

EXPERIMENTAL DESIGN AND INSTRUMENTATION FOR ANALYZING SOLUTE CONCENTRATIONS AND FLUXES FOR QUANTIFYING BIOGEOCHEMICAL PROCESSES IN WATERSHEDS

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Abstract. The quantification of solute fluxes in ecosystems is important for evaluating biogeochemical cycles of ecosystems. The fluxes of solutes include important pathways for elemental inputs, losses and internal cycling within ecosystems. Measurements of solute fluxes can be done at various spatial scales including plots and watersheds. The use of small watersheds has advantages for quantifying hydrological and associated solute inputs and outputs if accurate water budgets are available. Atmospheric deposition of elements includes both wet and dry inputs. The measurements of wet deposition are relatively easy compared to the quantification of dry deposition and many studies focus on this former measurement. Various methods for the quantification of wet deposition will be reviewed emphasizing those methods (e.g., bulk deposition) that can be used in remote and/or undeveloped regions. The same methods used for measuring precipitation can be used for estimating throughfall flux (precipitation that has passed through an overlying plant layer). Solute concentrations within the soil are generally measured using lysimeters. There is a large range of lysimeter designs including zero-tension and tension lysimeters some of which will be reviewed. Specific attention is placed on those lysimeters that can be used in remote locations. The use of other sampling devices for measuring ground water (e.g., piezometers and wells) and surface water discharge is also introduced. The importance of adequate experimental design including the replication in the distribution and location of sampling devices is emphasized. Doing accurate and precise measurements of solute concentrations is also important for making useful biogeochemical measurements.

INTRODUCTION

The quantification of solute fluxes in ecosystems is important for evaluating biogeochemical cycles of ecosystems. Important pathways for solute transfer include precipitation inputs, throughfall, stemflow, soil water, ground water and surface water. The quantification of these fluxes is important for evaluating elemental cycles in those ecosystems with substantial amounts of solute transport. The quantification can be done at various scales ranging from plots, small watersheds, landscapes up to entire regions. This paper will focus on quantification of fluxes in plots and small watersheds. Biogeochemical approaches as a tool for environmental research in small watersheds have been reviewed in Moldran and J. Cerny (1994). The watershed approach has been shown to be highly effective at locations in which water is in excess of evapotranspiration and where accurate water balances can be constructed. Some of the major pathways of solute transfer in a watershed are depicted in Figure 1. Advantages to the small watershed approach include the potential for

developing accurate budgets for some elements if an accurate water budget is available. Disadvantages may include 1) a lack of replication; 2) problems in some regions that do not have watersheds with easily quantifiable hydrology; and 3) extrapolation of watershed results to that of other compartments of the ecosystem (e.g., the cycling of an element within the biota may be decoupled from the overall watershed fluxes of the element).

PRECIPITATION

Precipitation inputs can take place in many forms including rain, sleet, snow and hail. There may also be substantial inputs via dry deposition (gaseous particles) and occult deposition (e.g., fog) depending upon the region, elevation, season and vegetation types. For many studies, the focus is on the measurements of precipitation inputs because this flux is often the major atmospheric source of elemental inputs (Johnson and Lindberg, 1992). The simplest devices for collecting precipitation are bulk deposition collectors. Such devices have been used throughout

the world and have been found to be highly effective. An example of such a device is shown in Fig. 2.

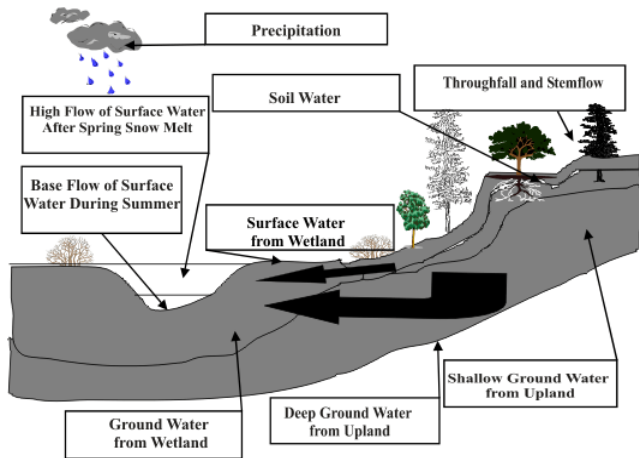


FIGURE 1. Major pathways of solute transfer in a watershed

Generally these devices include a funnel that is connected via tubing to a collecting vessel. It is important to minimize particulate matter from the input and this can be done using screening over the funnel or polyester fiber or glass wool at the base of the funnel. It is important to minimize evaporation and including a loop in the tubing has been often employed. Another concern with this type of collector is chemical transformation of the sample via biotic transformation, especially with warm temperature and light. Some investigators have used opaque or painted vessels to exclude light and preservatives to inhibit biotic transformations.

