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# Collection of Soil Solution

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The collection and analysis of the in situ soil solution is important for studies of pedological processes, environmental quality monitoring, and nutrient cycling (Zabowski and Ugolini 1990). Soil solution measurements are relevant for plant uptake and nutrient availability concerns, and estimates of solution fluxes from ecosystems are needed to balance ecosystem nutrient budgets and for research questions addressing losses of elements via leaching. Although laboratory soil extracts using chemical extractants or resin bags may measure an index of time-integrated nutrient availability, such extracts cannot measure fluxes within or between ecosystems.

Soil solution can be measured either by collecting field-moist soils and extracting solutions in the laboratory or by collecting solution in the field, usually with lysimeters. We will discuss three soil solution collection and measurement techniques here: field exchange resin membranes, soil lysimeters, and laboratory extraction of soil solution. Each technique measures something slightly different, and the technique needs to match the specific research question. Zero-tension lysimeters may be most appropriate for measuring fluxes through the soil profile and absolute losses from the system, while tension lysimeters can measure soil solution chemistry by depth and are indicated for questions relating to solution-solid phase equilibria or plant nutrition (Lajtha et al. 1995; Marques et al. 1996). Field resin measurements reflect both diffusion coefficients and mobile soil concentrations, and are often used to measure in situ nutrient availability. Laboratory extraction of soil water is generally less invasive and time-consuming than lysimeter installation and maintenance, and is useful for measurements of the intensity of soil solution. Detailed discussion of methods, as well as comparisons among methods, is offered in each section.

## Field Resin Membranes

Many authors have used field-placed resin bags, prepared as for laboratory resin bags (described in Chapter 7, this volume) to monitor in situ nutrient availability. An alternative technique is the use of anion and cation-exchange resin impregnated membranes to measure nutrient bioavailability in the field (Abrams and Jarrell 1992; Cooperband and Logan 1994). Since ion-exchange resins have the potential to mimic nutrient uptake by plant roots, resins placed in the field can provide a measure of nutrient supply in soils (Huang and Shoenau 1996).

Ion-exchange membranes (IEMs) are well-defined planar, ion-sink surfaces. As such, they offer a specific geometry, unlike mesh bags filled with resin beads. In addition, the exchanger surface is in direct contact with soil particles, eliminating potential interferences from mesh bag material. The membranes are less likely to disrupt the flow of water through soils than are resin bags, and there is less soil disturbance with membrane placement in soils. However, as for resin bags, the amount of a nutrient sorbed by the membranes is not a quantitative measure of a pool size or of nutrient mineralization but rather is a correlate of the amount of labile nutrients in soils.

Membrane-bound $NO_3^-$ has been shown to be highly correlated with soil $NO_3^-$ concentrations and net soil nitrification (Subler et al. 1995). However, Giblin et al. (1994) found that nutrient accumulations on ion-exchange resins did not correlate well with other measures of $NH_4^+$, $NO_3^-$, or phosphate availability in an arctic ecosystem, although landscape differences in N versus P accumulation corresponded well with N:P ratios in soils and soil solutions. Lajtha (1988) found that total mineral N sorbed by resins was correlated with laboratory N mineralization rates over a desert landscape, but this relationship was weak, and P accumulation was not related to other measures of P availability. Accumulation onto resins is significantly affected by water flux, whereas field and laboratory measures of mineralization do not allow for changes in water flux. Thus resins might well pick up subtle differences in ion supply in the field when water flux changes rapidly. Because resins cannot measure pool sizes or fluxes, this technique is recommended only when an index of ion supply in the soil solution is needed.

Advantages to the IEM technique include

- soil is not removed and is only minimally disturbed using this technique, allowing repeated measurements on a fairly small area;
- chemical processing is simple;
- analysis includes a dynamic component that cannot be reproduced in the laboratory;
- little waste is generated in the laboratory; and
- the analytical equation can be specifically solved to produce a "universal" quantity.

However, there are also several concerns with this technique related to IEM sensitivity to the field environment:

- IEMs are slightly sensitive to temperature (10% change per 10 °C temperature change);

- IEMs are sensitive to soil water content (Nye and Tinker 1977); and
- IEMs are potentially sensitive to the total concentration of anions; in most cases, this means $Cl^-$, $SO_4^{-2}$, and occasionally $HCO_3^-$.

