical conductivity, temperature, TDS) and the instrument model used
- Sampling method and equipment
- Well or piezometer water level (m)
- Channel details (distance from the bank, estimated river flow)
- Type of analysis required for the sample
- If a preservative was added to the sample, and what type of preservation
- At what temperature the sample was preserved
- If the sample was filtered
- Remarks such as: Sampling conditions (weather, relevant sample site observations)
- Signature(s) of sample collector(s)

See the appendix for a recommended **Water Sampling Record** format.

3.3 Chain of Custody Record

The Chain of custody is a mechanism for ensuring that data from the analysis of a sample is **credible** and **defensible**. Chain of custody records provides a record of all the personnel responsible for handing the samples. This record contains all information necessary for proper tracking of field and blank samples from the time of their collection until the laboratory analysis reporting. These records must accompany the samples at all times.

Note: Samples should change hands as few times as possible on their way to the analyzing laboratory. Chain of custody records should be available from the analysis lab. See the appendix for a recommended format.

Chain of Custody Procedures:
1. Chain of custody begins at the time and point of sample collection.
2. Record the sample number and other appropriate information on the chain of custody form. Always record transfer of custody with your signature, the signature of the person receiving the sample, the date, and time. Retain an original of this record with site sample files.
3. Chain of custody must be maintained until completion of the analysis of a sample and the reporting of the analytical results.
4. The chain of custody record should be kept in the site samples files.

4. PLANNING A SAMPLING EVENT

a. Verify the property owners and appropriate parties when samples will be collected.
b. Ensure that you have legal authorization to enter a property and collect samples.
c. Check with laboratory personnel to arrange for analyses within the appropriate sample holding time. Pick up all the necessary sample bottles, trip blanks, and blank water for preparation of field and equipment blanks.
d. Ensure that the samples will get back to the lab cooled, and as quickly as possible. Make shipment arrangements if the samples will need to be shipped.
e. Maintain a site map identifying well locations to ensure that wells, piezometers and drainage ditches can be found.
f. Know the diameter of wells being sampled in order to enable sampling equipment of the proper size be available.
g. Prepare as much of the sample documentation as possible before the sampling event (i.e. sample log records, chain of custody records).

5. PRE-TRIP EQUIPMENT DECONTAMINATION

All field equipment that will come in contact with samples must be thoroughly cleaned to prevent inadvertent contamination from used equipment.

Procedures
1. Disassemble equipment into parts
2. Submerge and scrub equipment in solution of **phosphate-free detergent** and rinse with water.
3. Rinse equipment with tap water, followed by 3 separate rinses of distilled water.
4. Seal and label clean and dried equipment in new polyethylene bags, noting the date of decontamination, decontamination procedures, and person performing the decontamination.
5. If possible, dedicate one set of sampling equipment per sampling point to minimize potential contamination.

6. WATER SAMPLING PROCEDURES

6.1 Water Level Measurements

Water level measurements are the basis data of any hydrogeological investigation, and are easy to perform. Results from the following procedures should be recorded on the **Well Sample Record.**

Procedures

With Electric Water Level Indicator

1. Turn meter on the lower the probe sensor down the well until the light or buzzer goes on.
2. Slowly reel in the probe until the light or buzzer goes off. This is the water level. Record the depth to the water level from the top of the well casing or protective casing, whichever has been or will be surveyed in to a common datum for all local wells (mark the measuring point for future use).
3. Raise the probe a little, then lower again. Check your measurement.
4. Turn the meter off.
5. Reel out the line until it goes limp. Measure this depth - it is the depth of the well. Check this depth against the well label, and determine if silting has occurred - make a note of this.

With Weighted Steel Tape

1. Chalk the bottom 0.5 m or more of the tape.
2. Reel out the tape while listening for a “plop” as the weight hits the water (little noise will be made with a pointed weight). Then drop the weight about another 0.25 m.
3. Record the depth from the top of the well casing or protective casing, whichever has been or will be surveyed in to a common datum for all local wells (mark the measuring point for future use). Do not raise and re-lower.
4. Reel in the tape, note where the water has wetted the chalk dust. Subtract that from the depth measurement in Step 3 above. This is the depth to the water level.

6.2 Purging the Well

Only the piezometers will need to be purged prior to ground-water sampling in order to remove stagnant water and to ensure that samples collected are representative of aquifer conditions.

Equipment

Pump or bailer, or point-source sampler

Procedures

Before groundwater sample is collected for analysis, entire water column in the piezometer will be pumped out one day before the sample is collected. Once the piezometer pipe is filled with fresh groundwater from the saturated zone, within 24 hours, water samples will be collected for analytical analyses.

6.3 Grab & Composite Samples

6.3.1 Grab Samples

These are samples collected in a short period of time (a few seconds) ad are typically less expensive than composite samples. They represent a "snapshot" of the water quality at a specific place and time. There are two kinds of grab sampling:

1. Discrete

A sample that is taken at a selected depth and time.

2. Depth-Integrated

A sample that is collected over a predetermined portion or the entire depth of the water column at a selected time.

6.3.2 Composite Samples

These are samples that combine portions of multiple grab samples. There are two kinds of composite sampling:

1. Sequential

A sample made by continuos, constant mixing of equal water volumes collected at regular time intervals.

2. Flow Proportional

A sample made by mixing volumes of water proportional to the volume of water flow collected during regular time intervals.

Usually composite sampling is chosen to provide a more representative sample of heterogeneous water conditions or for surface water sampling.

6.4 Fundamental Sample Collection & Preservation Procedures

The following procedures should be followed for all sampling events in order to maintain the integrity between the time of sample collection and the time of analysis.

6.4.1 Frequency

Shallow groundwater wells/piezometers (less than 7 m in depth) will be sampled twice a month. Deeper piezometers (>7 m in depth) will be sampled once a month for water quality analyses.

Open drains/irrigation channels will be sampled once a month recording both primary and secondary flow. Data on flow will be collected from approximately mid-March to the begging of December each year.

6.4.2 Sampling Equipment

Piezometers and water wells will be sampled with contamination-free pumps. Groundwater from piezometers and water wells will be analyzed for pesticides, nitrate, bacteria, and other parameters such as phosphorous at various levels within the saturated groundwater zone.

Surface water will be monitored and measured using simple flumes installed at selected locations at the end of the demonstration plots for evaluating the effects of conservation

tillage and manure management on production and water quality. These plots will be established in selected villages and outlet points in the fields within the selected areas. Each flume will collect water samples as a function of runoff flow volume. Surface runoff from the field plots will be analyzed for various agricultural and manure contaminants.

6.4.3 Sample Containers

Sample container and cap selection for water collection depends on the parameter analyzed for. Refer to Table 1 for the required sample container volume, proper container and cap material to be used for specific sampling containers. The analytical laboratory should be able to provide sampling containers.

6.4.3.1 Sample Containers for Pesticides Analysis

It is recommended that 1-liter amber glass bottles (if available) be used for sampling to minimize the potential for photo-oxidation.

Glass bottles, rinsed with pesticide grade acetone, followed by Milli-Q water, and pre-combusted at 350^0 C will be the storage container for herbicide samples. Cap liners will be made of teflon and/or aluminium foil. Glassware will be pre-combusted at 350^0 C.

6.4.3.2 Sample Containers for Nitrate Ion Analysis

The storage containers for nitrate ion will be glass or polyethylene bottles, rinsed with a non-phosphate detergents and rinse with tap water, followed by 3 separate rinses of distilled water.