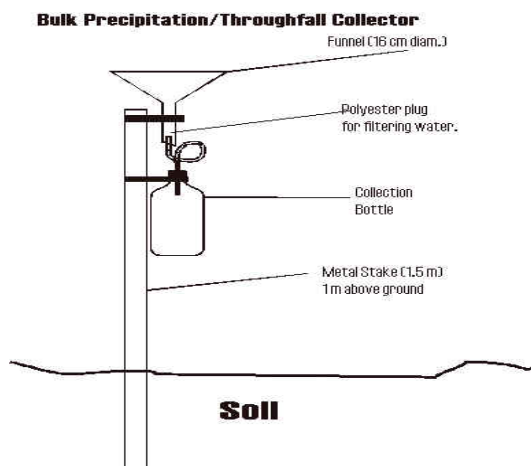


FIGURE 2. Bulk collector for precipitation or throughfall.

Routine cleaning of collecting devices and frequent collection of samples helps to minimize these

problems. Sampling intervals can be as short as individual precipitation events and as long as needed, but sampling over more than monthly intervals should generally be avoided. Another alternative to a collection vessel is to use ion exchange resins. The use of ion exchange resins may be especially useful at remote sites where frequent collection is not possible. Resin columns for anions can be constructed (Bio-Rad Laboratories, 1000 Alfred Nobel Drive, Hercules, CA 94547, USA). The actual amount of the resin added to a column will depend on the total sampling time and the estimated anion flux. After passing through a funnel, the solution passes through the anion exchange resin where SO_4^{2-} , NO_3^- , Cl^- , Br^- and PO_4^{2-} are trapped. Resin columns are replaced as needed (e.g., every 4 to 6 weeks) and extracted with 1 N KI. Recoveries of SO_4^{2-} , NO_3^- and Cl^- are >95% (Figure 3).



FIGURE 3. Bulk collector with ion exchange cartridge (Weathers et al., in prep) (do not duplicate without permission)

In those regions with snow, funnels need to be replaced by other collectors such as buckets. The buckets need to be of sufficient depth and width to allow snow to accumulate. The location and numbers of collectors depend on the study site, but sufficient collectors need to be installed to capture the variation in precipitation inputs. Also, attention should be given to how weather conditions can affect collection efficiency. For example, open sites with wind and snow make it especially difficult to accurately quantify precipitation inputs. For such sites, the use of snow courses combined with snow cores for estimating snow inputs are often useful. In some

studies it may be useful to have measurements of wet only precipitation and the installation of wet-only collectors would be suggested. In the United States there is an extensive network of wet-only collectors that are operated by the National Atmospheric Deposition Program (NADP). The NADP website (<http://nadp.sws.uiuc.edu/>) can be consulted that contains extensive information on protocols, actual data collected, publications and quality assurance. Other networks such as GAW, EMEP, and CAPMoN, and EANET are found in other regions of the world. The World Meteorological Organization (<http://www.wmo.ch/indexflash.html>) has organized some of this information (<http://marble.asrc.cestm.albany.edu/qasac/data.html>). Precipitation fluxes on an area basis can be calculated based upon the opening size of the sampling devices and the volume of precipitation collected.

THROUGHFALL AND STEMFLOW

Throughfall is the water that passes through the overlying plant canopy before it enters a lower stratum of the ecosystem (e.g., forest floor). For forested ecosystems, there may be substantial changes in solute chemistry as the water interacts with the canopy due to leaching from vegetation, biotic uptake and the wash off of dry deposited elements (Parker, 1983). The same devices that are used for collecting bulk precipitation can be used for collecting throughfall, but a more extensive network of collecting devices is required due to the heterogeneity introduced by the vegetation (Weathers et al., 1992, 2001). Alternatively, various other systems have been developed for collecting throughfall in troughs especially under forested canopies (Reynolds and Neal, 1991). These troughs may be interconnected to a central collecting device. Throughfall fluxes on an area basis can be calculated based upon the opening size of the sampling devices and the volume of throughfall collected. It is important that the throughfall collectors be stratified to encompass the range of vegetation types and other factors that can affect precipitation quantity and chemistry (Houle et al., 1999).

