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Soil Sampling, Preparation, Archiving, and Quality Control

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The saying "The devil is in the details" appropriately describes the many decisions that must be made when conducting soils research, particularly long-term investigations where consistency over time and among scientific staff is essential. In addition to technical and often sophisticated analytical methods, soils research also includes the basic sampling and processing of samples as well as adherence to general standards for quality control in the laboratory. Though many decisions about the more nonanalytical steps of soils research may seem inconsequential at the time, they often largely determine the quality of data and their general utility later on.

In this chapter we recommend general protocols for the sampling and general laboratory processing of soils for long-term studies. We discuss soil variability and make practical suggestions for determining sample numbers, collecting soils, and preparing soils for analysis. We propose three levels of soil sampling intensity for long-term research, the lowest level being a minimum standard and the highest level the most comprehensive. We also outline general quality control procedures for the laboratory, including the use of replicates, blanks, spiked samples, and reference materials. Finally, we recommend protocols for the archiving of soil samples and specify the elements of metadata that are essential for the soils database.

Soil Variability

The variability of soil properties in space and time presents a challenge for site assessment and the detection of changes within or among sites. Spatial variation includes horizontal variation across a landscape and vertical variation with horizon

depth. In nonagricultural systems this variability is due to numerous factors, including microrelief, animal activity, windthrow, litter and wood inputs, any human activity, and the effect of individual plants on soil microclimate and precipitation chemistry. Variability in agricultural systems is caused by amendments (e.g., fertilizers and lime), tillage, cropping sequences, animal dung and urine, and compaction from grazers and farm equipment. The spatial aspect of disturbance history is a key factor for many systems. Failure to appreciate and adjust for site variability can compromise an otherwise well-designed and carefully conducted investigation.

The literature on the spatial variability of soil properties (e.g., Zinke and Crocker 1962; Mader 1963; Beckett and Webster 1971; Biggar 1978; Riha et al. 1986; Grigal et al. 1991; Robertson and Gross 1994) is reasonably consistent. Generally, variance increases with size of area sampled, even for areas regarded as the same sampling unit; forest soils tend to be more variable than agricultural soils (though see Beckett and Webster 1971; Robertson et al. 1988, 1997); some properties (e.g., extractable cations) are more variable than others; and data often are not normally distributed. Also, horizontal soil variability in both natural and managed ecosystems can be spatially complex and may vary in scale from 1 m to over 100 m. Many investigators (e.g., Warrick et al. 1986; Robertson et al. 1988; Cambardella et al. 1994; Chien et al. 1997) have applied geostatistics as a means of evaluating spatial correlation in soils, although this technique generally has been limited to agricultural sites.

There are no general rules regarding spatial variance of soil properties within horizons and by depth. Although lower variances within horizons and with greater soil depth are often assumed (Petersen and Calvin 1986; Crêpin and Johnson 1993), the few data on this topic are ambiguous. Several investigators have found that variability may be high within horizons and may actually increase with depth. In forest soils the spatial heterogeneity caused by windthrows may contribute to variability of chemical properties within horizons. Cline (1944), who outlined some of the original principles of soil sampling, noted that physical heterogeneity vertically does not guarantee chemical heterogeneity. Mader (1963), in an analysis of several soil properties in Massachusetts red pine plantations, reported a wide range in variance by horizon. Coefficients of variation ranged from 7% for bulk density in the A horizon to 83% for exchangeable calcium and magnesium in the B horizon. Most properties showed no difference in variation between the A and B horizons. Mader (1963) concluded that variability in soil properties did not decrease with depth and suggested that variance may be higher when nutrient concentrations are low. Clearly, whenever possible, the variance of soil properties within horizons and by depth should not be assumed but rather should be determined directly for site-level work.

Temporal variation (from days to years) within a soil horizon or depth interval can be substantial for many soil properties. Temporal changes may reflect seasonal and annual variations in climate and microclimate as well as management regime (e.g., plowing and manuring, fertilization, liming, forest cutting) and alteration of the amounts and chemical quality of organic matter inputs. Many biological soil processes (e.g., microbial respiration and nitrogen mineralization) are strongly controlled by temperature and moisture and often have seasonal patterns specific to a particular site or ecosystem. The amounts, timing, and chemical quality of organic

matter inputs (leaf litter, dead wood, crop residues) also may influence temporal changes in soils. For both forest and agricultural systems there is a large collective literature variously documenting seasonal and interannual changes for nitrogen mineralization potential, total organic matter, active organic matter, microbial biomass, light-fraction organic matter, soluble carbon and nitrogen, and extractable cations (Gupta and Rorison 1975; Spycher et al. 1983; Bonde and Rosswall 1987; Boone 1992; Collins et al. 1992; DeLuca and Keeney 1994; Maxwell and Coleman 1995; Sollins 1998). If any characteristics subject to seasonal changes are compared over years or among sites, it is imperative that samples be collected at roughly the same time or under similar climatic and site management conditions.

Field Sampling

Preliminary Assessment

Site assessment prior to the establishment of experimental plots or the adoption of a sampling design should include exploratory soil sampling. For many purposes, soil in a potential field site can be rapidly assessed with hand probes or augers, or by exposing the upper part of the soil with a spade. Soil pits, if interpreted by knowledgeable pedologists, provide the most information on the pedogenic processes at a site and potentially on properties relating to site productivity (e.g., redox conditions, texture, rooting depth). Profiles can reveal evidence of deposition, erosion, and previous land use, and can sometimes serve as a rough gauge of time since previous major soil disturbances. Some profile features, such as plow (Ap) layers, may persist in soils for centuries after plowing has ceased. Indeed, determining past human impacts on the soil may be critical to understanding current soil conditions, how a soil will change in response to disturbance, and how a soil's physical and biological features will change with time. Further recommendations on site and landscape-level assessment are provided in Chapter 2, this volume.