### Materials

1. Ion-exchange resin membranes (available from a variety of sources including Soil-Plant-Water Quality, 125054 NW Cornell Rd., Portland, OR 97229). Both anion and cation IEMs are available; use anion-exchange resins to determine phosphate and nitrate; use cation-exchange resins to determine potassium, calcium, sodium, magnesium, and other divalent metals. Ion sinks are available in a range of sizes, from 0.45 $m^2$ sheets to 5 cm × 5 cm squares, or even smaller. The size used depends on the field sampling desired and ease of handling in the laboratory. The actual parameter determined, $M_t$, is independent of size, although a large ratio of perimeter to area can result in unacceptable edge effects. The 5 cm × 5 cm size is recommended.
2. 10 cm diameter petri plates, plastic or glass
3. Heavy-duty putty knife
4. 0.5 mol/L $NaHCO_3$
5. 0.5 mol/L HCl

### Procedure

1. Before use, chloride-saturated anion-exchange membranes must be converted to the bicarbonate form. Shake resin sheets for 10 minutes in three successive solutions of 0.5 mol/L $NaHCO_3$, rinsing with deionized water between each solution. Although the bicarbonate form is less stable, it is preferred for determining P availability, since P affinity for the resin is low relative to $Cl^-$ and $OH^-$.

   Cation-exchange membranes are usually supplied in the $H^+$-saturated form. Before use, the membranes should be rinsed thoroughly with fresh 0.5 mol/L HCl solution.
2. Prior to installation, ion sinks can be labeled by placing nylon monofilament line through a hole in one corner, tying it off with a knot, and connecting a label to the other corner. The label may be made of any material that maintains its integrity in the field. Membranes are inserted into slits opened in the soil with a broad-bladed tool like a putty knife. They can be placed at any depth; in most cases, the primary root zone is the region of greatest interest. Ideally they should be placed at a slight angle from the vertical, e.g., 15–30°, since this creates better soil-membrane contact. If desired, one cation sheet and one anion sheet can be placed back-to-back in each slit. They can then be treated as a unit through the desorption and analysis phases.
3. The membranes should not be left in soil longer than 100 hours in most cases. Beyond this time the membrane may no longer maintain a near-zero concentration of phosphate or nitrate at its surface. If the concentration near the surface becomes significant relative to the soil concentration, the simple model

described later no longer applies and interpretation is complicated. Even with resin bags, Giblin et al. (1994) noted that long deployment times gave lower estimates of nutrient availability than did a series of shorter deployments; they also noted that nitrate and phosphate could be desorbed from resins in the field.

The ion sink should be removed from the soil gently, although mild scraping of the soil from the surface causes little change in the amount extracted. Clinging soil particles should also be removed gently, and the membrane rinsed with deionized water to remove any additional soil. A small amount of soil on the membrane will not cause problems in the extraction except for trace metal determinations.

4. Keep the IEMs moist, e.g., in a Ziplock bag with a few drops of deionized water, prior to desorption. However, in most cases drying does not appear to adversely affect sorption properties. Dab the ion sink dry with a clean cloth, placed in 25 mL of 0.5 M HCl in a petri plate, and gently shake for 20 to 30 hours. The desorption sample solution can be stored in polyethylene bottles for analysis using appropriate laboratory techniques.

### Calculations

The defined planar geometry allows simple mathematical analysis of results. Vaidyanathan and Nye (1966) attempted to determine the effective P diffusion coefficient, $D_{eff}$, in soil by applying the following relationship to uptake by an exchanger sheet:

$$D_{eff} = \frac{1}{4} M_t^2/(4 \times t \times c^2)$$

where

$D_{eff}$ = effective diffusion coefficient, expressed as $cm^2/sec$

$M_t$ = mass sorbed on planar surface after time $t$, expressed as $\mu mole/cm^2$; divide the total amount of ion extracted from the resin, $\mu$moles, by the surface area of the resin. For a 5 cm × 5 cm sheet, with one side in contact with soil, the area is 25 $cm^2$. If both sides of the ion sink are exposed to soil, then both sides are counted in the area term (50 $cm^2$ for the preceding example).

$t$ = time after placement in soil in seconds

$c$ = effective diffusible P concentration in soil, as $\mu mole\ p/cm^3$ soil

Since $M_t$ and t are known from analysis, rearranging the preceding equation allow us to calculate a term $c^2D_{eff}$ designated the *ion sink bioavailability factor* (Abrams and Jarrell 1992):

$$c^2D_{eff} = \frac{1}{4} M_t^2/(4 \times t)$$

### Special Considerations

Huang and Shoenau (1996) describe the construction of an IEM probe that makes it easy to insert the membranes into the soil and ensures minimum disturbance of the surrounding soil, as well as permitting easy retrieval. Membranes are attached

to long stakes with the bottoms of the stake pointed for easy insertion, and a single probe spans the entire soil profile. After probes are retrieved (Huang and Schoenau [1996] used field placement times of 2 hours), sections of membranes corresponding to specific depths or horizons can be cut out and analyzed separately. To best compare basic fertility among several similar sites, ion sinks should be inserted after a soaking rain or irrigation, to make water content more comparable among treatments.