6.4.3.3 Sample Containers for Phosphate Ion Analysis

The storage containers for phosphate ion and total phosphorous will be glass bottles, rinsed with a non-phosphate detergents and rinse with tap water, followed by 3 separate rinses of distilled water.

6.4.3.4 Samples for Bacteria Analysis

Bottles of glass capable to be sterilised, and of 250, 500, and 1000 ml will be used for samples intended for bacteriological examination.

All glassware must be thoroughly cleaned, using a suitable detergent and hot water, rinsed with hot water to remove all traces of residual washing compound, and finally rinsed with distilled water.

Glass bottles should be sterilised not for less than 60 min at a temperature of 180^0 C, or in an autoclave at 121^0 C for 20 min.

6.4.4 Preservation and Storage of Water Samples

Nitrate, phosphate, pesticide residues and bacteria samples will be stored at 4^0 C. No additional preservation will be necessary. Samples are pre-filtered, if necessary. The

pesticides samples will be stored in the dark. Refer to Table 1 for preservation and storage condition.

6.4.5 Transport of Water Samples

Nitrate, phosphate, pesticide residues and bacteria samples will be transported to the laboratory in insulated containers at 4^0 C.

6.4.6 Maximum Holding Time

The Maximum Holding Time (MHT) is the length of time a sample be stored after collection and preservation, and before preparation and analysis significantly affecting the analytical results.

Nitrate ion, phosphate ion and pesticide residue samples will be analyzed within 24 hours. Bacteria samples will be analyzed within 6 hours. Refer to Table 1 for maximum holding times.

In the pesticides samples the extraction solvent should be added immediately after the samples collection.

6.6.7 Sampling Procedure

1. Person collecting the sample should wear clean gloves. Gloves should be changed for each well.
2. See Table 1 to identify the proper sample container volume and the cap material to be used for sample collection.
3. If preservation is required, preservatives should be added to the vial before the sample is collected, except when collecting samples in polyethylene bottles. In this instance, the preservation reagent should be added after the sample is placed in the polyethylene bottle. If a glass bottle is used for collecting samples, then the preservation reagent should be added before the sample is collected.
4. If preservatives are added to samples, then also add the preservative to the field blanks.
5. Immediate seal the container after sample collection and preservation (if necessary).
6. For bacterial examination sampling, the bottle will be kept unopened until the moment it is to be filled. The stopper and hood or cap will be removed as a unit, with care taken to avoid soiling. During sampling the stopper or cap and neck of the bottle will not be handed and will be protected from contamination. The bottle will be held near the base, filled without rinsing, the stopper or cap replaced immediately, and the hood secured around the neck of the bottle.
7. Assign the samples a unique sample number, with the details of each sample records in the **Sample Log Record**.
8. Keep samples cool (4^0 C) and in the dark, use cubes or crushed ice to chill samples as soon as they are collected, and ice packs to maintain internal temperature in the samples containers.
9. Deliver samples to the laboratory as soon as possible after collection, noting the recommended maximum holding time (MHT).

TABLE 1: WATER SAMPLE COLLECTION AND ANALYSIS PROCEDURES

PARAMETER	NITRATE ION	PHOSPHATE ION	PESTICIDE RESIDUES	BACTERIOLOGICAL EXAMINATION
• Container Volume (ml)	100	100	1000	1000
• Container/Cap Material	Glass bottles/ Polyethylene bottles	Glass bottles	Sterile (pre-combusted at 350^0C) glass bottles/teflon or aluminum foil cap liner	Sterile (pre-combusted at 350^0C) glass bottles
• Preservation (type & temp.)	Cool 4^0 C	Cool 4^0 C	Cool 4^0 C	Cool 4^0 C
• Max. Holding Time	24 hours	24 hours	24 hours, in dark	6 hours
• Current Analysis Method(s)	Phenol-disulfonic Acid Colorimetric or Spectro-photometric Method	Molybdo-phosphoric Acid - Hydrazine Sulfate Colorimetric or Spectro-photometric Method	Gas Chromatography Method	Multi-tube Fermentation Technique and/or Membrane Filter Technique
• Current Romanian Standards	STAS 3048/1-77	STAS 3265-86	STAS 12650-88	STAS 3001-91
• Proposed World Bank Analysis Method	Spectro-photometric Method using a Lachat Model AE ion analyzer.	To be completed	GC/MS Method	To be completed
• Proposed World Bank Method(s)	To be completed	To be completed	To be completed	To be completed

7. LABORATORY PREPARATION OF CHLORINATED HYDROCARBON PESTICIDES ANALYSIS (PROPOSED METHOD BASED ON ROMANIAN STANDARD STAS 12650-88)

7.1 Receiving Samples

A Chain of custody containing the number of samples, date, location, and all sample codes will accompany each shipment. A receipt will be returned to the sender after the chain of custody is verified against the samples shipped.

7.2 Sample Extraction

1. Stir the sampling bottle.
2. 500 ml sample into a separatory funnel.
3. Three separate extraction with 50, 50 and 25 ml petroleum ether strongly shaken for 10 min.
4. Remove the organic layers into an Erlenmeyer flash.
5. Separate the water from the solvent by adding 10 g anhydrous sodium sulphate for 15 – 20 min.
6. Filter through mineral wool.
7. Rinse the mineral wool with 10-ml petroleum ether and collect the liquid into the same flash.

7.3 Sample Concentration

1. Transfer the dried solution to an evaporative concentrator and reduce the volume at 2 ml.
2. Quantitatively transfer the solution to a 10-ml volumetric flash.
3. Rinse the concentrator twice with 2 ml petroleum ether each time.
4. Quantitatively transfer the rinsing solutions to the same 10-ml volumetric flash and dilute to volume.
5. Evaporate the solution to dryness at room temperature.

The concentrated samples could be hold maximum 4 weeks at temperature of – 15…-20^0 C.

7.4 Sample Analysis (GC)

7.4.1 Packing Preparation

Chromatographic columns may be purchased or prepared in the laboratory. The recommended column in the Romanian standard is 1.5% OV-17 and 1.95% QF-1/Chromosorb PAW-DMCS 0,125…1,50 mm.

1. Dissolve 0.3 g silicon oil type OV-17 and 0.39 g silicon oil type QF-1 in 60 ml acetone by strongly stirring with a magnetic stirrer for 1 hour.
2. Quantitatively transfer the solution into the evaporator beaker with acetone up to a volume of 70…75 ml.
3. Slowly add 20 g support – Chromosorb PAW-DMCS 0,125…1,50 mm (100…120 mesh) into the same beaker with stirring.

4. Gently swirl to mix the solution and the support for 10 min.
5. Evaporate the solvent and dry the support at 50^0 C.

7.4.2 Column Preparation

1. Rinse the column with sulphuric mixture, tap water up to a neutral pH, 50 ml ethylic alcohol, 50 ml ethylic ether, 50 ml benzene and 50 ml acetone and dry it into a drying stone at max. 50^0 C.
2. Fill the column with 10 % dimethil-dichlor-silan solution in toluene, keep the column filled for 10 min. and than empty it.
3. Rinse the column with 25 ml toluene, 25 ml methylic alcohol and 25 ml ethylic ether and dry it into a drying stone at max. 50^0 C.

7.4.3 Column Filling

1. Lightly pack a glass wool plug into one end.
2. Apply vacuum to that end.
3. Introduce the prepared packing (about 8 g) into the other end.
4. Vibrate the tubing until it is firmly filled.
5. Place a glass wool plug in the end.

