

Chapter 9

Analysis of Nitrogen in Soils and Biosolids

The reliability of a biosolids application rate depends on many factors, not the least of which is the accuracy of the analytical information on which the calculations are based. Knowing the amount of residual N in the soil and the amount and form of N in the biosolids—and being able to rely on that information—are critical links in the chain of N management.

Biosolids managers must know the concentrations of the forms of N in the biosolids and soil that are or can become available to plants. Although there are other forms of N in soils and biosolids, the only ones of concern here are organic and inorganic forms including nitrate (NO_3^- -N), ammonia (NH_3 -N), and ammonium (NH_4^+ -N). During analysis, NH_4^+ -N is often converted to NH_3 -N and analytical results are then reported as NH_3 -N. Because both forms are considered to be plant available, this combined analysis does not diminish the quality of the result.

Whenever N values are reported for biosolids samples, it is important to also include values for total solids and volatile solids content. The percent total solids value is used as a component of application rate determinations. The total solids value is also used to derive a dry weight value from a wet weight result and to verify the dry weight values reported. The volatile solids value (expressed as a percent of total solids) is used to draw inferences about expected and reported N values.

The analysis of soils and biosolids for N presents challenges to both the chemist and the biosolids manager:

- Both soils and biosolids may contain compounds capable of interfering with a chosen analytical methodology.
- The concentration of N in biosolids can be high relative to the effective range of some methods of analysis.
- Dilution of the sample may be required, which can lead to errors in analysis.
- Methods of sample processing and preparation can have an impact on analysis results.
- The high organic matter content of some biosolids can complicate sample digestion and some analytical methods.
- Biological activity can result in transformations and/or loss of nitrogen between the time of sampling and analysis.
- Analytical methods may not be precise enough to cleanly separate available and unavailable forms of N.

Ultimately, the best approach to managing these challenges is the consistent use of proper sampling, analytical, and reporting methods. This chapter addresses preparation of a sampling plan; collection, preparation, and analysis of samples; and reporting of results. Each of these steps includes many critical elements. It is beyond the scope of this chapter to present a detailed discussion of each element, but the major points are covered and good references are provided.

Preparing a sampling plan

A sampling plan—even a rudimentary plan—is an important tool in assuring that samples are properly collected, handled, and processed. For complex sampling projects, the assistance of a person experienced in designing sampling plans and programs may be required. A basic sampling plan should identify the medium to be sampled, the equipment and supplies needed for sampling (including forms, labels, and containers), the sample locations, and the methods for collecting, handling, storing, and transporting the samples. For soil sampling (or for large piles of biosolids), a map identifying specific sites to be sampled is important. If sampling at different depths is necessary, this should also be discussed. In some cases, many discrete samples may be needed. In other cases, composite samples (which are then subsampled) may be just as informative and less expensive.

Collecting samples

Sample collection is the first step in the process. If sample collection technique is poor, if samples are not representative, or if sample handling is careless, then the reliability of the data will be questionable and any decisions or conclusions based on the data will be suspect.

For biosolids, samples must be taken at the end point of the treatment process. If the biosolids are going directly from a digester to the application site, then samples should be taken from the digester. If the biosolids are going to a drying bed before being applied to the site, samples should be taken from the drying bed. If biosolids are going to be stored prior to use, then samples may need to be collected from the storage site.

For soils, the season of sampling may be most important. NO_3^- in soil may be measured after harvest (report card sampling) to determine whether the amount of N applied to the last crop was appropriate. Both NH_4^+ and NO_3^- may be measured before planting in dryland cropping and low rainfall areas; such sampling is not as necessary in higher rainfall zones because residual soil N may be leached from the soil during the winter. In some cases, soil N may be measured during the growing season to determine the possible need for additional fertilization.

Soil samples should be taken directly from the application site and should be representative of the soils on which the biosolids will be applied. This may require sampling at different depths in the soil profile and at different areas of the site, depending on soils and past management practices. Guidance on soil sampling can be found in the Washington State Department of Ecology's *Biosolids Management Guidelines* (WDOE 93-80) and the University of Idaho Cooperative Extension's *Soil Sampling Bulletin 704* (1994).

Whether sampling biosolids or soils, the time between sampling and analysis and between analysis and use of biosolids should be kept to a minimum. For more stable types of biosolids, such as aged biosolids that have been sitting in a drying bed or lagoon for many years, an additional period of time after analysis may make little difference. For other types of biosolids, delays between analysis and use can compromise the reliability of the determination of the biosolids application rate because of transformations and losses of N from the sample or the source.