## Lysimeters

Many types of lysimeters have been used in both agricultural and natural settings, and they collect water either with or without applied tension to extract water. Tension lysimeters are generally smaller and relatively easy to install, and they collect water from the soil matrix. They have been made of ceramic, glass, Teflon, and other materials, and partially filter water that enters the lysimeter. Zero-tension lysimeters collect gravitational water, generally have significantly larger collection areas than tension lysimeters, and have been constructed from pans or PVC pipe, among other materials.

Tension lysimeters and zero-tension lysimeters collect different pools of water, and thus deciding which lysimeter type to use in specific studies is not necessarily a simple matter. Any differences in the chemical composition of water collected by tension and zero-tension lysimeters could lead to biases in estimates of nutrient fluxes if one or the other types are used.

Zero-tension lysimeters can collect only saturated flow or macropore flow, not gravitational or matric flow (which occurs at 0.01–0.03 MPa tension). Water will not enter the collection vessel of a zero-tension lysimeter unless the water is saturated at some stage along the collection pathway, but this is probably true of the majority of water moving through the soil profile. Tension lysimeters, on the other hand, could in theory collect both matric and saturated flow components; however, in practice, the hydraulic conductivity of tension lysimeters is probably too low to proportionally sample saturated flow in many cases. This all remains a matter of conjecture, however, insofar as there have been no systematic studies of the degree to which tension lysimeters bias against saturated flow via macropores. Haines et al. (1982) compared volumes and chemistry of soil solutions collected by tension and zero-tension lysimeters at Coweeta, North Carolina. They found that the zero-tension lysimeters collected seven times more solution than the tension lysimeters in the litter, probably because the zero-tension lysimeters are more efficient at collecting macropore flow. In the deeper horizons, however, the zero-tension lysimeters collected 50% less water because they miss unsaturated flow.

Tension lysimeters could also, in theory, collect soil water at the appropriate volumes if their tension is set to exactly that of the soil. Commercially available Prenart systems include the option of having lysimeter tension set to that measured with tensiometers. With lysimeters set at a constant tension, however, there is almost always either an underestimate or an overestimate of soil water flux because the tension at the lysimeter usually differs from that of the soil, which can vary. This is sometimes referred to as *coning*. If tension is too low, water will move around the lysimeter and

flow though the soil as unsaturated flow in the matrix, which is always the case in the zero-tension lysimeter.

Several authors have compared the chemical composition of soil solutions collected by zero-tension versus tension lysimeters (Haines et al. 1982; Nyberg and Fahey 1988; Swistock et al. 1990; Hendershot and Courchesne 1991; others summarized in Marques et al. 1996). Although several found that soil solutions collected with the tension lysimeters had higher concentrations, as one would expect since they should collect a more tightly bound fraction of soil water, this varied a great deal depending on the ion examined and the site. In general, there have not been clear patterns of differences between lysimeter types across the many studies, although nitrate often appears to be elevated in tension versus zero-tension lysimeters.

### *Zero-Tension Lysimeters*

Zero-tension lysimeters can be used to assess both the quality and the quantity of water leaching through the soil profile, and thus are critical for complete ecosystem elemental budgets. However, collection efficiencies (volume of water collected divided by percolating volume, which is separately calculated from a water balance model) are often low, and thus zero-tension lysimeters may not be appropriate for use in fairly dry systems or when large volumes of water are needed. They have the advantage of continuously sampling moving water rather than sampling water only when tension is applied. However, this also means that water may collect in storage bottles between collection events, and even with preservatives there is the possibility of nutrient or elemental transformation or loss via denitrification, volatilization, or flocculation.

Published collection efficiencies of zero-tension lysimeters are generally less than 10% (Radulovich and Sollins 1987). Radulovich and Sollins (1987) found that by increasing catchment area to 2500 $cm^2$ and by pushing the lysimeter rim upward into the soil, collection efficiency was increased to 36% under grass and 17% under forest, and the failure rate of lysimeters was also substantially decreased. Jemison and Fox (1992) found a mean collection efficiency of about 50% for pan lysimeters even larger than those used by Radulovich and Sollins (1987) that were placed at a depth of 1.2 m in an agricultural soil in Pennsylvania; they also noted a large variation among lysimeters. The greater efficiencies of large pan area lysimeters is likely due to both the greater chances of collecting preferential flow water and a lower proportion of flow around the edges of the pan. Thus, it would appear that matric potential–driven water flow in soils can be a significant proportion of total soil water flux. Even in a highly sandy soil with high infiltration rates, Seely et al. (1997) found that large catchment area lysimeters at 15 cm depth captured only 25–75% of flow. Efficiency at 50 cm depth was reduced to 15–25% of calculated flow, and efficiencies at 100 cm were under 10%.