7.4.4 Column Conditioning

1. Place the column in the normal operation position in the gas chromatograph.
2. Pass through the column the carrier gas (nitrogen) with a flow of 15…25 ml/min.
3. After 30 min. start the heating with a rate of 50^0 C/30 min, up to 230^0 C.
4. Hold at that temperature for 48 hours.

7.4.5 GC Conditions

1. Column temperature: 215^0 C
2. Evaporator temperature: 225^0 C
3. Detector temperature: 275^0 C
4. Carrier gas: Nitrogen
5. Carrier gas flow rate: 75 ml/min.
6. Volume of injected sample: 1…5 µl
7. Compound approximate relative retention:

Pesticide	Relative Retention Time
α-HCH	2.6
β-HCH	3.3
γ-HCH	3.8
δ-HCH	4.4
Aldrin	4.9
o, p'-DDE	8.1
p, p'-DDE	9.8
Dieldrin	10.9
o,p'-DDT	13.4
p,p'-DDT	17.3

7.4.5 Instrument Performance

Sensitivity: 1 …5 ng/l for α, β, γ, δ HCH and aldrin.
10..15 ng/l for o, p'-DDE, p, p'-DDE, o,p'-DDT, p,p'-DDT and dieldrin.

7.4.6 Instrument Calibration

GC is calibrated using standard solution D containing 0.2 ng of each above-mentioned pesticides.

7.5 QA/QC for the Laboratory Analysis of Water Samples

7.5.1 Sample Analysis by GC

1. Each sample set to contain at least one blank and one control sample.
2. Samples are analyzed in-groups of 25. Following the first twelve, two calibration standards are reinjected for instrument recalibration.
3. First and last injection will be check standards. They must be within 20% of known values. If not, recalibrate before starting analysis.

7.5.2 Laboratory Notebook

Laboratory notebook containing all records of instrument maintenance conditions, sample ID, date extracted, etc. will be maintained.

8. LABORATORY PREPARATION FOR HERBICIDES ANALYSES (ALACHLOR, ATRAZINE, METOLACHLOR, METRIBUZIN) (PROPOSED METHOD)

8.1 Samples Receiving

A Chain of custody containing the number of samples, date location, and all sample codes will accompany each shipment. A receipt will be returned to the sender after the chain of custody is verified against the samples shipped.

8.2 Sample Extraction

8.2.1 Spiked Samples

Spiking level will be representative of the range of expected herbicide concentrations in the water sample.

8.2.2 Extraction Procedure

1. 500 mg C-18 cartridge is activated with 2 ml of methanol followed by 2 ml of water using. Cartridge must remain wet.
2. 250 ml of sample containing 0.5% methanol and 250 ng propazine (surrogate) is passed through the cartridge at a flow rate of approximately 10 ml/min.
3. Push air through cartridge for 10 minute to remove residual water (after the sample has passed through).
4. 100 µl of terbutylazine (internal standard: 10 ng/µl) in methanol is added.
5. Elution with 2 ml of ethyl acetate into a small test tube.
6. Small amount of pesticide-free sodium sulfate is added to eluate. Shake and let stand.

7. Transfer ethyl acetate to a CG vial, seal, and store at -20^0 C until analysis.

8.3 Sample Analysis (GC/MS)

8.3.1 GC Conditions

1. Column: HP Ultra-1 (Cross-linked 100% methylsilicone), 25 m by 0.2 mm i.d. with a 0.33 µm film thickness.
2. Carrier Gas: He.
3. Head Pressure: 25 kPa (flow rate of 1 ml/minute)
4. Temperature Program: 50^0 C for 1 minute, ramp at 6^0 C/min. to 200^0 C, hold one minute.
5. Injector temperature: 260^0 C.
6. Splitless injection: 2 µl.
7. Compound Approximate Relative Retention

Herbicide	Relative Retention Time	Time (Terbuthylazine)
Atrazine	20.7 minutes	0.97
Propazine	20.9 minutes	0.98
Terbuthylazine	21.3 minutes	1.00
Metribuzin	22.7 minutes	1.07
Alachlor	23.6 minutes	1.11
Metolachlor	24.8 minutes	1.16.

8.3.2 MS Conditions

Ionization Voltage: 70 eV
Ion Source Temperature: 250^0 C
Electron Multiplier: 600 V above autotune value
Tuning: Autotune daily using PFTBA (perfluorotributylamine).
Minimum acceptable criteria for tuning are determined using ions at m/z 69, 215, and 502. Using 69 as base peak (100%), 502 must exceed 2% and 215 must exceed 35%.
Dwell Time: 50 millisecond/ion
Analysis: SIM (Selected ion monitoring) as shown.

Compound	Base	Molecular	Confirming
Alachlor	160	269	188
Atrazine	200	215	173
Metolachlor	162	238	146
Metribuzin	198	214	172
Propazine	214	229	172
Terbuthylazine	214	229	173

Confirmation will be based upon the presence of two confirming ions 9with area counts ±20%), and a retention time match of ±0.2% relative to terbuthylazine.

8.3.3 Instrument Performance

1. Sensitivity: 0.05 ng atrazine injected gives s/n<3.
2. Chromatographic performance: 1.0 ng atrazine injected gives a PGF value greater than 0.8, but less than 1.2.

PGF (Peak Gaussian Factor) = {1.83 x W (1/2)}/W (1/10)

where: W (1/2) = peak width at 1/2 height
W (1/10) = peak width at 1/10 height

3. Column performance: 1.0 ng atrazine and terbuthylazine injected gives a resolution value > 0.7.

Resolution (R) = t/w

where: t = the difference in retention time between atrazine and terbuthylazine
w = the average peak width at the baseline of two peaks.

8.3.4 Instrument Calibration

GC/MS is calibrated using four calibration levels (approx. 0.05, 0.10, 0.50, 0.75, and 1.25 ng/µl).

Calibration is to be accepted when R > 95%. Prior to each analysis, a check standard is run. It must agree within 20% of known value. If failure, recalibration is required. Analytical runs are made in-groups of 40. Two calibration standards are run midway through for calibration.

8.3.5 Method Quantification Limit

Detection limit is 0.2 ng/µl (ppb) for atrazine and metolachlor, metribuzin, and alachlor.

8.4 QA/QC for the Laboratory Analysis of Water Samples

8.4.1 Sample Analysis by GC/MS

1. Each sample set to contain at least one blank, and one control. Each sample wil contain a surrogate.
2. Samples are analyzed in groups of 25. Following the first twelve, two calibration standards are reinjected for instrument recalibration.
3. First and last injection will be check standards. They must be within 20% of known values. It not, recalibrates before starting analysis.

8.4.2 Laboratory Notebooks

Laboratory notebooks containing instrument maintenance and services records, sample ID, date extracted, surrogate level, etc., are maintained.

9. LABORATORY ANALYSIS OF NITRATE ION (CURRENT METHOD BASED ON ROMANIAN STANDARD STAS 3048/1-77)

9.1 Sample Receiving

A Chain of custody containing the number of samples, date, location, and all sample codes will accompany each shipment. A receipt will be returned to the sender after the Chain of custody is verified against the samples shipped.

9.2 Sample Extraction

No extraction is necessary. Samples are pre filtered, if necessary.