Number of Samples

The objective in measuring a soil property is most often to precisely estimate its mean; for example, to produce an estimate that has a 90% confidence of being within 10% of the mean. Many physical, chemical, and biological soil properties (e.g., aggregate sizes, exchangeable bases, soil gases, bacterial numbers) are not normally distributed but are more nearly lognormally distributed, so this objective requires careful consideration. If the properties are lognormally distributed, then fewer samples are usually required to achieve similar precision of their estimated mean than if they are normally distributed (Grigal et al. 1991). What level of accuracy is necessary? Do we believe that soil-dependent processes are markedly different at two sites whose mean values differ by 10% (e.g., exchangeable Ca^{+2} of 4.5 versus 4.1 cmol (+) kg^{-1})? At what level of differences in properties do we expect differences in processes: at 20% of the mean, or 50%, or even at differences of an order of mag-

nitude (e.g., from 4.5 to 0.4 cmol (+) kg^{-1})? Acceptable levels of precision will vary by study and soil property. For most of the soil protocols described in this volume, reasonable care will keep analytical variability lower than field variability. In general, as a consequence of high variability in the field, the presence of lognormal distributions, the triviality of small differences, and the limited resources with which to process many samples, acceptable laboratory procedures need not be as precise as those presented in many methods manuals, and the investigator will need to strike a reasonable balance between precision and accuracy.

Testing for Normality

The first step in calculating the number of samples to collect is to ascertain whether the frequency distributions for the soil properties of interest are normally or lognormally distributed. This is best done by examining sample data from previous analyses. Good sources are data sets from a pilot study or from other investigators. In this regard, databases on the World Wide Web may be useful if values for samples (versus means alone) are included. Generally, frequency distribution information is limited or unavailable from data in the published literature.

Normality (or lognormality) of data can be assessed visually by graphs and more rigorously by statistical tests. One simple approach is to construct a histogram, which will reveal obvious skewness. If data are lognormally distributed, they often obtain a normal distribution after a natural log–transformation (Parkin and Robinson 1994), although this may not always be the case (Grigal et al. 1991). An alternative and more diagnostic graphical method for identifying normality is a probit plot (Miller 1986; Parkin and Robinson 1992). Statistical methods that can be used to test for normality (or lognormality) include the W or Shapiro-Wilk test for sample sizes of up to 50 (Shapiro and Wilk 1965; Parkin and Robinson 1994) and the D'Agostino test (Gilbert 1987; Parkin and Robinson 1992) for sample sizes greater than 50 but less than 1000. If only data summary statistics are available, asymmetry is indicated by a high coefficient of variation (CV), a wide difference between the mean and median (or geometric mean), and a high coefficient of skewness (Parkin and Robinson 1994).

Sample Number Calculation

If data are distributed normally, then the number of samples that are necessary for a given level of accuracy can be found relatively simply by using the relationship

$$n = t^2C^2/E^2$$

where

n = the number of samples to be collected
t = Student's t statistic that is appropriate for the level of confidence and number of samples being collected
C = the coefficient of variation (standard deviation divided by the mean)
E = the acceptable error as a proportion of the mean

For example, to collect sufficient samples for the sample mean to be within 10% of the true population mean with a 95% probability, the t statistic is approximately 2 (1.96 for a 95% confidence interval for a sample of infinitely large size) and $E = 0.1$. Prior data from similar samples, either collected on site or from the literature, can be used to estimate C. Several studies and reviews (e.g., Mader 1963; Beckett and Webster 1971; Blyth and MacLeod 1978; Grigal et al. 1991) provide useful tables with CVs for numerous chemical and physical soil properties.

If data are distributed lognormally, the necessary number of samples can be calculated by using log-transformed data in the preceding equation. This will give lower sample numbers than would be obtained if a distribution mistakenly were assumed to be symmetrical. For many soil data, scaling by multiplying by 100 or 1000 eliminates values less than 1, making the use of logarithms more straightforward.

Composite Sampling

Compositing or combining sampling units into a single sample for analysis is an effective method for obtaining an accurate estimate of the population mean while reducing cost and analytical time. The requirements for compositing samples are (1) the sample volume represents a homogeneous sample, (2) each sample contributes an equal amount to the composite, and (3) there are no interactions between the sample units within the composite that would significantly affect the composite value. When these conditions are met, values from composites agree well with means obtained from single sampling units (Jackson 1958; Cline 1944). However, compositing does not provide a direct estimate of the population variance, which may be no less important than the mean. For hypothesis testing, at least two composites must be collected from a population to obtain a measure of the variance of the estimated mean. In that case, the estimated mean is the average of the two composites, and the standard deviation of the two composite values can be considered an approximation of the standard error. Field and laboratory costs, the desired accuracy of the estimate, and the expected error of laboratory measurements ultimately should determine the optimum number of field composites after the required number of field samples has been determined (see Mroz and Reed 1991).

Sampling Time and Frequency

Sampling time and frequency are determined by the conditions and objectives of the study. For comparison of flux measurements (e.g., nutrients, gases, water) among sites or across years, we recommend that measurements of all fluxes be carried out on at least a growing season basis, but preferably for a full calendar year. Determining interannual variation in flux measurements certainly is an essential component of a long-term program and is necessary for legitimate site comparisons. Often winter fluxes can be a significant fraction of total annual fluxes and should be measured if at all possible, especially at sites where summer drought limits biological activity. Soil chemistry (e.g., extractable cations, pH, nitrate, active carbon) and soil biotic pools (microbiota and soil animals), which change with season, vegetation phenology, weather, and site conditions, should be determined under common

conditions among years whenever possible and ideally during those periods that are most stable or at least repeatable.

Sampling Intensity

Debate continues concerning the costs and benefits of sampling soil by uniform depth increments versus sampling by horizons. Reasons to favor depth-increment sampling are that:

- A large number of samples can be collected relatively easily with augers or similar devices so that variation in soil properties can be adequately captured. Excavating pits for horizon sampling is more costly and time-consuming.
- If several crews are used, lack of uniformity among crews is a valid concern. Differences in horizon descriptions and subsequent analytical results could be attributed to a "lumper" versus "splitter" approach to description and sampling.
- Budgeting often requires a firm estimate of the number of samples to be analyzed. Estimating sample numbers is difficult when sampling is by horizon because of variation in soil profiles and potentially in personnel.
- A major objective of many studies is an inventory of the total elemental or water content of the soil, requiring analysis of the entire soil. There is a risk when sampling by horizon that some thin or discontinuous horizons may not be included when a profile is sampled; if they are combined with another horizon, the concept of sampling by horizon is violated.