#### Materials and Procedure

1. Because of low collection efficiencies, we recommend constructing lysimeters to be the largest size possible for the money and labor available. Jemison

and Fox (1992) used 0.5 $m^2$ catchment areas, while Radulovich and Sollins (1987) used 0.25 $m^2$ areas; we recommend areas within this range. However, collection efficiency is never 100%, and thus chemical data must be combined with a water balance model (see later discussion) for calculation of element flux.

The material used to construct the lysimeter should be chemically inert. Pan-type lysimeters are often constructed of aluminum. If these are custom made, the height of the side walls can be varied and thus favor water flow to the lowest corner of the pan with the outlet port. Seely et al. (1998) constructed lysimeters from 10 cm diameter PVC pipe that was cut in half lengthwise and had caps at each end. The latter design has the advantage of easier installation into long but narrow tunnels, although edge area:volume is greater than in square pan lysimeters. If asymmetrical pan lysimeters are constructed, outlet ports are placed at the lowest corner. If pipe is used, outlet ports are installed at one end, and lysimeters must be installed at an angle to ensure gravity flow of water to collection bottles. To prevent soil from collapsing into the lysimeter, lysimeters are filled with polypropylene pellets, acid-washed silica sand, or other inert materials to a level a few millimeters below the edges of the lysimeter.

2. Install lysimeters from large pits. To measure element flux from below the rooting zone, lysimeters must be placed at a depth below where at least 90% of roots are found. This should be determined in advance and will vary among ecosystems. Pits should be dug to at least 0.5 m below the lowest lysimeter depth, and should be sufficiently wide for easy manipulation of collection bottles. In many soils wooden support structures inside the pit will be needed if pits are to be maintained for several years. Plywood pit covers also protect the pits from disintegration. Side tunnels from the pit faces are excavated at the appropriate depths for lysimeter installation so that each lysimeter collects solution water from underneath an undisturbed soil profile. At least 50 cm space between the pit face and the edge of the lysimeter is needed to avoid edge effects, and lysimeters placed at different depths should not overlap.
3. Place lysimeters in the tunnel and push them up against the bottom of the soil horizon to maximize contact. Because the fill material does not come up to the top edge of the lysimeter, the top of the lysimeter will cut into the soil profile, and soil will fill the very top of the lysimeter. This last step is critical because matric potential will change between the soil and the lysimeter fill material, and water flow tends to follow matric potential; thus water will tend to flow laterally around the outside edges of the lysimeter unless a physical barrier (i.e., the top edge of the lysimeter wall) is present. Boards or other materials are often used to add pressure to the bottom of the lysimeter to ensure a close contact with the bottom of the soil profile.
4. Connect the outlet port via Tygon tubing to collection bottles that sit at the base of the pit. The tubing should enter the bottle through a tightly fitted hole in a cap. A smaller hole with smaller-diameter tubing must also be placed in the cap as a pressure equilibration port, and the tubing should be wrapped in circles to minimize evaporation losses. The volume capacity of the collection

bottle will depend on the area of the pit and the estimated maximum precipitation per area for each rainfall event. Because bottles will sit for several hours, or perhaps days, between collection, the possibility exists for nutrient loss or transformation. The addition of several drops up to 1 mL of chloroform will prevent microbial transformation, but chloroform evaporates and thus will need to be renewed often. It is important to collect water after each rainfall event.

5. Pump and discard several water collections. Although disturbance to the overlying soil pit is minimal, most researchers have suggested an equilibration period to counteract disturbance effects. Some authors have suggested equilibration periods of up to 2 years. We recommend a period of at least 6 months with indicators of disturbance, such as elevated $NO_3^-$ leaching, used to judge when disturbance effects are past.

### *Tension Lysimeters*

Perhaps due to their relative ease of installation and their premade commercial availability, tension lysimeters have been used more extensively than have zero-tension lysimeters. Large soil pits do not need to be dug because lysimeters can be installed from soil cores. However, the use of tension lysimeters requires disturbing the soil column immediately above the tube lysimeter, and in contrast to zero-tension lysimeters, it is not clear what area of soil is being sampled with a tension lysimeter, although the depth of soil water collection can be regulated.