Collected samples must be preserved and stored. Preservation and storage requirements will vary with the sample matrix, the analytes targeted, and the methods of analysis chosen. There may be specific regulatory requirements related to sample preservation, holding time, and chain of custody that must be followed. The best way to determine requirements is to review any available discussion of the analytical methods to be used and consult with the laboratory that will be doing the analysis.

Preparing and analyzing samples

The way a sample is analyzed depends to a certain extent on the preferences of the chemist and the laboratory, and the way a sample is prepared depends on the selected method of analysis. Generally, preparation involves some type of extraction, digestion, or distillation. The resulting products are then analyzed quantitatively for the selected form of N. Laboratories should be prepared to justify the use of the methods in terms of meeting permit and other regulatory requirements. Biosolids managers may use less exacting methods of analysis as a "litmus test" but not as a substitute for meeting regulations. For example, an in-house laboratory may have limited capabilities to analyze biosolids or soils that can serve as a quick and relatively inexpensive periodic indicator of compliance.

The preparatory process may have effects on the final N content of the sample. For example, drying and grinding processes may lead to a loss of NH_3 and some acid digestion processes may liberate forms of N for analysis that are not plant available. Therefore, it is important to have knowledge of the biosolids or soil matrix being sampled and of the potential sources of interference from the specific method of sample preparation or analysis. Most analytical methods provide information on such interference.

This section lists four documents that contain methods for analysis of N that are directly or indirectly applicable to biosolids. For purposes of analysis, biosolids fall somewhere between the realm of water and waste. The final use for biosolids is either agricultural, or closely related to agricultural use, and biosolids often more closely approximate soil than either waste or water, especially when biosolids have been dewatered.

The four documents are as follows:

- *Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods* (U.S. EPA). This document is cited in the federal biosolids rule for the analysis of inorganic pollutants (40 CFR 503.8). It is used primarily by those concerned with analyzing and managing solid wastes and contains limited methodologies for the analysis of N in soils or biosolids.
- *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association, 1992). This document is also cited in 40 CFR 503.8, but for purposes other than the analysis of N. It is used primarily by those working in water quality and wastewater analysis. It describes a number of analytical methods that are acceptable for the analysis of N in soils and biosolids. **It is a recommended reference.**
- *Methods of Soil Analysis, Part 2—Chemical and Microbiological Properties* (American Society of Agronomy and Soil Science Society of America, 1982). This extensive document is specifically designed to address laboratory methods for the chemical and microbiological analysis of soils. The procedures described may also be applicable for the analysis of biosolids. **It is a recommended reference.**
- *Plant, Soil, and Water Reference Methods for the Western Region* (Gavlak et al., 1994). This is a collaborative effort specifically written with the agricultural community in mind. **It is a recommended reference.**

Figure 9.1 presents a simplified flowchart that shows the general methods for preparation and analysis of samples for inorganic and organic N in soils and biosolids. The figure is followed by descriptions of specific methods listed in the three recommended reference documents.