9.3 Sample Analysis

9.3.1 Instruments

Spectrophotometer or colorimeter for use at 410 nm for concentrations up to 10 mg/l or 480 nm for concentrations of 10…100 mg/l, with a light path of 1 cm
Magnetic stirrer

9.3.2 Reagents

Phenoldisulfonic acid
Sulphuric acid 10% solution
Ammonium hydroxide 25% solution
Hydrogen peroxide 3% solution
Aluminium sulphate 10% solution
Lead carbonate
Standard nitrate solution at 100 ppm NO_3-N
Silver sulphate solution at 1000 ppm Cl

9.3.3 Interference Removal

a. Chloride removal

1. Determinate the chloride content of the water (Romanian standard STAS 3049-52)
2. Treat 100 ml of sample with an equivalent amount of standard silver sulphate solution.
3. Remove the precipitated chloride either by centrifugation or by filtration, coagulating the silver chloride if necessary.
1. Evaporate the solution up to 100 ml over o hot water bath.

b. Nitrite conversion

1. Add 0.1 ml sulphuric acid to 100 ml of sample and stir.
2. Add dropwise (2…3 drops), with stirring hydrogen peroxide solution.
3. Let the treated sample to stand for 15 min to complete the conversion of nitrite to nitrate.
4. Make the proper deduction at the end of the nitrate determination for the nitrite concentration (STAS 3048/2-77).

c. Hydrogen sulphide removal
1. Add 0.2 g lead carbonate.
2. Aerate with the magnetic stirrer at maximum speed for 15 min.
3. Remove the precipitated sulphide either by centrifugation or by filtration.
4. Take 10 ml of supernatant for nitrate analysis.

d. Colour removal
1. Add 0.5 ml of aluminium sulphate solution to 100 ml of sample
2. Stir very thoroughly using the magnetic stirrer for 2 min. at maximum speed and other 5 min. at minimum speed.
3. Remove the precipitate by standing for a few minutes or by centrifugation.
4. Take 10 ml of supernatant for nitrate analysis.

e. Evaporation and colour development
1. Transfer 10 ml of sample into a casserole, and evaporate to dryness over o hot water bath.
2. Add 0.5 ml of phenoldisulfonic acid reagent and insure dissolution of all solid.
3. Allow standing for 15 min.
4. Add ammonium hydroxide solution by portion of 1 ml each until the maximum colour is developed.
5. Transfer the solution to a 10 ml volumetric tube and dilute to the mark.

f. Photometric measurements
1. Make photometric readings in cells with a 1/cm longer light path at a wave-length of 410 nm for concentrations up to 10 mg/l or 480 nm for concentrations of 10…100 mg/l.
2. Make readings against a blank prepared from the same volumes of phenoldisulfonic acid reagent and ammonium hydroxide solution as used for the sample.
3. Determine nitrate concentration using the calibration curve.

g. Colorimetric comparison
1. Transfer in 100 ml volumetric flashes different volumes of standard nitrate solution.
2. Transfer 10 ml of sample into a casserole, and evaporate to dryness over o hot water bath.
3. Add 0.5 ml of phenoldisulfonic acid reagent and insure dissolution of all solid.
4. Allow standing for 15 min.
5. Add ammonium hydroxide solution by portion of 1 ml each until the maximum colour is developed.
6. Transfer the solution to a 10 ml volumetric tube and dilute to the mark.
7. Make colorimetric readings against a blank prepared from the zero solution.

Prepare a calibration curve.

9.3.4 Instrument Calibration

Calibrate prior to each run using several levels.

Acceptable calibration is r > 0.9.

9.3.5 Method Quantification Limit

Detection limits are ± 0.02 ppm NO_3-N in water samples.

9.4 QA/QC for the Laboratory Analysis of Water Samples

9.4.1 Instrument Calibration

Instruments are re-calibrated at the beginning of each set. Calibration standards run once each ten samples. If the value varies from the known value >10%, instrument is re-calibrated.

9.4.2 Laboratory Notebooks

Laboratory notebooks containing instrument maintenance and service conditions, sample ID, date extracted, etc., are maintained.

10. LABORATORY ANALYSIS OF NITRATE ION (PROPOSED METHOD)

10.1 Sample Receiving

A Chain of custody containing the number of samples, date, location, and all sample codes will accompany each shipment. A receipt will be returned to the sender after the Chain of custody is verified against the samples shipped.

10.2 Sample Extraction

No extraction is necessary. Samples are pre filtered, if necessary.

10.3 Sample Analysis

10.3.1 Instrument Configuration of Lachat AE

Proportioning pump
Micro-sample loop
Colorimeter equipped with a 10 mm, 80 µl flow cell, and 520 nm filter
Manifold #10-107-04-I-E with cadmium reduction column

10.3.2 Reagents

15 M sodium hydroxide
Ammonium chloride buffer, pH=8.5
Sulfanilamide colour reagent
Stock standard at 1000 ppm NO_3-N

10.3.3 Instrument Performance

Sensitivity: 1 ppm NO_3-N at s/n > 3
Cadmium column performance: 100 ppm NO_3-N gives value >0.6 absorbance units.

10.3.4 Instrument Calibration
Calibrate prior to each run using several levels.
Acceptable calibration is r > 0.9.

10.3.5 Method Quantification Limit
Detection limits are 0.5 ppm NO_3-N in water samples.

10.4 QA/QC for the Laboratory Analysis of Water Samples

10.4.1 Instrument Calibration
Samples are run in sets of 60. Instruments are re-calibrated at the beginning of each set. Calibration standards run once each ten samples. If the value varies from the known value >10%, instrument is re-calibrated.

10.4.2 Laboratory Notebooks
Laboratory notebooks containing instrument maintenance and service conditions, sample ID, date extracted, etc., are maintained.

11. LABORATORY ANALYSIS OF PHOSPHATE ION (CURRENT METHOD BASED ON ROMANIAN STANDARD STAS 3265-86)

11.1 Sample Receiving
A Chain of custody containing the number of samples, date, location, and all sample codes will accompany each shipment. A receipt will be returned to the sender after the Chain of custody is verified against the samples shipped.

11.2 Sample Extraction
No extraction is necessary. Samples are pre filtered, if necessary.

11.3 Sample Analysis
11.3.1 Instruments
Spectrophotometer or colorimeter for use at 720 nm or with a red filter for concentrations of 0.1…1.0 mg/l
Hot plate
Distillation apparatus

11.3.2 Reagents
Hydrochloric acid 10% solution
Sulphuric acid d = 1.84 diluted at 1 + 4 and 5N
Phenolphthalein indicator solution
Sodium hydroxide or potassium hydroxide, 2N solution
Molybdate – hydrazine solution
Stock phosphate solution at 1000 ppm PO_4^{3-}
Standard phosphate solution at 10 ppm PO_4^{3-}

11.3.3 Interference Removal

a. Chloride and calcium removal

1. Determinate the chloride content (Romanian standard STAS 3049-52) and calcium content (Romanian standard STAS 3662-90) of the water.
2. If the chloride or calcium contents are bigger than 200 Cl^- mg/l or 200 Ca^{2+} mg/l, dilute the samples in order to reach lower Cl^- or Ca^{2+} concentrations.

b. Free phosphate analysis

1. Transfer 25 ml of sample in a 100-ml conic flash.
2. In case of higher contents of calcium (>200 mg/l), chloride (>200 mg/l) or phosphate (>1 mg/l), transfer a smaller volume of sample and dilute to 25 ml.
3. Add 20 ml of molybdate – hydrazine reagent.
4. Heat to boil the solution
5. Transfer the solution, after cooling in a 50-ml volumetric flash and dilute to mark.
6. Make photometric readings in cells with a proper light path at a wavelength of 720 nm or with a red filter.
7. Make readings against a reagents blank prepared from 25 ml distilled water and 20 ml of molybdate – hydrazine reagent
8. Determine phosphate concentration using the calibration curve.