Lysimeter installation always involves some degree of soil disturbance, even when performed from tunnels as in the plate system or at an angle as in Prenart™ lysimeters. This disturbance can result in anomalously high soil solution concentrations of nitrate and/or silica bicarbonate (the latter in soils with large amounts of weatherable minerals; Liator 1988; Shephard et al. 1990; Lajtha et al. 1995). The best way to account for this effect is to simply wait until several year's data can be collected and regular seasonal patterns can be observed, allowing the anomalous period to be identified. The waiting period for this can range from 2 to 4 months to 2 years. Johnson (1995b) found a very large nitrate pulse (>7,000 $\mu$eq $L^{-1}$), which lasted over a year after lysimeter installation in a beech forest soil in the Great Smoky Mountains.

The most common commercial tension lysimeters consist of a PVC or other tube of inert material that is of a variable length, with a round-bottomed ceramic cup at the bottom that serves as the filtering membrane for soil water. A neoprene access tube, fitted into the PVC tube by a rubber stopper, extends above the surface of the soil and is connected to the vacuum source for water collection. Ceramic cups can be purchased and lysimeters can be customized for specific applications (e.g., Stone and Robl 1996). Alternatively, lysimeters can be made of the "plate" type: a ceramic plate can be installed in the soil sideways from a soil pit, as for zero-tension lysimeters, with direct connection to an access tube.

Other, more inert materials than ceramic have been used for the collection-filtering membrane of both tube and plate lysimeters, including fritted glass, fritted stainless steel, glass-steel mixtures, and Teflon or Teflon-glass mixtures. These ma-

terials address concerns raised by some about the chemical inertness of porous ceramic, even with acid leaching or equilibration as pretreatments Zimmerman et al. 1978; McGuire et al. 1992). The material used for the soil interface must be hydrophilic in order to maintain the capillary tension necessary to keep tension between rain events. If the lysimeter material is hydrophobic, lysimeters may be coated with hydrophilic materials such as silica flour. By their very nature, these materials interact to some degree with the solutions passing through them. Liator (1988) provides a comprehensive review of chemical interactions with various types of lysimeters; see also Grossmann and Udluft (1991) and McGuire et al. (1992). Suffice it to say that results vary depending on contact time, the ion in question, and soil characteristics.

We have found that fritted glass or Prenart Teflon-glass lysimeters equilibrate with most ions rather quickly and are slightly superior to ceramic in terms of phosphate retention. Prenant lysimeters are also small and can be installed at an angle, thus minimizing soil disturbance. Glass is clearly less desirable in cases where Si or B (borosilicate glass) is of interest but would be superior to the alundum in ceramic in cases where Al is of interest. Krejsl et al. (1994) found that excessive filtering in ceramic lysimeters made them unsuitable for collecting and quantitatively measuring microbial constituents; they recommended using sand-filled or fritted glass lysimeters. In cases where soil pits can be dug, plate lysimeters might be preferable because the overlying soil column is left relatively intact; when many lysimeters must be employed or when soil disturbance is to be kept to a minimum, tube lysimeters are probably preferable.

The amount of tension that should be applied to draw soil water into the tubes has also come into question; it should be remembered that radically different tensions will draw on different sources of soil water, with potential repercussions for chemical analysis. Because tension is applied, it cannot be assumed that the water collected by tension lysimeters is chemically equivalent to water that leaches through the soil profile, although it is this latter quantity that is to be measured in ecosystem-level budget analyses. Tension lysimeters can collect too little water if there is saturated flow that is flowing in faster than the hydraulic conductivity of the lysimeter material. Coning toward the tension lysimeters (too much water) can occur if tension is set too high.

Finally, as for zero-tension lysimeters, an accurate water balance model must be constructed for each site to translate soil solution concentrations into ecosystem-level fluxes.

### Materials

1. Soil water samplers of desired lengths. A wide variety of premade lysimeters of different ceramics and lengths can be purchased from Soilmoisture Equipment Corp. (P.O. Box 30025, Santa Barbara, CA 93105; 805-964-3525); Prenart Equipment ApS (Buen 14, DK-2000 Frederiksberg, Denmark, phone: +45 3874 1664) makes lysimeters of a variety of materials.
2. 2–4 inch soil corer (a larger soil core will be needed for more rocky soils)
3. Bentonite clay (optional, available from Soilmoisture Equipment Corp.)