Certainly, fixed-depth sampling is not without problems. It may skew results, obscure soil changes, and lead to false conclusions, particularly on sites where erosion, deposition, or compaction has occurred (see later discussion). Horizon-based sampling in some cases effectively reduces both depthwise and horizontal variability (though see Mader 1963) and is fundamental to studies of pedogenesis. In the end, which sampling approach is "best" depends on the site conditions and study objectives.

For long-term research and for cross-site comparisons, we recommend a hierarchical sampling scheme, with depthwise sampling at the lowest intensity level (I), horizon sampling at the highest intensity level (III), and a blend of approaches at the intermediate level (II). The lowest level (I) provides the minimum amount of information acceptable for cross-site or long-term studies, while the highest level (III) is designed to capture at least 90% of the variation in a property at a site (e.g., 90% of total net N mineralization over the full soil profile). Sampling is by fixed depth (20 cm) at Level I and by horizon at Level III; sampling by horizon is encouraged when appropriate at Level II. All three sampling levels provide soil data on at least a 20 cm depth basis. We have deliberately chosen the 0–20 cm depth as a minimum standard because it extends below the plowing depth in most agricultural soils and includes the majority of root biomass. Samples taken from 0–15 cm depth are discouraged because they often do not include the full plow depth in soils. Level III information is recommended as the goal for long-term research sites and for the most meaningful cross-site comparisons.

Level I Sampling (Least Intensive)

The minimum intensity for long-term and cross-site research includes

- sampling of organic horizons;
- sampling of mineral soil from 0 to 20 cm depth;
- description of horizons or distinct soil layers within the sampling zone on a site basis; and
- collection of ancillary soil profile information allowing conversion of data to a 20 cm soil depth basis, if soils are sampled from 0 cm to below 20 cm depth.

Level II Sampling (More Intensive)

An intermediate sampling intensity is preferable for long-term and cross-site research and includes

- sampling of organic horizons;
- sampling of mineral soil at 0–10, 10–20, 20–50, and 50–100 cm depths;
- further subdivision of depth intervals into horizons if there are obvious changes in pertinent soil properties; and
- field description of soil profile, including characterization of all horizons (depth, color, and texture) and determination of rooting depth.

Level III (Most Intensive)

A comprehensive sampling ensures valid site comparisons and includes

- sampling by horizon over the full profile;
- certification (based on previous work) that more than 90% of the soil property's level has been captured by the sampling;
- collection of ancillary data as required to allow determination of properties over 0–20 cm mineral soil depth; and
- full soil profile characterization according to Natural Resources Conservation Service (NRCS) format.

Outside expertise will most likely be required to characterize the soil according to the NRCS format, which is not a trivial task.

"Equivalent depth sampling" (Crépin and Johnson 1993) may be appropriate when depth sampling alone (Level I) is employed and control soils are compared with those that have been physically disturbed. To illustrate, consider a comparison of organic matter contents between a heavily compacted cultivated soil and an uncultivated soil that has not been obviously compacted. If both are sampled to the same depth, the cultivated soil will have a greater "effective depth" (Davidson and Ackerman 1993) and soil mass because of the inclusion of material from deeper horizons. Accordingly, the value for a given property may be skewed. One means of adjusting for this is to sample the less compacted soil more deeply to obtain an equivalent soil mass, though this method is generally feasible only when soil rock content is low and not variable.

Field Procedures

Organic horizons, which consist of undecomposed and partially decomposed litter, are sometimes difficult to sample because they may have variable thickness and poor delineation, may be held together tightly by fine roots, and are not always visually distinct from the mineral soil. The Soil Survey Division Staff (1993) defines an organic horizon as one that

- is never saturated with water for more than a few days and has 20% or more organic carbon (by weight); or
- is saturated for longer periods, or has been artificially drained, and has an organic-carbon content (by weight) of 18% or more if 60% or more of the mineral fraction is clay; 12% or more if the mineral fraction has no clay; or 12 + (clay percentage multiplied by 0.1)% or more if the mineral fraction contains less than 60% clay.

Federer (1982) reviewed the problems associated with identification of organic horizons in forest soils and proposed that 40% organic matter (determined by loss on ignition) is a more convenient definition for organic horizons. The NRCS (1996) has defined standards of "rubbed fiber content" for the Oi, Oe, and Oa organic horizons, though this assay is not commonly used by ecologists. Because most investigators identify organic horizons subjectively, based on composition and color, field separations should be calibrated against the quantitative criteria. This calibration is particularly important when there is a change of field personnel, and when organic horizon data are used in cross-site comparisons or to examine changes over time.

Organic horizons can be collected with a knife and spatula or other flat blade to lift away material from a uniform area marked with a template or frame. Garden clippers or scissors may be useful for separating organic horizons from one another and from the mineral soil if roots make sampling difficult. Surface moss, if present, can be removed by hand if loosely attached to the soil surface, or it can be cut away. Investigators should decide prior to sampling and based on their scientific questions and objectives whether or not to include well-decomposed deadwood (often embedded in the ground) in soil samples (see Chapter 11, this volume).

A bucket or screw auger or a drive-type corer can be used for depthwise sampling of the mineral soil; these corers permit rapid collection of a sample of uniform cross-section area and minimize contamination. A relatively undisturbed sample collected with a corer can be used for measurements of physical properties, including total pore volume, field capacity, and bulk density, which is necessary to convert weight or concentration data to a volume or area basis. A tapered tip on a corer allows the cutting of a sample with a diameter less than the tube, thus facilitating sample removal. Coring devices do not work well in stony soils or dry sandy soils, though augers are available for these conditions. Coring devices obviously exclude rock fragments larger than the core diameter but also minimize the collection of smaller rocks. The degree to which rocks are excluded by the sampling method should be considered when soil concentration data are expressed on a volume or area basis.

Often a soil pit is necessary for sampling by horizon. When loose samples are

collected by horizon from a pit, it is usually best to sample from the "bottom up." That is, after horizons have been delineated and described, the deepest horizons should be sampled first. As samples are collected, soil materials slough to the bottom of the pit, and deeper horizons can become contaminated or even buried by material from above. Soil from horizons, which can be collected with a blade (trowel, spade, or knife), should be a composite of samples from more than one face of the pit and should represent the full horizon depth interval equally. Complete sampling of the full horizon depth interval is generally difficult if cores or short augers are used. An alternative to horizontal sampling from the bottom up is to sample a profile from the top down, removing each horizon after sampling to produce a flat surface for the sampling of the next horizon. Determination of both rock content (see Chapters 2 and 4, this volume) and bulk density (i.e., the ratio of the total mass of solids to the total or bulk volume) is necessary for conversion of soil measurements from weight to an area basis if sampling area is not known.