c. Total phosphate analysis

1. Transfer 50 ml of sample and 1 ml of sulphuric acid 5N solution in a 100-ml balloon.
2. Attach the refrigerator to the balloon and boil for 90 min.
3. After solution cooling add 1 drop of phenolphthalein and then titrate with sodium hydroxide or potassium hydroxide solution till the end point of titration – the pink colour.
4. Transfer the sample in a 100-ml volumetric flash, dilute to the mark and homogenate.
5. Take 25 ml of sample or a smaller volume (see interference removal) and transfer in a 25-ml volumetric flash, diluting to the mark.
6. Transfer 25 ml of sample in a 100-ml conic flash.
7. Add 20 ml of molybdate – hydrazine reagent.
8. Heat to boil the solution
9. Transfer the solution, after cooling in a 50-ml volumetric flash and dilute to mark.
10. Make photometric readings in cells with a proper light path at a wavelength of 720 nm or with a red filter.
11. Make readings against a reagents blank prepared from 25 ml distilled water and 20 ml of molybdate – hydrazine reagent
12. Determine phosphate concentration using the calibration curve.

d. Preparation of calibration graph

1. Transfer in 100-ml conic flashes different volumes of standard phosphate solution (0, 1.0, 1.5, 2.5, and 5 ml) and dilute with water to 25 ml.
2. Add 2.0 ml of molybdate – hydrazine solution.
3. Make photometric readings in cells with a proper light path at a wavelength of 720 nm or with a red filter.

4. Make readings against blank prepared from zero concentration solution and 20 ml of molybdate – hydrazine reagent.
5. Prepare a calibration curve.

11.3.4 Instrument Calibration

Calibrate prior to each run using several levels. Acceptable calibration is $r > 0.9$.

11.3.5 Method Quantification Limit

Detection limits are ± 0.02 ppm PO_4^{3-}-P in water samples.

11.4 QA/QC for the Laboratory Analysis of Water Samples

11.4.1 Instrument Calibration

Instruments are re-calibrated at the beginning of each set. Calibration standards run once each ten samples. If the value varies from the known value >10%, instrument is re-calibrated.

11.4.2 Laboratory Notebooks

Laboratory notebooks containing instrument maintenance and service conditions, sample ID, date extracted, etc., are maintained.

12. BACTERIOLOGICAL EXAMINATION OF WATER SAMPLES (CURRENT METHOD BASED ON ROMANIAN STANDARD STAS 3001-91)

12.1 Sample Receiving

A Chain of custody containing the number of samples, date, location, and all sample codes will accompany each shipment. A receipt will be returned to the sender after the Chain of custody is verified against the samples shipped.

12.2 Tests for the Fecal Coliform Group

12.2.1 Culture Media

1. Composition – Bromcresol Red Lactose Bile Broth (Mac Conkey Culture):

Peptone-Trypticase	20	g
Lactose	10	g
Bile salts	1.5	g
Sodium chloride	5	g
Distilled water	1,000	cm^3
Red bromcresol	12	cm^3

2. Composition – Brilliant Green Lactose Bile Broth:

Peptone	10	g
Lactose	10	g

Oxgall	20	g
Brilliant green	0.0133	g
Distilled water	1,000	cm^3

12.2.2 Most Probable Number Procedure

The fecal coliform test may be expected to differentiate between coliforms of fecal origin and coliform from other sources. The test may be performed by multi-tube procedures. This procedure yield adequate information as to the source of the coliform groups (fecal and nonfecal) when used as a confirmatory test procedure.

Transfers should be made from all positive presumptive tubes to total coliform tests. This examination may be performed simultaneously with the confirmatory procedure using 1-2 drops of red bromcresol lactose bile broth or green lactose bile broth. Inoculated tubes are incubated in a water bath at 44±0.5 ^{0}C for 24 hours.

12.2.3 Interpretation

The color change (turns in yellow) and the gas production in a fermentation tube within 24 hours or less is considered a positive reaction indicating fecal origin. Failure to produce gas constitutes a negative reaction indicating a source other than the intestinal tract of warm-blooded animals. Fecal coliform densities are calculated based on Estimation of Bacterial Density procedure.

12.3 Tests for the Fecal Streptococcal Group

12.3.1 Culture Media

1. Composition – Buffer water:

To prepare *stock phosphate buffer solution*, dissolve 34.0 g potassium dihydrogen phosphate (KH_2PO_4) in 500 cm^3 distilled water, adjust to pH 7.2 with 1 N NaOH, and dilute to 1 liter with distilled water.

To prepare working solution, add 1.25 cm^3 stock phosphate solution to 1 liter distilled water. The solution is homogenized and sterilized at 121 ^{0}C for 20 min.

2. Composition – Sodium Azide Broth

Beef extract	4.5	g
Proteose-Peptone	15	g
Glucose	7.5	g
Sodium Chloride	7.5	g
Sodium Azide	0.2	g
Distilled water	1,000	cm^3

The components are dissolved in warm water, the pH is adjusted at 7.2…7.4. The solution is sterilized at 115 ^{0}C for 20 min.

3. Composition – Double Concentrated Sodium Azide Broth

Beef extract	9	g

Proteose-Peptone	30	g
Glucose	15	g
Sodium Chloride	15	g
Sodium Azide	0.4	g
Distilled water	1,000	cm^3

The components are dissolved in warm water, the pH is adjusted at 7.2…7.4. The solution is sterilized at 115 ^{0}C for 20 min.

4. Composition – Red bromcresol sodium azide broth for confirmation

Proteose-Peptone	20	g
Glucose	5	g
Sodium Chloride	5	g
Potassium hydrogen phosphate (K_2HPO_4)	2.7	g
Potassium dihydrogen phosphate (KH_2PO_4)	2.7	g
Sodium Azide	0.4	g
Red bromcresol 1.6% sol. in ethanol 98% vol.	2	cm^3
Distilled water	1,000	cm^3

The components are dissolved in warm water (except the red bromcresol solution), the pH is adjusted at 7.2…7.3. The solution is sterilized at 115 ^{0}C for 30 min.

12.3.2 Multiple-Tube Technique

1. Presumptive Test

a. Procedure

1) Inoculate a series of tubes of double concentrated sodium azide broth with appropriate graduated quantities of the water to be tested.
2) Incubate inoculated tubes at 37±0.5 ^{0}C for 48 hours. All tubes showing turbidity with or without sediment after 48 hours incubation must be subject to the Confirmed Test.

2. Confirmed Test

a. Procedure

1) Transfer one or two drops from each sodium azide broth tube to a tube containing red bromcresol sodium azide broth.
2) Incubate the inoculated tubes for 24 hours at 44±0.5 ^{0}C. The presence of fecal streptococci is indicated by the color charge in yellow and by sediment formation at the bottom of the tube, or occasionally by a dense turbidity. Record all positive results.

3. Computing and Recording of MPN

Fecal streptococci densities are calculated based on Estimation of Bacterial Density procedure.

B. SAMPLING & ANALYSIS OF SOIL

13. QUALITY ASSURANCE / QUALITY CONTROL SOIL SAMPLING

A proper Quality Assurance / Quality Control (QA/QC) program should be establish to ensure that data obtained is **accurate** and **representative** of actual soil conditions.

Quality Control is a set of procedures followed to measure and, when necessary to correct data quality. **Quality Assurance** is a set of procedures followed to provide documentary assurance of the proper application of quality control and of the resulting data quality.