4. 200-mesh silica sand (available from Soilmoisture Equipment Corp. or hardware stores)
5. Field soil sieve to remove pebbles and rocks from backfill material
6. Ehrlenmeyer flask with two-hole stopper for soil water collection
7. Vacuum hand pump or battery-operated pump with a tension gauge

### Procedure

Lysimeters come with fairly detailed installation instructions for different situations, and virtually all materials needed for installation and collection can be purchased from the manufacturer. The following procedure is for the commonly used ceramic cup lysimeters; Prenart systems come with pointed ends for insertion, and directions are provided. Grossman and Udluft (1991) also provide installation guidelines. We recommend using the most complex, but the safest, installation method that isolates the ceramic cup from the soil below the depth to be measured, and that guards against channeling of water down the installation hole.

1. Dig soil cores to the desired depth, and sieve the extracted soil for use as backfill material.
2. Pour a small quantity of wet bentonite clay into the bottom of the core to isolate the sampler from the soil below.
3. Pour a small layer of silica sand into the hole and insert the lysimeter, followed by at least 6 inches of silica sand to completely cover the ceramic cup of the lysimeter.
4. Add a small quantity of bentonite clay to guard against channeling of water down the installation hole, and backfill the hole with the sieved native soil with continuous tamping with a metal rod to ensure that large air pockets do not form. The main concern with installation is that the ceramic cup should be in tight, intimate contact with the soil (or with the silica sand that is in contact with the soil) so that soil moisture can move readily from the pores of the soil through the pores in the ceramic cup and into the soil water sampler. It may be necessary to protect the top of the lysimeter and the access tubing from native fauna with metal screening.
5. After equilibration, soil water may be collected in a number of ways. In general, tension is applied using a hand pump, and the lysimeter is allowed to draw in soil moisture for 12–24 hours. A pinch clamp at the end of the neoprene access tube allows the hand pump to be removed while leaving the lysimeter under tension. To retrieve the collected water from the lysimeter into a collection flask, tension may be applied to tubing that is inserted into one hole of the two-hole stopper in the Ehrlenmeyer flask, while plastic tubing from the other hole of the stopper is inserted into the lysimeter via the neoprene access tube.

### Special Considerations

Lysimeters can be adapted for under-snow sampling by adding vent and sample collection lines to the collection bottles or to the lysimeter tube itself (Johnson et al.

1977; Johnson 1995a). The vent and sample collection lines are elevated on poles or on trees and closed while the vacuum is on and samples are being collected. During collection, both lines are opened, and samples are simply withdrawn from the sample line with a vacuum pump and collection vessel from above the snowpack.

### Calculations for Both Zero-Tension and Tension Lysimeters

To obtain nutrient flux data from lysimeters, one must obtain a volume-weighted average annual concentration for the site measured and multiply this by the "true" estimate of water flux obtained either from a model or from the use of $Cl^-$ as an inert tracer. In the latter case, it is assumed that $Cl^-$ flux into the system equals $Cl^-$ flux out, and soil solution water balance is calculated as the one unknown variable:

$$\text{Soil water flux} = [Cl^-(dep)/SS(Cl^-)] \times F$$

where

$Cl^-(dep)$ = chloride deposition
$SS(Cl^-)$ = weighted average soil solution chloride concentration
$F$ = the factor for converting volumes of water to centimeters

Many hydrology models are available that differ substantially in the attention paid to processes such as interception of rain and snow, snowmelt, and saturated/preferential flow. These processes differ in importance by site, and thus a model suitable for one site may not be suitable for another. Because of this, we make no attempt to recommend hydrology models. Instead, we list criteria by which a model might be selected, given site hydrologic characteristics.

Most hydrology models are geared toward predicting streamflow (hydrographs) and thus devote considerable attention to subsoil and channel processes. Such processes are irrelevant to predicting flow past surface soil lysimeters; thus in choosing a model, it is important to pay close attention to the model representation of surface soil and litter moisture processes, and to the processes that control them. Specifically, note the following:

- For soils in which most of the water drains via saturated and/or preferential flow, the model needs to deal with such flow; models that assume that waters drain via unsaturated flow are not recommended for sites at which this does not happen.
- If a snowpack forms at the site, then the model must deal with the timing of snowmelt; moreover, if lysimeters are located under the canopy, the snowmelt model has to deal with the influence of the canopy on the snowpack energy balance.
- If lysimeters are located under different types of plant cover, then the model must consider effects of plant cover on transpiration, interception, and evaporation from the canopy.
- Finally, if lysimeters are located directly beneath the litter layer, then the model needs to predict drainage from the litter layer.

Most hydrology models are tested by comparison with streamflow data. Given our interest here in predicting flow past lysimeters, we recommend that the model be tested instead by comparison with time-series data on soil moisture for the layers above the lysimeters (see Chapter 3, this volume). In addition, comparison of simulated and measured throughfall, snowpack moisture, and litter moisture content is highly recommended. Annual or seasonal streamflow totals can provide a valuable check on model predictions of evapotranspiration, but a model's ability to predict short-term (i.e., daily or hourly) variation in streamflow is generally not a good test of its ability to predict flow past lysimeters.