We recommend that soils collected for biological and chemical assays be sealed in plastic bags, stored in coolers with blue ice or ice packs, and returned promptly to the laboratory for analysis. Polyethylene bags (1–2 mil thickness), which are convenient and commonly used, are relatively gas-permeable and somewhat permeable to water vapor. Thicker-gauge polyethylene bags or double bags may be required to reduce the possibility of tears or punctures when samples contain a large number of rocks, sticks, or sharp roots. Thicker bags better retard moisture loss but also can more readily lead to anaerobic conditions. Cooling and rapid processing are not as necessary for samples collected for physical measurements, though maintenance of field moisture may be important for some variates (e.g., aggregation and texture).

Laboratory Processing

Soil Handling

The techniques chosen and the time required for preparation of soil samples returned to the laboratory should be considered carefully to minimize changes in properties of interest and to avoid compromising future analyses. In the absence of information from laboratory trials, the analyst should not assume that soil properties are stable during sample preparation. Changes in properties after soil sampling and during processing can be assessed through the use of field addition samples (see section "Spiked (or Fortified) Samples," below). The processing protocol should be the same for all samples, and field and laboratory replicates should be randomized before processing to minimize systematic errors.

Storage and Drying

The soil variates of interest, the questions asked, and sometimes the soil type determine how samples should be best stored in the laboratory and whether they should be analyzed field-moist or dried. Investigators should recognize that soils can undergo significant changes under any storage condition, whether soils are refriger-

ated, frozen, or dried before analysis, and that long-term effects of storage on soil properties have not always been examined adequately. Readers are directed to the following chapters for variate-specific recommendations on storage conditions and the advisability of using field-moist versus air-dried samples. Here we discuss generally the more common approaches.

Air drying (at ambient laboratory temperature and humidity) is convenient and often appropriate for measurement of many nonbiological soil properties. Air-dried soil has relatively constant weight and minimal biological activity. Soils after collection can be spread to air-dry in a thin layer in trays or on paper or plastic in a room free of contaminants. If maintaining soil structure is not important for analyses, the soil can be rolled gently with a roller and clods can be broken to facilitate drying. Air drying notably can cause variable and significant changes in soil chemistry (e.g., soluble organic matter, pH, total S, and extractable K^+, NH_4^+, and NO_3^-; Schalscha et al. 1965; Bartlett and James 1980; Kalra and Maynard 1991; Bates 1993; Tan 1996), and changes can continue even after soils have been air-dried. Especially in the case of soils rich in allophane and other amorphous clay, air drying can cause irreversible aggregation and substantial changes in texture (Schalscha et al. 1965; Bartlett and James 1980). Air-dried soils that are remoistened should be allowed sufficient equilibration time before analysis. *Oven drying* at 35 °C to accelerate drying may be acceptable, although oven drying at higher temperatures is strongly discouraged because of large effects on soil properties (Hesse 1971).

Refrigeration or cooling (near 4 °C) of field-moist samples often is justified provided that storage time is minimized if biological or biochemical properties are assayed. Long-term storage of moist samples in a refrigerator (several months or more) is not recommended because of possible major shifts in the microbial community (Stotzky et al. 1962) and the potential development of anaerobic conditions (Gordon 1988). Using field-moist samples is often preferable for biological assays and some physical properties (e.g., water retention) but may be problematic given that field-collected samples can range from air-dry to saturated. Adjusting water content (amendments, or removal by evaporation) may be necessary for biological assays.

Freezing at low temperature (≤ -20 °C) can be suitable for long-term storage, given that microbial activity is effectively minimized, though it too has some drawbacks. Freezing promotes desiccation, lyses microbial cells, and disrupts soil organic matter (SOM) structure, and it may alter exchangeable NH_4^+ and soluble P concentrations (Allen and Grimshaw 1962; Nelson and Bremner 1972; Bartlett and James 1980). Typically there is a flush of biological activity in thawed soils due to the decomposition of soil microbial cells lysed by the freezing.

In summary, no storage condition is perfect, and the absence of a storage effect on soil properties should be checked rather than assumed.

Sieving and Grinding

Conventionally, mineral soil samples for chemical and physical analyses should be passed through a 2 mm sieve to obtain representative subsamples and to exclude larger particles (small surface-to-volume ratio) that are relatively less reactive.

Aggregates, unless otherwise examined and considered, can be forced through the mesh by hand or with a larger rubber stopper. Whenever possible, samples should be sieved or ground in an air-dry condition; moist samples can be sieved and ground but often with difficulty. Subsamples from the sieved fraction subsequently may be ground to pass at least a 0.5 mm sieve (40-mesh) to reduce subsampling error for micro- or semimicro-analyses that require lower sample weight (micrograms to several grams). Organic horizons with macro-organic matter can be passed through a coarse sieve (e.g., 5.6 mm) to remove sticks and stones before grinding for chemical analysis. In some cases, hand picking of larger coarse fragments from organic horizons may be appropriate. Common grinding devices are mortar and pestle, ball or rod mill, Wig-L-Bug shaker, and SPEX mill for mineral soil; a Wiley mill or manual meat grinder can be used for organic material. Stainless steel or nylon sieves and mortar and pestle should be considered to minimize the possibility of sample contamination when trace elements are measured.

Allophanic soils, and others rich in amorphous clays, again deserve special mention because of their tendency to aggregate irreversibly upon air drying. Such soils may need to be sieved fresh, as best possible, or hand-picked to remove rocks and large plant fragments, then ground after air drying to break up aggregates formed during drying. Cautious air drying of the fresh soil prior to sieving may lower the moisture content to a level at which samples can be sieved but aggregates will not yet have formed.

Often soils should be analyzed unsieved or after passage through a coarse sieve only. This is true when maintenance of soil structure or retention of all particle sizes is important for biological and physical assays. Sieving of mineral soil, for example, breaks aggregates and exposes formerly physically protected SOM to soil microbiota. This may not be a trivial consideration for interpretation of nutrient dynamics, microbial respiration, and microbial biomass during laboratory incubations. In the case of organic horizons, using material that passes through a 2 mm sieve often is impractical because of the large fraction left on the screen. Conveniently, organic material can be passed through a coarser sieve (e.g., 5.6 mm) before biological assays.