The first step that should be undertaken in a sampling program before any field investigation commence, is the development of **a sampling protocol** - a written description of the detailed sampling procedures that should be followed throughout the program. It should contain the following elements described later in details:

- sampling locations (use a map)
- sample collection method to be used
- equipment used, including calibration, maintenance and decontamination procedures (if necessary)
- number of required field samples
- quality control samples (number and type)
- type, number, and size of sample containers to be used
- sample volumes to be collected
- order of sampling (least contaminated to most)
- preservation instructions (the laboratory should provide the necessary preservatives, if needed)
- procedures for maintaining chain of custody records
- plans for storage and transportation of samples.

14. QUALITY CONTROL SAMPLES

14.1 Control Site Sample

This sample is used to determine background levels of chemicals in the clean soil for comparison with the contaminated soil. One control site sample (sample blank) should be obtained and analyzed for each overall site that is being assessed.

The control site sample should have common soil characteristics with the contaminated site, but should obviously not be contaminated. It should be located near the

contaminated site, and upgradient from the contamination. If there is no suitable sample blank location nearby, a site in the general region should be chosen. The control site sample should be taken just prior to the field samples.

14.2 QC Duplicates

The collection of duplicate samples provides for the evaluation of the laboratory performance by comparing analytical results of two samples of the same location. A minimum of one duplicate should be collected for every 20 samples.

Obtaining duplicate samples in soil requires **homogenization** of the sample aliquot before the filling sample containers. This should be accomplished by filling a properly decontaminated stainless steel tray or bowl and mixing it with a clean instrument. Once mixing is completed it should be divided in half and containers should be filled by scooping sample material alternative from each half.

For the project purpose, it is recommended that duplicate samples will account 5% of the samples taken for nitrate, phosphate and pesticide residue analyses. The duplicate samples will be spiked upon return to the laboratory for later analysis.

14.3 Spikes Samples

Spiked samples are prepared in the field at the same time as sample collection to provide a quantitative measure of analyte loss by microbial degradation, volatilization, adsorption of sampling equipment, and other mechanisms. To avoid cross-contamination, spiked samples should not be carried in the same cooler as the field samples.

Samples are prepared by adding a known mass of the target compounds or elements of interest to a known volume of contaminant-free water. The concentration levels of target compounds should be about **10 times** the analytical detection limit. The concentration of target compounds in spiking solutions and their stability must be independently verified.

For the project purpose, the duplicate samples will be spiked upon return to the laboratory for later analysis.

14.4 Split Samples

For the project purpose, the split samples will account for 1% of the samples taken for nitrate, phosphate and pesticide residue analyses. A fraction of the split samples are sent to the QA/QC laboratory.

14.5 Identification of Quality Control Samples

Each quality control sample should be assigned a unique number in the same time with the field samples, with the details of each sample recorded on a **Sample Log Record**.

15. RECORD KEEPING AND DOCUMENTATION

Record Keeping is an integral part of the sampling procedure. If the sampling is not adequately documented, the sample results may well be meaningless. The documentation can be grouped into three areas: **sample identification**, **sample log record**, and **chain of custody record**.

15.1 Sample Identification

Each sample should be assigned a unique number in the same sequence as the field samples were taken. The details of each sample should be recorded in a sample log record. To avoid laboratory bias during the analysis, the only information that the laboratory should be provided with is the sample number.

15.2 Sample Log Record

A detailed record should be kept of the sampling procedures and should contain the following:

- Sampling site details (site ID, Magellan GPS coordinates, other available coordinates)
- Sampling date and time
- Soil sample identification number
- Unique sample number
- If the sample is a field sample, a control site, a QC duplicate, a spike, or a split sample
- Sampling method and equipment
- Type of analysis required for the sample
- If a preservative was added to the sample, and what type of preservation
- At what temperature the sample was preserved
- Remarks such as: Sampling conditions (weather, relevant sample site observations)
- Signature(s) of sample collector(s).

See the appendix for a recommended **Sample Log Record** format.

15.3 Chain of Custody Record

The Chain of custody form provides a record of all the personnel responsible for handing the samples. It must accompany the samples at all times. Samples should change hands as few times as possible on their way to the analyzing laboratory. Chain of custody acts as a mechanism for ensuring that data from the analysis of a sample is credible and defensible.

Chain of Custody Procedures:

1. Chain of custody begins at the time and point of sample collection.
2. Record the sample number and other appropriate information on the chain of custody form. Always record transfer of custody with your signature, the signature of the person

receiving the sample, the date, and time. Retain an original of this record with site sample files.
3. Chain of custody must be maintained until completion of the analysis of a sample and the reporting of the analytical results.
4. The chain of custody record should be kept in the site samples files.

16. PLANNING A SAMPLING EVENT

a. Verify the property owners and appropriate parties when samples will be collected.
b. Ensure that you have legal authorization to enter a property and collect samples.
c. Check with laboratory personnel to arrange for analyses within the appropriate sample holding time. Pick up all the necessary sample bottles, trip blanks, and blank water for preparation of field and equipment blanks.
d. Ensure that the samples will get back to the lab cooled, and as quickly as possible. Make shipment arrangements if the samples will need to be shipped.
e. Maintain a site map identifying soil sample locations.
f. Prepare as much of the sample documentation as possible before the sampling event (i.e. sample log records, chain of custody records).

17. EQUIPMENT CLEANING

A wire brush will be used to remove any soil near the cutting edge of the soil probe. The tip of the probe will be washed with methanol after each sample to remove any soil residue. If a hydraulic coring machine will be used, the power wire brush is used to clean the soil tubes.

18. SOIL SAMPLING PROCEDURES

18.1 Grab & Composite Samples

There are two common methods of soil sampling: **grab samples** and **composite samples.** A grab sample is a sample taken from one specific location, at one time. A composite sample is a combination of smaller samples taken at different locations or at different times.

18.2 Fundamental Sample Collection & Preservation Procedures

The following procedures should be followed for all sampling events in order to maintain the integrity between the time of sample collection and the time of analysis.

18.2.1 Frequency

Soil sampling will occur within fields of varying sizes and thus may cover a range of soil types within a single field. The number of samples collected will be representative of each field and some guidelines will be established for each site as to its variability. These guidelines will become available through some structured sampling with an ancillary parameter, e.g. bulk density, organic matter, or nitrate concentration, which may provide an analysis of the patterns of variability within a field. As many studies have shown, a

random sampling can accomplish the objectives of most studies, given that the surface properties are somewhat uniform. The resources available for data collection, processing, and analysis also may govern the number of samples.

18.2.2 Sampling Equipment

Soil sampling tubes and hydraulic driven soil probes are being used more recently. A number of liners for zero-contamination field penetration devices for both hand and machine soil coring tubes are available with caps of different colors to differentiate depth. The liners are made of cellulose acetate polymers and range from 2.5 – 5.0 cm in diameter, and from 20 – 200 cm in length. Using waterproof, permanent markers, these liners are marked with the plot sample code immediately after removal from the soil coring tube.

In sample collection, the tube is inserted to its full length at once to avoid contamination from soil falling into the tube. This poses some difficulties with the longer tubes in hard soil; and, in that case, a shorter tube length is used with care taken to avoid contamination. Each field and farming system presents different problems, and precautions will be taken to obtain a sample, which is not compressed by excess force.

18.2.3 Processing of Soil Samples

Samples are sectioned in a pesticide-free environment into depth increments and sub-sampled, if necessary, before they are transported to the analyzing laboratory. The sample size ranges from 100 – 150 g.

18.2.4 Sampling Containers

Sample container and cap selection for soil collection depends on the parameter analyzed for. Refer to Table 2 for the required sample container volume, proper container and cap material to be used for specific sampling containers. The analytical laboratory should be able to provide sampling containers.