Stemflow is precipitation that passes directly along the stems and boles of trees. Stemflow measuring devices generally consist of various types of collars fitted along the boles of trees that direct solution into a collecting vessel. Collars have been constructed of molded polyurethane (Likens and Eaton, 1970) and latex (Cape et al., 1991). Others (e.g., Zhang, 1989)

have longitudinally sliced the top one-quarter circumference of flexible plastic tubing to produce a trough and then stapled one edge to a tree. The interface between the bark and tubing is sealed with silicone cement. The collars are spiraled down the bole of the tree into collection vessels. Some form of filtering device can be used to remove particulate matter from the samples. For most conifer forest species stemflow is a very minor component of the total input the forest (<5%) while for hardwood there is substantial variation among species. Smooth-barked trees with centripetal branching patterns [e.g., American beech (*Fagus grandifolia*) and young sugar maples (*Acer saccharum*)] can produce > 50 L of stem flow per tree during intense rain events (McGee, 1998; Shepard et al., 1989). Determining stemflow input on an area basis requires extrapolating from either replicated plots in which all stemflow is measured or using a measurement of the representiveness of the trees from which stemflow information was obtained. Depending on the forest type, this form of input can vary.

SOIL WATER AND LYSIMETERS

Lysimeters are used to sample soil water. There are a wide variety of lysimeter types some of which are available commercially. Soil column lysimeters include the entire soil profiles and allow complete quantification of the soil water flux. This type of lysimeter has usually been confined to agronomic research and has not been extensively used in ecosystem research. Lysimeters can be constructed of various materials and attention must be paid on whether the fabrication materials will affect the chemistry of the collection solution.

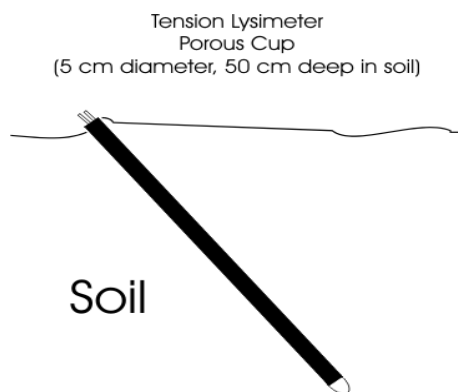


FIGURE 4. Porous cup tension lysimeter

A major dichotomy in lysimeters is whether they are zero tension or tension lysimeters. Zero-tension

lysimeters only collect gravitational water while tension lysimeters collect different portions of the soil water depending on the amount of negative pressure that is applied. The chemistry differs with the type of lysimeter used (Grossman and Udluft, 1991; Hendershot and Courchesne, 1991; Marques et al., 1996).

A common method for constructing zero tension lysimeters is to use an open-faced container that is filled with washed quartz sand or other relatively inert material. The container is placed horizontally in the soil and is equipped with a port in which tubing is connected to a collecting bottle. Tension lysimeters are often constructed of glass or ceramic media which are formed into plates or cups. Stainless steel lysimeters are also available and have been used for looking for contaminants within polluted areas. Teflon has been used in the construction of some lysimeters to ensure that there is no contamination from the porous medium (see for example: <http://www.prenart.dk/>). Lysimeters can be constructed and/or purchased over sizes ranging from a few mm (microlysimeters) to 15 cm (large plates). Tension lysimeters can be evacuated to different tensions and these tensions can be held constant or allowed to decrease.



Driving 1 1/2" pipe to develop hole for lysimeter installation

FIGURE 7.



Delivering soil slurry to bottom of hole



FIGURE 8.



Probing soil to locate promising location for lysimeter installation

FIGURE 5.



Inserting lysimeters



FIGURE 9.



Digging soil pit to obtain material to make slurry for seating porous lysimeter cup at bottom of hole

FIGURE 6.