## Laboratory Collection of Soil Water from Soil Samples

Soil solution has been extracted from soils in a number of ways in the laboratory. In many cases, a simple extraction using a low ratio of water to soil provides an adequate estimate of soil solution composition. A relatively large soil sample can be used, which helps to minimize effects of heterogeneity in the soil. This procedure can be performed, which works best for field-moist samples.

### *Saturation Paste Extract*

The saturation extract method is commonly used to extract soluble salts from soils (Richards 1954; Janzen 1993). The composition of this extract is generally closely related to that at field-moist water contents, with the advantage that the solution can readily be extracted using a Buchner funnel vacuum system. The technique can be used to assess the quantities of nitrate and other nonsorbing ions in the soil. For elements that are highly buffered in soils, such as P, cations, and trace metals, the effects of soil water content on concentration in solution are small.

The method also allows simultaneous determination of two physical parameters that can be informative: saturation percentage and saturated bulk density. Saturation percentage is a reasonable indicator of the texture of the soil and micropore space (sands are low, clays are high in saturation percentage). The saturated bulk density can indicate the average particle density of the soil solids; this is especially useful where coarse organic matter constitutes a significant (>5–10%) volumetric fraction of the soil.

We recommend that the analysis be performed on field-moist soils. Frozen samples can be thawed and analyzed, although it is preferable to analyze the sample within 48 hours of collection. The final saturated water content is corrected for the sample's field-moist water content. Air drying the field soil can precipitate salts that redissolve only slowly upon rewetting, if at all.

#### Materials

1. Balance weighing to 1 kg
2. 500 mL graduated plastic, glass, or aluminum container
3. 500 mL graduated cylinder

4. Spatula
5. Buchner (vacuum) funnel apparatus

### Procedure

1. Determine the tare weight of the beaker and add 400 g of field-moist soil.
2. Determine the gravimetric water content of a separate subsample as per Chapter 3, this volume.
3. Add deionized water gradually with regular mixing with a stainless steel spatula. Allow samples to stand without mixing at several points in the procedure. The sample will be saturated when free water at the soil surface causes the surface to change from a dull sheen to a brighter glistening. In most cases, the soil will flow slightly when the beaker is tilted, but it will not drip out. After the soil appears to be saturated, it should be checked after an hour to determine if it needs more water. Once it is saturated, the beaker is weighed and the volume of saturated soil in the containers estimated.
4. After the sample has been fully saturated, allow it to equilibrate for $4 \pm 1$ hours. The saturation paste is then filtered through Whatman no. 42 filter paper in a 10 cm Buchner funnel. Smaller-diameter funnels are more likely to clog and result in slow filtration rates.
5. Refrigerate the filtrate until analysis. After pH and electrical conductivity have been determined, the filtrate can be stabilized further with 2 mL of 1 mol/L HCl.

### Calculations

Solution composition: In most instances, results are expressed in terms of "concentration in the saturation extract," in mg/L or mol/L. For nonsorbing species such as nitrate, composition may be related back to dry mass of soil and expressed as mg $NO_3^-$–N/kg dry soil.

$$\text{Saturation percentage (estimate of pore volume)} = 100 \times [(\text{mass of saturation paste} + \text{beaker}) - \text{mass dry soil} - \text{mass beaker}]/\text{mass dry soil}$$

$$\text{Saturated bulk density} = (\text{mass dry soil})/\text{volume saturated soil}.$$

#### *Centrifugation*

In soils that are not excessively dry during most months of the year, centrifugation of soil water has proved to be an easy and effective way to collect soil water. Most collectors are handmade, thus requiring a large commitment to initial startup time. A common design uses a standard centrifuge tube that has been fitted with an internal screen to isolate particles from the centrifuged soil water, although others have simply decanted the solution successfully (Giesler et al. 1996). Clearly the largest problem with this technique will be limitations to the volume of soil water that may be collected, and thus this procedure is not recommended for chemical analyses that require large amounts of soil water. Soon and Warren (1993) discuss remoistening

field-moist soils to 90% of field capacity and reequilibrating the samples for 48 hours before attempting to extract the soil solution. However, it is most likely that mineralization and dilution, and thus sorption-desorption, will occur, and significantly change the chemistry of the extracted solution, so we do not recommend it here for measures of the in situ soil solution.