18.2.4.1 Sample Containers for Pesticides Analysis

It is recommended that amber glass vial (if available) be used for sampling to minimize the potential for photo-oxidation.

Glass jars, rinsed with pesticide grade acetone, followed by Milli-Q water, and pre-combusted at 350^0 C will be the storage container for herbicide samples. Cap liners will be made of teflon and/or aluminium foil. Glassware will be pre-combusted at 350^0 C.

18.2.4.2 Sample Containers for Nitrate Ion Analysis

The storage containers for nitrate ion will be glass jars, rinsed with a non-phosphate detergents and rinse with tap water, followed by 3 separate rinses of distilled water.

18.2.4.3 Sample Containers for Phosphate Ion Analysis

The storage containers for phosphate ion and total phosphorous will be glass jars, rinsed with a non-phosphate detergents and rinse with tap water, followed by 3 separate rinses of distilled water.

18.2.5 Storage of Soil Samples

After removing the core, the extra volume in the upper end of the tube will be packed with sterile cotton. This will keep the surface of the soil sample undisturbed. The marked and capped tube will be immediately placed horizontally into a container of dry ice or ice depending on site protocol.

18.2.6 Transport of Soil Samples

Each soil core will be placed in an insulated container at 4^0 C to transport it from the field to the freezer. The insulated containers, which are of sufficient length to horizontally accommodate the soil core, have airtight lids and handles for lifting and carrying.

18.2.7 Maximum Holding Time

The Maximum Holding Time (MHT) is the length of time a sample be stored after collection and preservation, and before preparation and analysis significantly affecting the analytical results.

Samples will be placed in -20^0 C freezers within 24 hours after coring and/or processing.

TABLE 2: SOIL SAMPLE COLLECTION AND ANALYSIS PROCEDURES

PARAMETER	NITRATE ION	PHOSPHATE ION	PESTICIDE RESIDUES
• Container Volume (ml)	100	100	100
• Container/Cap Material	Glass jar	Glass jar	Sterile (pre-combusted at 350^0C) glass jar/teflon or aluminum foil cap liner
• Preservation (type & temp.)	Cool -20^0 C	Cool -20^0 C	Cool -20^0 C
• Max. Holding Time	24 hours	24 hours	24 hours, in dark
• Current Analysis Method(s)	Phenol-disulfonic Acid Colorimetric or Spectro-photometric Method	Molybdo-phosphoric Acid - hydrazine Sulfate Colorimetric or Spectro-photometric Method	GC Method
• Current Romanian Standards	ICPA Method	ICPA Method	ICPA Method
• Proposed World Bank Analysis Method	Spectro-photometric Method using a Lachat Model AE	To be completed	GC/MS Method

	ion analyzer.		
• Proposed World Bank Method(s)	To be completed	To be completed	To be completed

19. LABORATORY PREPARATION FOR SOIL EXTRACTS/ANALYSES – HERBICIDES (ALACHLOR, ATRAZINE, METOLACHLOR, METRIBUZIN) (PROPOSED METHOD)

19.1 Soil samples receiving

A Chain of custody containing the number of samples, date location, and all sample codes will accompany each shipment. A receipt will be returned to the sender after the Chain of custody is verified against the samples shipped.

19.2 Storage of soil samples

Samples are stored at -20^0 C.

19.3 Soil samples holding time

Samples are extracted within 6 months following receipt at the analyzing laboratory. Extracts are analyzed by GC techniques within 30 days of preparation.

19.4 Extraction of soil samples for herbicide residue

19.4.1 Spiking

Soil sediment samples are spiked with terbutryne (surrogate).

19.4.2 Extraction Procedure

The extraction procedure uses a robotic system from Zymark. Sequenced operations include:

1. Weigh 10 g of soil into a 50 ml centrifuge tube (manual).
2. Add 20 ml of extraction solvent. Vortex and let stand 12 hours at room temperature to facilitate partitioning (manual).
3. Position the centrifuge tube on the Zymark robotic system rack.
4. Centrifuge at 2700 rpm for 10 minutes. Transfer the extraction solvent to another centrifuge tube.
5. Repeat with an additional 14 ml of extraction solvent.
6. Evaporate the combined extracts under nitrogen at 50^0 C for 65 minutes.
7. Transfer the extract to a C-18 cartridge activated with 2 ml of methanol followed by 2 ml of water.
8. Elute the herbicides with 2 ml ethyl acetate containing the internal standard (terbuthylazine).

19.4.3 Soil Moisture Content

Soil moisture content is defined on a wet-weight basis and is determined gravimetrically on one 20 g sample dried at 105^0 C for 12 hours in an oven.

$$\% H_2O = \{(Wet-Dry)/Wet\}\ 100$$

19.5 Soil Sample Analyses

19.5.1 GC Conditions

1. Column: HP-5 (cross-linked 5% phenyl, 95% methylsilicone), 25 m by 0.32 mm i.d. with a 0.52 µm film thickness.
2. Head Presure: 80 kPa.
3. Carrier Gas: He, flow rate of 1 ml/minute.
4. Temperature Program: 60^0 C (hold 1 minute) to 150^0 C (hold 0.3 minutes), then ramp at 4^0 C/min to 210^0 C (hold 1 minute).
5. Injector temperature: 250^0 C.
6. Detector temperature: 280^0 C.
7. Splitless injection: 2 µl.

19.5.2 Detector

1. Hydrogen: 3 ml/min.
2. Air: 120 ml/min.
3. Helium, make-up gas: 30 ml/min.

19.5.3 Instrument Performance

1. Sensitivity: 0.2 ng antrazine on column gives s/n<3.
2. Chromatographic performance: 1.0ng antrazine on column gives a PGF value greater than 0.8, but less than 1.2.

   PGF (Peak Gaussian Factor) = {1.83 x W (1/2)}/W (1/10)

   where: W (1/2) = peak width at 1/2 height
   W (1/10) = peak width at 1/10 height
3. Column performance: 1.0 ng antrazine and terbuthylazine on column gives a resolution greater than 0.7.

   Resolution (R) = t/w

   where: t = the difference in retention time between antrazine and terbuthylazine
   w = the average peak width at the baseline of two peaks.

19.5.4 Instrument Calibration

GC is calibrated using four calibration levels (approx. 0.1, 0.25, 0.5, and 1.0 ng/µl). Calibration is to be accepted when R > 95%. Prior to each analysis, a check standard is run. It must agree within 20% of known value. If failure, recalibration is required.

Analytical runs are made in-groups of 40. Two calibration standards are run midway through for calibration.

19.5.5 Method Quantification Limit

Detection limits are 5 ng/g (ppb). Attenuation and injection volumes are adjusted to give full-scale response for a 1 ng of atrazine on column.

19.6 QA/QC for the Laboratory Analysis of Soil Samples

18.6.1 Sample Analysis

Laboratory QA/QC is done on each group of 40 samples according to the following protocol:

1. One blank is used to measure method contaminants and will be an extract of the soil representative of the field site. A reagent blank may be run as a substitute if pesticide-free soil cannot be found.
2. Four matrix spikes on soils representative of the site are added. Spiking levels will vary to bracket the expected herbicide values.
3. Terbuthyne (surrogate) is added to each sample. 2% of all positive samples are confirmed by GC/MS using SIM. The same parameters are used for soil as for water analysis.
4. Following analysis representative extracts are sent to an external laboratory for confirmatory analysis.

19.6.2 Laboratory Notebooks

Laboratory notebooks containing instrument maintenance and services records, sample ID, date extracted, surrogate level, etc., are maintained.