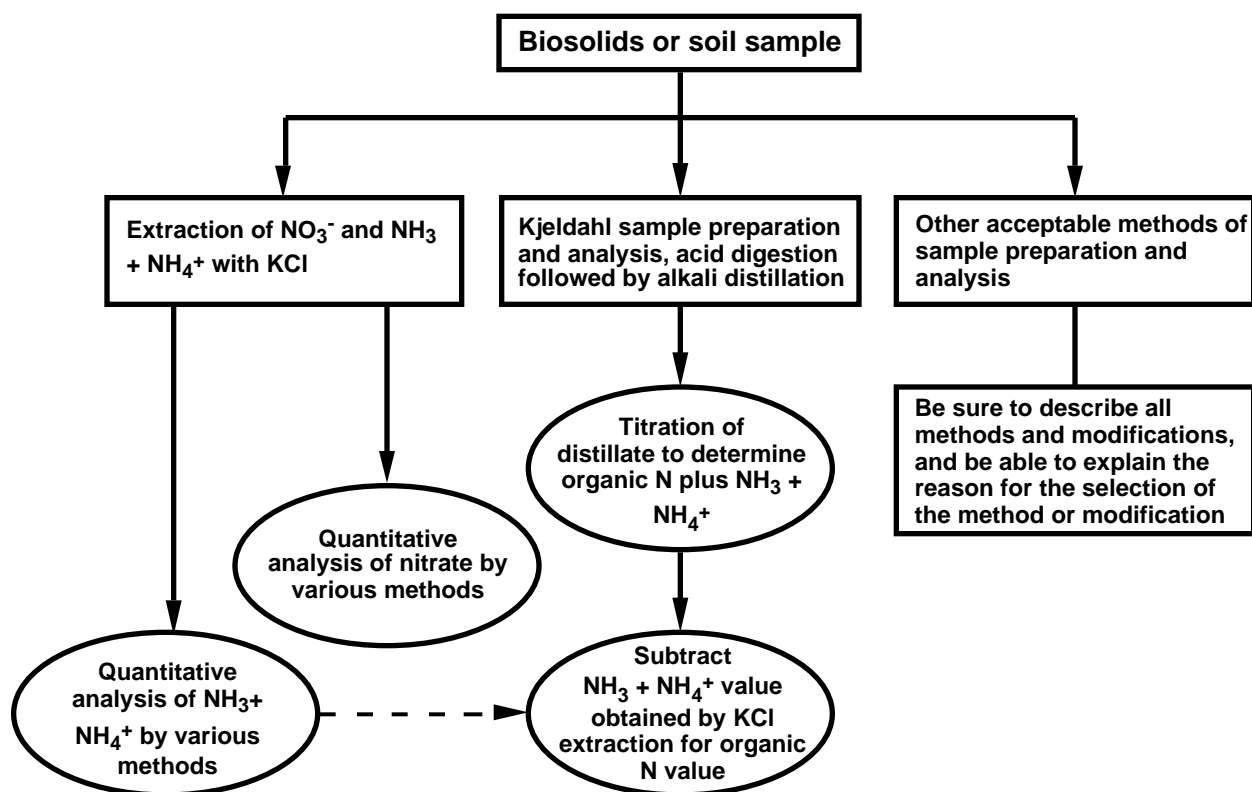


Figure 9.1 Simplified flowchart for analysis of nitrogen in biosolids and soils.

Inorganic nitrogen

Standard Methods for the Examination of Water and Wastewater addresses N in the NH_3 , NH_4^+ , and NO_3^- forms. It includes Method 4500 for analysis of NH_3 and NH_4^+ . Method 4500-NH3 - B describes a preliminary distillation procedure, after which methods 4500-NH3 - C (Nesslerization), D (phenate), E (titrimetric), and H (automated phenate) can be used for quantitative analysis. Methods F and G rely on the use of electrodes and are not recommended for the analysis of soil or biosolids N. Several methods are described under 4500-NO3- for NO_3^- . Methods 4500-NO3 - E (cadmium reduction) and F (automated cadmium reduction) are in common use. Method 4500-NO3 - B is for screening only and is not accurate in other than relatively clean water samples. Some labs have reportedly found methods 4500-NO3 - C and D, which use chromatography and electrodes, to be difficult or unreliable.

Methods of Soil Analysis (Chapter 33) also addresses N in the NH_3 , NH_4^+ , and NO_3^- forms. Method 33-3 discusses the use of potassium chloride to prepare an extract of exchangeable NH_4^+ and NO_3^- that can then be quantitatively analyzed by various methods. The potassium chloride extraction method is in common use. Method 33-4 discusses steam distillation methods for exchangeable NH_4^+ and NO_3^- with many possible variations. Anecdotal information suggests that

there can be significant differences in the results obtained by steam distillation, and it is therefore not recommended. Methods 33-7, 8, and 9 provide for quantitative colorimetric analysis of NH_4^+ and NO_3^- . These methods are used after samples are prepared by extraction or distillation. The methods discussed in 33-10 are not applicable because they deal with non-exchangeable NH_4^+ that is not considered to be plant available.

Plant, Soil, and Water Reference Methods for the Western Region is conveniently separated into matrix-specific sections. The potassium chloride extraction method, discussed in the preceding paragraph on *Methods of Soil Analysis*, is recommended for NH_4^+ and NO_3^- analysis.