All sample weights (whether air-dry or field-moist) should be converted to an oven-dry (105 °C) basis, determined by oven drying subsamples (>24 hours) taken at the time of sample analysis. Prior to some analyses (e.g., total nitrogen), it may be appropriate to dry soils at a lower temperature (e.g., 70 °C) to avert volatilization losses. In this case, an additional conversion to 105 °C weight equivalent may be necessary. When a sieved fraction is used for analysis, the material larger than mesh diameter should be oven-dried (105 °C) and weighed to provide a correction factor between sieved oven-dry weight and unsieved oven-dry weight.

Analytical Issues

Here we focus on general aspects of analytical methods that are critical to the quality of long-term data. Problems associated with accuracy and analytical bias must be avoided in assessing long-term trends or making cross-site comparisons. Thus the analytical data set must contain information reflecting and verifying method

accuracy. The most important approach for assessing and documenting accuracy is the use of reference materials or external standards that can be analyzed regularly by each laboratory. Analytical methods for specific soil constituents are described by Sparks (1996) and in other standard soil methods volumes.

The analyst must be prepared to make a major commitment to quality control and good laboratory procedures (Taylor 1987; Association of Official Analytical Chemists-International 1990; American Society for Testing and Materials 1991; American Public Health Association 1992). In addition to the use of reference materials, each analytical laboratory involved in producing long-term data sets must develop well-documented, standard operating procedures and incorporate regular analyses of blanks (field and laboratory) and spiked or fortified samples to enable detection of contamination or loss during storage and analysis and to document method accuracy. Blanks, spikes, reference materials, and replicates will constitute a substantial part of the sample load, analytical time, and cost.

When implementing a new method, the analyst should establish its precision and accuracy by analysis of replicate field samples and reference materials, respectively. Problems associated with the method will be reflected by these "trial runs." Control charts with various action levels established (e.g., warning versus shutdown) must be used to follow, and to react to, changes in method performance. A formal system of data quality flags and codes should be established to maintain uniformity across all work groups.

Blanks

Blanks are a critical component of the analytical scheme for detecting contamination from sample containers, analytical reagents, and sample handling. For blanks to be meaningful, cleaning, sampling, and sample handling techniques must be evaluated and standardized for all sample containers, sampling apparatus, and laboratory glassware and plastic ware used in the procedure. Sample containers that minimize blank values should be chosen whenever possible. For example, glass containers should not be used for samples to be analyzed for silica or trace metals, while plastic materials should not be used for organic components. Sample bottles manufactured from many other polymers, including low-density polyethylene (LDPE) and especially fluorinated LDPE, after detergent and acid washing, are suitable for dissolved organic carbon (DOC) sample collection, though DOC storage in these bottles has not been adequately tested. Appropriately cleaned Teflon (PTFE, PFA, FEP) is compatible with analysis of total organic carbon, DOC, many trace organic compounds, and nearly all inorganic compounds.

Two types of blanks should be incorporated into the sampling and analytical protocol. *Field blanks* should be used to detect possible contamination associated with sampling and storage. To the extent possible, field blanks (sample containers) should be exposed to all steps in the sampling and analysis scheme. These blanks are generally more critical for aqueous soil solution samples and soil extracts than for solid soil samples. For soil solution sampling, pure water should be added to the sampling container and carried through all field and laboratory steps such as sample transfers, filtrations, digestions, and reagent additions. Field blanks should represent at least

2% of the field samples, but a higher frequency may be appropriate for procedures unavoidably subject to contamination.

Laboratory blanks or reagent blanks should be incorporated at the beginning of the laboratory analysis scheme. Laboratory blanks monitor reagent purity and the overall laboratory procedure. Again, laboratory blanks should represent at least 2% of the samples. More frequent blanks should be used when contamination is problematic, when new reagents are incorporated into the analysis, and when sample and blank values are not so different (trace level analyses). Replicate spikes should be used to establish the limit of detection and limit of quantification for the method in use. Results (including those for blanks) below these values should be flagged as "below the limit of detection" or "below the limit of quantification." Preconcentrating the analyte may be necessary to achieve concentrations above blank values for accurate quantitation. If quantitation at this level is essential, the availability of more sensitive and less variable alternative methods should be explored.

Spiked (or Fortified) Samples

Spiked (or fortified) samples are necessary for monitoring analyte losses during sample storage and analysis and for determining the accuracy or bias of the analytical procedure. Spikes should be included at two points in the analytical scheme. Field spikes should be used for soil solution samples, which involves adding standards to the field sample container and to a subset of the field samples, then carrying the spiked samples through the remainder of the analytical scheme. These samples serve to detect analyte adsorption by the sample container. Laboratory spikes should be used for both soil and soil solution samples to monitor analyte recovery and matrix effects (either positive or negative interferences). For soil samples, the standard should be added to the soil extract. For soil solution samples, the standard should be added when the sample is transferred from the field sample container to the first container used in the laboratory analysis. Spikes should be made at concentrations approximately twice that expected in the sample, and spike frequency should correspond to at least 10% of the field samples. Spikes should not be used to correct analyte values for the regular samples because the spike may be more easily recovered or more readily detectable than that occurring in the samples naturally, and the spike may be reduced or otherwise altered by the sample and the sample matrix. Although any recovery standard is somewhat subjective, spike recovery of 80–120% is acceptable for most analyses (Klesta and Bartz 1996).

Laboratory Replicates

The degree of replication must be sufficient to document the precision of the sampling and analysis scheme. Field replicates monitor the precision of the overall procedure and overall field variability. Laboratory replicates or split samples (i.e., splits from a homogeneous sample in the laboratory) monitor the precision of the lab method. Precision of laboratory replicates can be assessed by calculating a CV for analytical replicates, referred to in the quality assurance/quality control (QA/QC) literature as the relative standard deviation

$$RSD = (s/x) \times 100$$

where

s = standard deviation
x = mean

RSD values ≤10% for laboratory replicates indicate that analyses are sufficiently precise. The number of replicates required will vary by protocol and should be evaluated carefully on a laboratory-by-laboratory basis. For example, some analyses will require even triplicate replicates to bring analytical CVs to ≤ 10%.