20. LABORATORY ANALYSIS OF NITRATE ION (PROPOSED METHOD)

20.1 Sample Receiving

A Chain of custody containing the number of samples, date, location, and all sample codes will accompany each shipment. A receipt will be returned to the sender after the Chain of custody is verified against the samples shipped.

20.2 Sample Storage

Samples are frozen at -20^0 C.

20.3 Soil Samples Holding Time

Samples are extracted within 6 months of receipt at the analyzing laboratory. Extracts are analyzed within 14 days.

20.4 Extraction of Soil Samples for Nitrate Ion

20.4.1 Extraction Procedure

1. 20 g of soil is weighed into a 250 ml Erlenmeyer flash.

2. 100 ml of 2 M potassium chloride is added, shaken for 1 hour.
3. Extract is filtered through Whitman #4 into a 20 ml scintillation vial.

20.4.2 Soil Moisture Content

Soil moisture content is defined on a wet-weight basis and is determined gravimetrically on one 20 g sample dried at 105^0 C for 12 hours in an oven.

$$\% H_2O = \{(Wet-Dry)/Wet\}\ 100$$

20.5 Soil Sample Analysis

20.5.1 Instrument Configuration

Autosampler
Proportioning pump
Micro-sample loop
Colorimeter equipped with a 10 mm, 80 µl flow cell, and 520 nm filter
Reaction module #12-107-1-B with cadmium columns.

20.5.2 Reagents

15 M sodium hydroxide
Ammonium chloride buffer, pH=8.5
Sulfanilamide colour reagent
2 M potassium chloride .

20.5.3 Instrument Performance

Sensitivity: 0.5 ppm NO_3-N at s/n > 3
Cadmium column performance: 20 ppm NO_3-N gives absorbance of >0.10.

20.5.4 Instrument Calibration

Calibrate prior to each run using 0.2, 0.5, 1.0, 5.0, 10.0 ppm standards.
Acceptable calibration is r > 0.9.

20.5.5 Method Quantification Limit

Detection limits are 0.5 ppm NO_3-N in soil samples.

20.6 QA/QC for the Laboratory Analysis of Soil Samples

20.6.1 Instrument Calibration

Lachat Autoanalyzer is calibrated prior to each autosampler run. Every tenth sampler tube is a check standard. If the value varies by greater than 20% from the accepted value, instrument requires recalibration. One control soil sample is run with each group to verify extraction and instrument performance.

20.6.2 Laboratory Notebooks

Laboratory notebooks containing instrument maintenance and service conditions, sample ID, date extracted, etc., are maintained.

21. QA/QC EVALUATION CRITERIA

21.1 Quality Control Checks

Laboratory quality control practices for the analytical aspects of this project include:

1. Compliance by the laboratory analyst to all approved or certified protocols.
2. Parallel analysis of method or reagent blanks is carried out with each test run.
3. Duplicate samples are analyzed.
4. Spiked samples with known concentration are analyzed.
5. Known reference standards for preparing calibration curves to calculate results are used.
6. Quality Control standards, if provided, are analyzed against certified laboratory standards to verify calibration accuracy.
7. Instruments are calibrated and standardized, as specified in the instrument manuals, and in the approved laboratory protocol.
8. The certified Quality Control standard results are plotted prior to calculating sample results to verify that results are within established ranges of acceptability.
9. All laboratory results are reviewed by at least two individuals prior to release.
10. All results not within excepted ranges for the particulate analyte are flagged.
11. Acceptability of duplicate analysis results are evaluated using a statistical comparison.
12. Acceptability of spiked samples is evaluated using a statistical comparison.

22. CORRECTIVE ACTION PLAN

22.1 Spiked Samples

Corrective action is taken when the analysis of spikes and/or controls result in values greater than 3 standard deviations from the accepted value (standard deviations are determined from updated averages).

22.2 Duplicate (Water only)

Corrective is taken when percentage of deviations between duplicates (one by local lab, other by external lab) exceeds 100% at 0.2 to 1.0 ppb and 50% at 1.0 to 20.0 ppb.

22.3 Audits

Corrective action is taken if there is a failure to comply with the requirements of an audit.

22.4 Non-standard Procedures

Corrective action is taken if nonstandard procedures, i.e. deviations from the approved laboratory protocol, are used.

22.5 Corrective Action

If corrective action is necessary, the analyst will take the following steps to remedy the problem:

1. Recheck all calculations and measurements data.

2. Check instruments to ensure proper calibration and operation.
3. Check reagents for proper reactivity.
4. Insure that proper operating procedures are followed.
5. Reanalyze all samples that were run during the problem sequence.
6. Seek assistance from the instrument manufacturer if the problem continues.

23. MANDATORY PROCEDURES FOR GOOD FIELD / LABORATORY PRACTICES

23.1 Field Equipment

23.1.1 Surface Water Samplers

The time setting on the surface water samples is checked weekly and recorded in the field notebook along with the exact time from a standard clock. A verification of the sample bottle identification and the position of the sampler, as well as a visual check of the sampler tube connections and condition, of the system is made and recorded.

23.1.2 Piezometer/Water Well Pumps

The volume of the well is calibrated every three month and the value recorded. The condition of the pumps and the sampling tubes is checked during each field collection sequence. The positioning of the pumps and the verification that the pump is in a level position is checked for each field setup.

23.1.3 Soil Sampling

The condition of the hydraulic core is checked weekly. The cutting bit is sharpened and maintaining during each sampling sequences. The condition of the augers is checked before and after each field sampling sequence.

23.1.4 CR10 Data Acquisition System

The time setting on the Campbell Scientific CR10 Data Acquisition System is checked weekly and recorded in the field notebook along with the exact time from a standard clock. The operation of the program is verified on a weekly basis and recorded in a field notebook. Data, which are stored from the CR10, are referenced by file name and location in the field notebook.

23.2 Laboratory Instruments

Checks on laboratory equipment are recorded in the laboratory notebook.

23.2.1 Balances

Balances are calibrated monthly using a recognized standard weight and the auto-calibration procedure on the balances.

23.2.2 Pipettes

Digital pipettes are checked monthly for accuracy.

23.2.3 Ovens

Cleaning and drying ovens are monitored weekly for accuracy of temperature.

23.2.4 Refrigerators

Refrigerators and freezers are monitored daily for accuracy of temperature.

23.2.5 Analytical Instruments

The analytical instruments and other hardware are maintained daily according to manufacturer's specifications. Repairs and semi-annual preventive maintenance are to be performed only by certified, manufacturer-trained service engineers.

23.3 Safety

The toxicity or carcinogenic of each reagent used inn these methods has not been precisely defined; however, each chemical must be treated as a potential health hazard. Accordingly, exposure to chemicals must be reduced to a minimum. The laboratory is responsible for maintaining a current awareness file of Safety Inspectorate regulations regarding the safe handling of all chemicals specified in these methods. A reference file of Material Safety Data Sheets (MSDS) issued by the Research Institute for Work Safety is available to all personnel involved in chemical analysis. Additional references to laboratory safety are available from the Facility Safety Officer.

24. PERSONNEL/CHAIN IN COMMAND

Each monitoring site will be under the direction of the UPP Project Manager. A Field Manager (Environmental Consultant) and two Analytical Lab Managers (one from the local Environmental Protection Inpectorate and another from the Public Health Directorate) report directly to the UPP Project Manger. The Field Manager is responsible for all field operations and field personnel. The Analytical Lab Managers are responsible for the operation and personnel involved in chemical analysis. Individual investigators interact with the Project Manager, Field Manager and Lab Managers on individual project needs.