Zabowski and Ugolini (1990) compared low-tension lysimeter and centrifuged soil solutions in a subalpine Spodosol over the course of a year. Differences in centrifuge speeds, corresponding to soil solutions held with tensions of about 0–30 kPa versus 30–3000 kPa by soils, did not seem to affect solution chemistry, suggesting that micropore water was fairly constant. However, lysimeter water and centrifuge-collected soil solutions did vary, with centrifuge solutions generally yielding higher concentrations at certain times of the year. The authors suggested that lysimeters are more likely to collect preferential (macropore) flow water, and micropore water, collected by centrifugation, would be more affected by biological activity and would have longer residence times in the soil. Giesler et al. (1996) compared the chemistry of zero-tension versus centrifuged collected soil solutions and concluded that centrifugation would avoid the hydrologic anomalies introduced by lysimeters and thus would be a more accurate reflection of the true soil solution.

There is no standard procedure for this technique. In one design, 60 mL centrifuge tubes have been cut in half crosswise, one half fitted with a mesh screen to support a filter, and then the two halves fastened together again. A glass fiber or smaller filter is placed on top of the screen, and soil is added to the top of the tube; after centrifugation, soil water is collected from the base of the tube. For drier soils, large centrifuge bottles and a high-speed refrigerated centrifuge (capable of $>10{,}000$ g) is recommended. Giesler et al. (1996) centrifuged soils for 80 minutes in centrifuge bottles without screens or filters, but we suggest that the time required, as well as the necessary g-force, will vary depending on the soil examined. Soon and Warren (1993) used the following materials:

### Materials

1. The bottom half of a disposable 60 mL plastic syringe (the top half is cut off)
2. The bottom half of a 50 mL polypropylene centrifuge tube
3. Centrifuge with horizontal 50 mL container rotors. High speed and refrigeration may or may not be needed, depending on the soil and the moisture content.
4. Glass wool
5. Optional: no. 42 filter paper cut into 27 mm diameter disks or glass fiber filters of the largest pore size available
6. Parafilm
7. 1 mol/L HCl
8. 0.45 μm filters (e.g., Gelman or Nucleopore)

### Procedure

1. The cut disposable syringe is used as the soil container. Plug the drainage hole with glass wool and line the bottom with a paper or glass fiber disk. Rinse this

entire apparatus by pouring in several milliliters of 1 mol/L HCl, followed by several deionized water rinses. Dry by centrifuging for several minutes or overnight in a warm oven. If glass fiber disks are used, the wool, the tube, and the filter can all be acid-washed separately beforehand, and the glass filters can be ashed.

2. Place approximately 25 g of field-moist soil into the top of this container.
3. Place the bottom half of a 50 mL polypropylene centrifuge tube into the rotor shield to serve as a solution collecting cup, and place the soil container into the shield and into the cup. Be sure to balance opposite sides of the rotor. Centrifuge at the maximum speed of the centrifuge for at least 30 minutes; experimentation will determine the time needed to extract the maximum amount of solution.
4. Immediately filter the solution through acid-washed 0.45 μm filters and store frozen or acidified for further analysis.

### *Immiscible Displacement with Centrifugation*

An immiscible displacement technique (Whelan and Barrow 1980; Soon and Warren 1993) is more elaborate than the centrifugation-only technique, but it may be best suited for soils where centrifugation alone does not yield sufficient solution for chemical analysis. A dense, immiscible liquid is used to displace the soil solution, which, when centrifuged, floats on top of the immiscible liquid. Disadvantages of this technique include the fact that most of the immiscible liquids used are either relatively toxic or require special material centrifuge tubes to avoid tube dissolution, and generally, the use of a high-speed centrifuge. Advantages include a high yield of soil solution and the use of intact centrifuge tubes without filters or glass wool. The various immiscible liquids used are discussed in detail in Whelan and Barrow (1980) and Soon and Warren (1993). We will follow the recommendation of Whelan and Barrow (1980) in using tetrachloroethylene ($C_2Cl_4$).

#### Materials

1. Polyallomer 50 mL centrifuge tubes with caps
2. Tetrachloroethylene
3. Transfer pipettes or disposable syringes, 10 mL
4. High-speed centrifuge with 50 mL rotor

#### Procedure

1. Weigh 20 g field-moist soil into acid-washed polyallomer tubes.
2. Add 20 mL tetrachloroethylene to each tube. Balance the centrifuge by adding drops of tetrachloroethylene to one pair of tubes until the members of the pair are within 0.002 g of one another.
3. Centrifuge the capped tubes for 1 hour at approximately 20,000 × g.
4. After centrifuging, remove the displaced soil solution with either a transfer pipette or else a 10 mL syringe, and filter through a 0.45 (m filter prior to storing the samples as above.

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# STANDARD SOIL METHODS

FOR

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