Quality Control Check Samples

Quality control check samples (distinct from calibration standards) are certified reference materials or in-house standards used to determine analytical precision and accuracy. Quality control check samples should be matched with respect to matrix and the analyte concentration range of the routine samples, and should be handled the same as routine samples in the processing and analytical stream. In-house standards and calibration standards should come from different sources. Quality control samples should be used only during their known shelf life (i.e., the period of stability for the parameter of interest). If the shelf life is not known, the integrity of quality control check samples can be examined by comparison with fresh certified reference standards or by participation in an interlaboratory sample exchange program (see later discussion). Mean values (and standard deviations) for in-house standards should be determined upon repeat analysis and should be traceable to certified reference standards whenever possible. Analyses are regarded as sufficiently precise if the value for quality control check samples is within two standard deviations of the mean value (Klesta and Bartz 1996). Otherwise a problem with the analysis (method or instrumentation or both) is indicated.

Reference Materials

Incorporation of reference materials or external standards in a quality control scheme is necessary to determine analytical bias caused by the measurement protocol and the analyst. *Reference material* is defined as "a material or substance, one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials" (National Institute of Standards and Technology 1995). Primary or certified reference materials are those with properties certified by a national standards laboratory or other organization with appropriate legal authority and are accompanied by a certificate from the issuer (Ihnat 1993). The National Institute of Standards and Technology (NIST), formerly the U.S. National Bureau of Standards, uses the term *standard reference material* (SRM) for its certified reference materials. The philosophy of certification is that the value for a given measured property is independent of method.

Soil reference materials with certified values for chemical constituents are un-

common, and the assays (reflecting predominantly the needs of geochemists, geologists, and reclamation specialists) are biased toward metals and cations. There are few reference soils with certified values for total nitrogen, total carbon, organic carbon, and extractable cations, or for any physical properties. NIST reference soils include Peruvian Soil (SRM 4355), Buffalo River Sediment (SRM 2704), San Joaquin Soil (SRM 2709), and Montana Soil (SRMs 2710 and 2711). Although all have certified values for numerous metals, only Montana Soil and Buffalo River Sediment have certified values for carbon, and none have certified values for nitrogen. Mineral soils available from several other agencies outside the United States (e.g., the Community Bureau of Reference, or BCR, program of the European Commission) also tend to have certified values for metals and cations only. The Canadian Centre for Mineral and Energy Technology (CANMET) offers several reference soils and sediments with consensus values (means based on participating labs, each using methods of its choice) for major elements and some metal oxides. CANMET soil samples SO-2, SO-3, and SO-4 have consensus values for carbon, nitrogen, and loss-on-ignition, but the precision of their nitrogen values is low. Notably, mineral soils with NIST-traceable values for carbon, nitrogen, and sulfur may be obtained from some companies that manufacture soil nutrient analyzers (e.g., LECO Corporation).

We know of no certified material for soil organic material. However, several types of leaves (tomato, apple, peach, pine) are available from NIST with certified values for carbon and nitrogen. Similarly, 10 different plant reference materials (including beech and spruce leaves) are available from the BCR Reference Materials program of the European Commission, with consensus values for metals and cations (all materials) and for carbon and nitrogen (leaves only). Simulated rainwater reference materials with certified values for major cations and anions also are available from the BCR program. Several companies (e.g., SPEX CertiPrep, Inc.) offer certified standards for trace metals, minerals (e.g., calcium, magnesium, sodium, potassium), anions, and nutrients (e.g., ammonium, nitrate, total nitrogen and phosphorus) in a water matrix.

Certified reference materials should be used to calibrate in-house standards and to determine analytical bias. Although many labs commonly use in-house standards for quality control purposes and to measure precision, these do not provide a measure of accuracy or analytical error unless compared against certified standards. Certified reference materials are particularly critical for intersite work and for measurement of long-term changes in soil properties. NIST is now initiating inclusion of certified values for carbon and nitrogen in all of its soil SRMs (B. MacDonald, NIST, personal communication), although the process is likely to take 3 years. Discussions within the LTER Network are now under way to develop a library of certified soil standards designed to cover properties of common interest to ecologists. Table 1.1 lists a selection of current soil reference material providers.

Interlaboratory Exchanges

An interlaboratory exchange program is one means of judging values for in-house standards and promoting comparability of results among laboratories. The largest and most extensive sample exchange program is the International Soil-Analytical

Table 1.1. Selected Providers of Soil Reference Materials

Provider	Address
NIST	Standard Reference Materials Program National Institute of Standards and Technology Gaithersburg, MD 20899-0001 Phone: 310-975-6776 FAX: 301-948-3730 email: SRMINFO@enh.nist.gov http://www.nist.gov
CANMET	Canadian Certified Reference Materials Project (CCRMP) Natural Resources Canada 555 Booth Street Ottawa, Ontario Canada K1A 0G1 Phone: 613-995-4738 FAX: 613-943-0573 email: ccrmp@nrcan.gc.ca http://www.nrcan.gc.ca/mets/ccrmp
BCR	BCR Reference Materials European Commission, Joint Research Centre Institute for Reference Materials and Measurements (IRMM) Management of Reference Materials (MRM) Unit Retieseweg B-2440 Geel Belgium Phone: +32-14-571211 FAX: +32-14-590406 http://www.irmm.jrc.be/mrm.html
BAM	Bundesanstalt für Materialforschung und-prüfung [Federal Institute for Materials Research and Testing] Section 1.01, Quality Assurance and Methodology in Chemical Analyses Rudower Chaussee 5 D-12489 Berlin Phone: +49-30-63 92 58 47 FAX: +49-30-67 77 06 10 http://www.bam-berlin.de/e3org.html

Notes: See text for a description of available materials.
A more comprehensive listing can be found in Ihnat (1993).

Exchange Programme operated by the Wageningen Evaluating Program (WEPAL) of Wageningen Agricultural University in the Netherlands. For a subscription fee, participating laboratories receive in common four soil samples every 3 months for analysis of parameters (only those they decide are useful to them) by methods of their choice. Consensus values (with statistics) for measured parameters subsequently are compiled by WEPAL and distributed back to the member laboratories. Laboratories additionally may submit their own samples and in-house standards to WEPAL for interlaboratory measurements. Currently nearly 300 laboratories world-

wide participate in the WEPAL program, which is described in more detail at www.benp.wau.nl/wepal.