Porous cups can be purchased from various manufacturers (e.g., Soilmoisture Equipment Corp, PO Box 30025, Santa Barbara, CA, 93105, <http://www.soilmoisture.com/>). Mitchell et al. (2001) have used 1 bar, high flow porous cups (Cat # 653X02-B01M3). These are cemented to a 3.8 cm (1.5 in.) dia. PVC pipe using PC-11® epoxy. This is a paste epoxy which bonds to both plastic and ceramic and is easily applied to the outer lip of the cup and the

edge of the pipe to form a good seal. The epoxy paste can easily be smoothed over the outer surface with a finger (latex gloves recommended). A 3.8 cm (1.5 in.) PVC pipe cap is glued to the top of the PVC pipe using standard PVC cement. Two holes (0.95 cm) (3/8 in.) are drilled into the caps. Rigid, 0.95 cm (3/8 in.) OD 0.16 cm (1/16 in.) wall, polycarbonate tubing is inserted into the holes and glued using liquid 5-minute epoxy. A bead of flexible silicone cement placed over the epoxy helps to reduce weathering and damage to the rigid seal. A long tube for removing solution is inserted into the lysimeter until it touches the bottom of the cup, and then pulled back slightly before securing it in place. A shorter tube is used for evacuating the lysimeter using a pump prior to sampling and also for removing the accumulated solution by adding pressure inside the lysimeter. Flexible plastic tubing, with clamps, is attached to the rigid polycarbonate tubing. If sampling is to occur during sub-freezing conditions, be sure that tubing remains pliable. For colder temperatures silicone tubing is superior to polyvinyl chloride (PVC) tubing. The lysimeters are installed by hammering a steel pipe into the ground at a 45° angle. A wooden frame is constructed with a larger diameter pipe mounted at the 45° angle, and into which the steel pipe of sufficient length is inserted. This wooden frame holds the pipe at the proper angle while it was being driven into the ground. This technique worked relatively well. "False starts" can be minimized by using a "tile probe" to determine where large obstructions are located. It is often useful to grind new, sharp edges on the pipe every day (especially in bouldery soils), but this may not be required in finer-textured soils. Using a pipe, rather than an auger helps make straight holes and avoids loosening stones on the hole wall that might cause cave-ins or obstruct the insertion of the lysimeter. For the lysimeter to efficiently maintain tension between the porous cup and the surrounding soil, the cup must be seated in a fine-textured soil matrix. We have made a slurry with water and soil taken from the same horizon at which the porous cup is located to fill any spaces between the lysimeter and surrounding soil. The soil for making the slurry is obtained from a soil pit evacuated near the site of lysimeter installation. After the hole is established, a 2.5 cm diameter PVC pipe is inserted to the bottom. Soil slurry is loaded into the top of the pipe and a plunger used to push the slurry to the bottom of the hole. After removing the pipe and plunger, the lysimeter is ready to be installed. The lysimeter needs to be seated firmly into the slurry at the bottom of the

hole. After installation the lysimeters are excavated to 276 kPa or other tension as required by the study. An example of a porous cup tension lysimeter is shown in Figure 4. Some examples of lysimeter installation are shown in Figures 5-9.

The installation of lysimeters can result in substantial disturbance to the soil. This disturbance can have a marked effect on soil water chemistry. A notable example of such disturbance effects is associated with the stimulation of nitrification (Shepard et al., 1990). Thus, it is desirable to install the lysimeters and monitor chemistry to ascertain when the disturbance effects are no longer affecting the results. These disturbance effects can last for one year or longer. Also, the lysimeters need to be routinely checked for damage by small and large animals. The former tend to chew on tubing while the latter (e.g., bears) have been known to remove whole lysimeters.

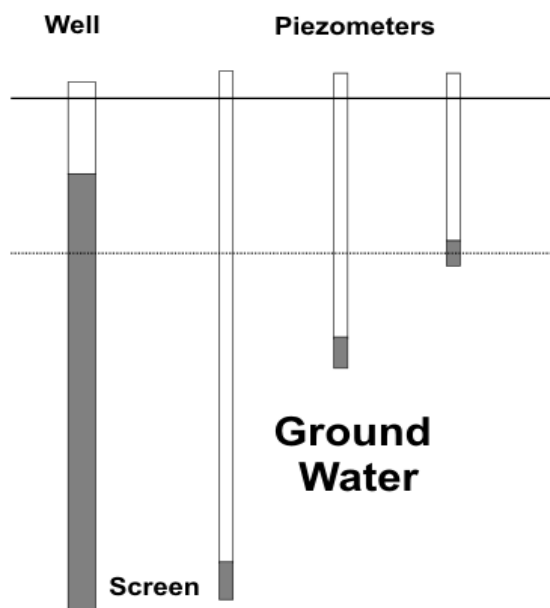


FIGURE 10. Groundwater well and piezometers

Translating chemical measurements to flux cannot be done directly using the volume of water obtained from the lysimeters alone unless the lysimeters sample the water from the entire soil column (e.g., soil column lysimeters). Generally, the amount of water collected by zero tension or tension lysimeters cannot be used to directly estimate water flux. Thus, another estimate of water flux is required. Mitchell et al. (1996, 2001) have used both BROOK2 (Mitchell et al., 1996) and BROOK90 (Mitchell et al., 2001) to calculate water flux for soils in the Adirondack Mountains of New York, USA.