Organic nitrogen

The Kjeldahl method is the most common method in use for determining mineralizable organic N (ON) in biosolids, and is appropriate for soils (although measure of soil ON is typically only done for research purposes). The standard Kjeldahl method involves a two-step process. First, the sample undergoes a sulfuric acid digestion that converts ON compounds to NH_4^+ . Second, the converted NH_4^+ , along with any NH_4^+ that was originally present, is further converted to NH_3 in an alkali distillation process. The NH_3 liberated in this process is then quantified to determine the total N in the original digest. A separately determined value for NH_3 and NH_4^+ is then subtracted from the value obtained by the Kjeldahl method, and the difference is considered to be the mineralizable, or potentially plant-available, ON.

The Kjeldahl method does not strictly account for all forms of N in a sample, including NO_3^- and nitrite or other compounds with direct N-to-N bonding. The method may recover some of the NO_3^- and other forms of N that are not specifically intended for quantification. The amount accounted for by this incidental recovery is variable. In any case, the Kjeldahl method accounts for the greatest majority of nitrogenous compounds, and the result therefore is often referred to as "Total Kjeldahl Nitrogen" (TKN), or sometimes simply (and less correctly) as "total nitrogen."

The Kjeldahl method can be modified to recover NO_3^- and other forms of N. Although some of these modifications may yield better results, others are not appropriate for the purposes of biosolids application rate determinations because they may liberate forms of N that are not considered to be plant available. Generally, modifications should not be necessary. Any modifications used should be specifically noted on the laboratory report form. The term "total nitrogen" should not be used with the standard Kjeldahl method unless the Kjeldahl method has been deliberately modified in an effort to recover all nitrogenous forms present.

Standard Methods for the Examination of Water and Wastewater describes two variations of the Kjeldahl method. Either method 4500-Norg B (Macro-Kjeldahl) or 4500 Norg C (Semi-Micro Kjeldahl) may be used. Because the concentration of N in most biosolids samples is expected to be relatively high, the macro method is recommended. For highly liquid biosolids samples and soils expected to be low in N, either method is recommended. Soils with high quantities of ON, such as those where large amounts of manure or other organic materials have been applied, may require the macro method.

Methods of Soil Analysis describes the Kjeldahl method (Chapter 31) and two other methods. The electrode method discussed in Section 31-4 is not recommended; the hydrofluoric acid modification in Section 31-5 should also be avoided because it will liberate N that is not considered to be plant available.

Plant, Soil, and Water Reference Methods for the Western Region also relies on the Kjeldahl method. It should be noted that the total nitrogen method described in this reference is different from the Kjeldahl method, and is not recommended.

Reporting

It is important to keep good records of all sampling and analytical events. The records can be used for later reference, as evidence of regulatory compliance, and to ensure proper interpretation of the data. Inadequate or unclear reporting reflects on the laboratory and chemist and can jeopardize a project or result by inviting additional regulatory scrutiny because of suspect application rate calculations. Leave no doubt!

The following items should be reported:

- Dates of sampling events and sample analysis
- Sample numbers (tied to results)
- Origin of sample (field, digester, pile)
- A brief sample description (liquid, solid, semi-solid; clear, dark, gritty)
- Methods of preparation and analysis, including any modifications
- Results reported on both wet and dry weight basis and the units used (mg/kg, mg/L)
- Percent of total solids of the sample and volatile solids content as a percent of total solids
- Name of the technician or other contact person in case of questions

When reporting the various forms of N, the following terms or notations should be used (the form followed by "-N" means that the results are reported as mass of N instead of the entire compound):

- Total Kjeldahl Nitrogen or TKN
- Organic nitrogen or (ON-N)
- Nitrate nitrogen or (NO_3^- -N)
- Ammonia nitrogen or (NH_3 -N)
- Ammonium nitrogen or (NH_4^+ -N)

References

American Public Health Association. 1992. Standard Methods for the Examination of Water and Wastewater. 18th ed.

American Society of Agronomy and Soil Science Society of America. Methods of Soil Analysis, Part 2—Chemical and Microbiological Properties.

Gavlak, R.G., Horneck, D.A., and Miller, R.O. 1994. Plant, Soil, and Water Reference Methods for the Western Region.

Mahler, R.L. and Tindall, T.A. 1994. Soil Sampling. Bulletin 704 (Revised). University of Idaho Cooperative Extension System, Moscow, ID.

U.S. Environmental Protection Agency (U.S. EPA). Test Methods for Evaluation of Solid Waste, Physical/Chemical Methods. EPA Publication SW-846 (various editions and revisions).