Calculations

For cross-site purposes we recommend that soils data be expressed on an areal basis, whenever possible and practical, and that soil sampling depth always be specified. In some cases it may be useful and appropriate to express soils data additionally by soil mass, volume, or horizons. However, these units alone do not lend themselves as well to cross-site comparisons. The disadvantage to comparing soil data among sites on a soil mass basis, for example, is that differences in coarse fragment content and bulk density are commonly ignored. Adopting the standard of expressing soils data on an areal basis whenever possible should facilitate cross-site comparisons and synthesis, and better ensure the comparability of long-term data sets.

The steps required to express soil data on an areal basis depend on whether samples are collected from a fixed surface area. If soil samples are collected quantitatively within a fixed surface area (e.g., defined by a sampling frame or coring device), soil nutrient concentration data are easily converted to an area basis by the equation

$$y = a \times b$$

where

y = variate mass/m^2
a = soil nutrient concentration (mass, equivalents, molar quantities)/soil mass
b = mass of soil/m^2

The mass of the sieved fraction must be used for b in the equation, assuming that soils are sieved before analysis. Conventionally, soil mass is defined as oven-dry (105 °C) mass.

If samples are not collected from a fixed area, the equation must include bulk density, rock content, and soil volume m^{-2} for the given sampling depth, and becomes

$$y = a \times b \times c \times d$$

where

y = variate mass/m^2
a = soil nutrient concentration (mass, equivalents, molar quantities)/soil mass
b = bulk density of sieved material
c = soil volume for 1 m^2 at given sampling depth
d = (1 − [% rock volume/100])

Bulk density of sieved material can be determined by subtracting the rock fragment volume (best measured by water displacement) from a bulk density sample of unsieved soil. Note that the equation becomes increasingly sensitive to rock content

as rock content increases, and correspondingly less sensitive to bulk density. Certainly a major impediment to comparing sites is the scarcity of reliable data on rock content (see Homann et al. 1995). Methods for determining rock volume are given in Chapters 2 and 4, this volume.

Sample Archiving

The archiving of soil samples is an essential component of a long-term soils research program. Archived soils are invaluable "time capsules" for assessing temporal changes in soil properties, particularly as new analytical tools become available. Examples of the profitable use of archived soils include detection of reduced soil lead levels following the banning of leaded gasoline (Siccama et al. 1980; Friedland et al. 1992) and refined measurements of soil organic matter turnover based on changes in the ^{14}C bomb signal (Trumbore 1993). Certainly the creation and maintenance of an archive for soil or other physical samples (e.g., leaf litter, tree cores, sediments) is not trivial and requires continued financial support and institutional commitment. One option for reducing the costs of an archive facility, particularly for research sites with a smaller sample inventory, may be to share existing archives or to establish a national-level facility or network.

The following are commonsense recommendations for long-term storage of soil samples, based in part on the experience of scientists who have developed the Sample Archive Building (a library of nearly 10,000 physical samples) at the Hubbard Brook LTER site:

- Samples should be kept air-dry at room temperature in a secure location with low probability of water damage (e.g., broken pipes, flooding from weather or storm events), chemical contamination, fire, or other catastrophes. Temperature fluctuations in the archive should be minimized because of the potential for condensation inside containers. Dehumidification may be necessary during warmer months. Long-term storage of field-moist samples in refrigerators or freezers generally is not recommended because of inevitable power failures and the cost of backup power units.
- Containers should have secure lids and should be made of long-lasting materials (plastic or glass) with low potential to contaminate the sample and alter soil chemical properties.
- Container labels should be carefully evaluated for permanence. Labels should always be placed on the container itself rather than placed only on the lid. If there is significant risk that labels will be defaced or that they will not be permanently affixed, a copy of the label on plastic or similar material should be placed inside the container with the sample.
- Labels should include both sample number and the degree of fineness of the sample (e.g., <2 mm).
- Records of sample collection (investigators, location, method, sampling time), processing (e.g., prior storage conditions, sieving, grinding), and available data, including analytical methods, should be readily accessible and main-

tained by personnel responsible for the archive. A copy of the records should be kept in a location near the archive if convenient. The location of the records can be written on the sample container. Ideally the soil archive inventory and sample data should be electronically cataloged and made accessible electronically both on-site and remotely.

- Each archive should have a written policy regarding use and access, and a log of activities and users should be maintained. The original investigator should have free and easy access to samples.
- Subsampling of archived soil is wasteful. People often take more material than they need. It is better for users to take the complete sample, use only the amount necessary, and return the sample. To protect against loss of a sample, archives can maintain a subsample for use only in the event that the "working" sample is lost.
- Changes in properties will occur during sample storage and should be monitored by periodic analysis of archived soil reference materials or in-house standards.

The amount of soil for archiving cannot be easily fixed because it depends on the projected number of future users, the amount required for analyses, and the cost and logistics of soil storage. A minimum of several hundred grams may be appropriate. Destructive sampling of archived material should be minimized.

Metadata

Metadata, or the supporting documentation necessary to interpret a data set, are essential for data sufficiently valuable to preserve for potential reuse. Without such documentation the value of data depreciates rapidly due to human and institutional memory loss; the loss of field and laboratory notes; and career changes, retirements, and deaths of the data originators. Metadata are particularly critical for data from long-term studies given the high reuse value of such data and because long-term research projects generally have a changing group of investigators. Without adequate accompanying metadata, which can be tedious, time-consuming, and expensive to assemble, soils data may have limited value beyond the original study.

We strongly encourage researchers conducting long-term soils research to include sufficient metadata with data that have future potential value. What metadata are sufficient? Michener et al. (1997), in a thorough review of metadata (costs, benefits, and implementation), propose a metadata standard for nongeospatial ecological data similar to that already established for geospatial data (e.g., National Institute of Standards and Technology 1992; Federal Geographic Data Committee 1994). We adapted their version to accommodate long-term soils work (Tab. 1.2). Data from long-term studies should be able to meet the "20-year test" (Webster 1991; Strebel et al. 1994; Michener et al. 1997), meaning that someone unfamiliar with a study should be able to readily utilize data 20 years after their collection. The monetary costs associated with developing and maintaining metadata are not trivial but must be considered obligatory for those conducting and funding long-term research.