GROUND WATER – WELLS AND PIEZOMETERS

Water can be collected either from the entire vertical column (wells) or at a specific depth (piezometers) as noted in Figure 4. Generally wells and piezometers are used for looking at ground water height and sometimes chemistry. They are constructed of PVC pipe and can be slotted or screened. In addition to water sampling the wells can also be equipped with various devices for measuring the height of the water table. Most recently, we have used a combination capacitance rod and data logger manufactured in New Zealand (Malcolm Barth, Tru Track Ltd., 130 Petrie Street, Christchurch 8001, New Zealand, Email: <m.barth@trutrack.com>) for monitoring water table height. As for lysimeters, the data from wells and piezometers cannot be used alone to calculate fluxes, but other sampling procedures are needed that often include some measurement of water flow pathways and model calculations.

SURFACE WATER – WEIRS AND FLUMES

If possible, it is most helpful to have within the watershed a gauging device that measures the height of the surface water. It is most convenient if the surface water can be routed through a discharge measuring system such as a flume or weir. Flumes and weirs can be calibrated for the relationship between stage height and discharge rate. This information can be used to provide information on discharge from a catchment. Various agencies throughout the world construct water discharge monitoring devices. In the United States, the Geological Survey (USGS) and the U.S. Forest Service have installed such devices in a wide variety of watersheds and small catchments. Sites in the United States with a history of hydrology, biogeochemistry and long term ecological research at the catchment level include 1) Coweeta, NC, (<http://coweeta.ecology.uga.edu/>); Hubbard Brook Experimental Forest, NH (<http://www.hbrook.sr.unh.edu/>) Andrews Forest, OR (<http://www.fsl.orst.edu/lter/>). A short general review of some of the concepts related to ground and surface water can be found in Winter et al. (1998).

CHEMISTRY

To obtain accurate information on elemental fluxes in solution it is critical that accurate measurements of the chemistry are obtained. Accurate and precise chemical measurements require a number of steps including 1) avoiding contamination of

sampling containers 2) preventing or at least minimizing chemical transformations from the time of collection to the time of analyses 3) having a good quality assurance and quality control (QA/QC) procedure in the laboratory where the chemical determinations are done and 4) maintaining a data base that can be used for checking for various problems. The contamination of samples can be avoided by doing careful cleaning of the sampling devices, being aware of any artifacts introduced in device installation, regular cleaning of sampling devices and being sure that sample bottles are free of any contaminants. Periodic sampling of blanks from collection devices is important for QA/QC. Minimizing of chemical transformations is highly dependent on the solute of interest with certain forms (e.g., NO_3^- and NH_4^+) being very labile while other solutes (e.g., SO_4^{2-} , Ca^{2+}) being more inert. Samples should be handled in a manner to minimize change (e.g., keeping samples cold, precluding light, using preservatives if necessary) and sampling over the shortest interval that is compatible with study's resources and objectives. A good quality assurance program includes the use of certified standards, analysis of blanks, careful record keeping, etc. It is useful if the laboratory doing the chemistry is involved with a program where samples of known chemistry are analyzed by different laboratories and differences in the results among laboratories provided. A recent report from HBEF describes the chemical methodology used at that LTER site (Buso et al., 2000).

CONCLUSIONS

The quantification of solute fluxes is often an important component in the evaluation of the biogeochemistry of an ecosystem. Important fluxes include precipitation, throughfall, stemflow, soil water, ground water and discharge. The instrumentation of a study area depends on the goals of the research, site characteristics and available resources for equipment. It is important that the limitations of measurements be recognized and that the installation of instrumentation accounts for variation in ecosystem properties. Replicated measurements are needed for doing statistical comparisons. Attention is also needed on the various steps of sample handling, chemical determinations and data management to help ensure the validity of the results and the potential for doing both within and across site comparisons.

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