Table 1.2. Metadata Descriptors

Descriptor	Explanation
Class I. Data Set Descriptors	
Data set identity	Title or theme of data set
Data set identification code	Accession number or code specified by the data set originator or data management personnel to identify a data set
Data set description	Summary of research objectives, data set contents (including temporal and spatial context), and potential uses of the data
Originators	Name(s) and address(es) of principal investigator(s) associated with data set
Abstract	Summary of research objectives, data set contents (including temporal and spatial context), and potential uses of the data
Keywords	Theme and contents, ecosystem type, location
Class II. Research Origin Descriptors	
Overall project description	(Note: this section may be essential if the data set represents a component of a larger or more comprehensive database; otherwise relevant items may be incorporated into the subproject description, below.)
Identity	Project title or theme
Originator(s)	Name(s) and address(es) of principal investigator(s) associated with the project
Study period	Start date and end date or expected duration
Objectives	Scope and purpose of research project
Abstract	Summary of the broader scope of the overall research project
Funding source(s)	Name(s) and address(es) of funding sources, grant and contract numbers, and funding period, if available
Subproject description	
Site description	
Location	Latitude and longitude, political geography, permanent landmarks or reference points
Physiographic region	Ecoregion, physiographic province, major land resource area
Landform component	Backslope, summit, floodplain, stream terrace
Watershed(s)	Size, boundaries, receiving waterways (streams, rivers)
Terrain attributes	Slope, aspect, slope curvature, elevation, microtopography, catchment area, catena position
Soils	Taxonomic unit (order and series if available), depth, texture, thaw depth, pans, presence of upper organic horizons or organic debris
Predominant soil parent material type	Residuum, alluvium, glacial drift, colluvium, lacustrine deposits, etc.
Lithology of predominant soil parent material	Sandstone, shale, limestone, granite, gneiss, etc.
Geomorphic history and approximate age of geomorphic features	Erosional and depositional events, slumps, etc.
Predominant vegetation communities	Tall-grass prairie, eastern temperate forest, tilled agricultural field, etc.
History of land-use and natural disturbances	Management activity (e.g., plowing, fertilization, liming, grazing, cutting, clearing, scarification), wildfires, drainage, depositional and erosional events, pest outbreaks, severe storms, severe climatic events, and other "acts of God" (e.g., volcanoes and earthquakes)

(*continued*)

Table 1.2 (*continued*)

Descriptor	Explanation
Climate	Summary of climate statistics
Experimental or sampling design	
Design characteristics	Experimental design, field replication, subsampling and compositing, decisions regarding inclusion or exclusion of heterogeneous features (e.g., deadwood, rocks, furrows)
Permanent plots	Dimension, location, vegetation characteristics
Data collection period and frequency	
Sampling area, depth, horizons	Area, depth, and horizons sampled for each analysis
Research methods	
Field and laboratory	Description of protocols, including references to standard methods
Sample processing	Sieving, storage time and conditions (e.g., refrigeration, freezing, air drying), removal or inclusion or roots, grinding
Instrumentation	Type, manufacturer, and model
Standards	Use and frequency of standards (certified and other)
Project personnel	Principal and associated investigator(s), technicians, and students
Class III. Data Set Status and Accessibility	
Status	
Latest update	Date of last modification
Latest archive date	Date of last data set backup
Metadata status	Date of last metadata update and current status
Data verification	Status of data quality assurance checking
Accessibility	
Storage location and medium	Pointers to where data reside (including redundant archival sites)
Contact person(s)	Name and address, phone, fax, electronic mail address, and web home page
Copyright restrictions	Whether copyright restrictions prohibit use of all or portions of data set
Proprietary restrictions	Any other restrictions that may prevent use of all or portions of data set
Release date	Date when proprietary restrictions expire
Citation	How data may be appropriately cited
Disclaimer	Any disclaimer that should be acknowledged by secondary users
Costs	Costs associated with acquiring data (may vary by size of data request, desired medium)
Class IV. Data Structural Descriptors	
Status	
Identity	Unique file names or codes
Size	Number of records, record length, number of bytes
Format and storage code	File type (e.g., ASCII, binary), any compression schemes used
Header information	Description of any header data or information attached to file (Note: may include elements related to "Variable information" [below]; if so could be linked to appropriate section[s])
Alphanumeric attributes	Mixed, uppercase, or lowercase
Special characters/fields	Methods used to denote comments or to flag modified or questionable data

(*continued*)

Table 1.2 (*continued*)

Descriptor	Explanation
Authentication procedure	Digital signature, checksum, actual subset(s) of data, and other techniques for assuring accurate transmission of data to secondary users.
Variable information	
Variable identity	Unique variable or code
Variable definition	Precise definition of variables in data set
Units of measure	SI units of measurement associated with each variable
Data type	
Storage type	Integer, floating point, character, string, etc.
List and definition of variable codes	Description of any codes associated with variables
Range for numeric values	Minimum and maximum
Missing value codes	Description of how missing values are represented in data set
Precision	Number of significant digits
Data format	
Fixed, variable length	
Columns	Start and end columns
Optional number of decimal places	
Data anomalies	Description of missing data, anomalous data, calibration errors
Class V. Supplemental Descriptors	
Data acquisition	
Data forms or acquisition methods	Description or examples of data forms, automated data loggers, digitizing procedures, etc.
Location of completed data forms	Physical location (address, building name, room, or office number)
Data entry verification procedures	Methods employed to identify and correct errors during data entry
Quality assurance/quality control procedures	Identification and treatment of outliers, description of quality assessments
Supplemental materials	References and location of maps, photographs, slides, videos, GIS data layers, physical specimens, field notebooks, comments, etc.
Computer programs and data-processing algorithms	Description or listing of any algorithm or software package used in deriving, processing, or transforming data
Archiving	
Archival procedures	Description of how data are archived for long-term storage and access
Redundant archival sites	Locations and procedures followed to provide redundant copies as a security measure
Publications and results	List of publications resulting from or related to the study, graphical and statistical data representations, primary Web site(s) for the data and the study
History of data set usage	
Data request history	Log of who requested data and for what purpose
Date set update history	Description of any updates performed on the data set
Questions and comments from secondary users	Questionable or unusual data discovered by secondary users, limitations or problems encountered in specific applications of data, unresolved questions or comments

Sources: Adapted from Michener et al. (1997) and Chapter 2, this volume.

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FOR

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