Chapter 13
Measurement and Importance of Dissolved Organic Carbon

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Abstract The flux of dissolved organic carbon (DOC) from an ecosystem can be a significant component of carbon (C) budgets especially in watersheds containing wetlands. Although internal ecosystem cycling of DOC is generally greater than the fluxes to ground or surface waters, it is the transport out of the system that is a main research focus for carbon accounting. In watersheds containing organic wetland soils or peatlands, the flux from the watershed can be 4–8% of annual net primary production, a significant fraction that should be addressed when performing a carbon mass balance. Recent literature suggests that DOC transport from watersheds is increasing as a result of climate change or changes in sulfur deposition. As changes occur in land use, atmospheric deposition, and climate, response variables such as DOC will become even more critical to document the effect of those changes.

Keywords DOC, forest floor, soil carbon, TOC analyzer, wetlands

13.1 Introduction

Dissolved organic carbon (DOC) is operationally defined as organic molecules that pass through a filter, most often 0.45 μm. This is usually the major form of carbon transported with soil solution and in streams. The importance of DOC lies in its role

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of being able to hydrologically transport carbon between different pools in the ecosystem. Most significant is the transport from the forest floor to the mineral soil. The internal fluxes of DOC within the ecosystem are in general higher than the net loss of DOC to ground water and surface waters.

DOC concentrations in rain water are generally very low but increase as the water passes through the canopy and forest floor. Fluxes of DOC in throughfall of temperate forests range from 4–16 g m^{-2} $year^{-1}$, whereas the flux in the O horizon is usually is in the range 10–40 g m^{-2} $year^{-1}$ (Michalzik et al. 2001). In the mineral soil DOC concentrations and fluxes decrease with depth and under the B horizon the flux is usually well below 10 g m^{-2} (Michalzik et al. 2001). The difference between O and B horizons is widely thought to be mainly due to physical and chemical retention rather than rapid mineralization (Kalbitz et al. 2000).

DOC transport in runoff increases with increasing proportion of wetlands present in the watershed, especially with organic soil wetlands or peatlands present (Aitkenhead et al. 1999). DOC exiting peatlands can be upwards of 4–8% of annual net primary productivity. Fluxes of DOC from watersheds containing wetlands typically range from 2–10 g m^{-2} $year^{-1}$ (Kolka et al. 1999, Elder et al. 2000). In watersheds or sites with few wetland soils, the loss of DOC is minimal in relation to other carbon pools and fluxes. In these systems, the error associated with measuring larger carbon fluxes is probably greater than DOC fluxes.

DOC fluxes are small compared to some other carbon fluxes in the ecosystem, but DOC may be important for carbon balances of litter and the O horizon. In relation to the annual aboveground litter fall, the annual transport of DOC from the O horizon to the mineral soil is on average 17%, with a range from 6–30% in temperate forests (Michalzik et al. 2001). DOC is also a significant source of organic carbon in the mineral soil (e.g. Neff and Asner 2001).

13.2 Sample Collection

Dissolved organic carbon is typically measured at either the plot or watershed scale. At the plot scale lysimeters, wells or piezometers are used. Lysimeters are typically used in unsaturated soils while wells and piezometers are used where water tables are present. There are two main types of lysimeters, zero tension and tension lysimeters. There are some differences between these two that need to be taken into consideration, as both the quantity and sources of DOC may be different, depending on the type of lysimeter used. Zero-tension lysimeters better reflect water that is moving through soils, as they mainly collect water in large pores. However, they create a discontinuity in the soil pore system and require the build up of a temporary local water table before they start collecting water. Therefore it may, in areas with moderate rainfall intensities, be difficult to get a sample of the soil solution with zero-tension lysimeters, at least in mineral soil. For minimum disturbance it is recommended that zero-tension lysimeters are installed laterally from pits, rather than by cutting through the forest floor from above.

Tension lysimeters consist of a porous cup connected to a collection flask where vacuum has been applied. Tension lysimeters are in contact with the soil pore system and collect soil water representing smaller pores than zero-tension lysimeters. They are more likely than zero-tension lysimeters to collect water in the mineral soil, but may be less representative of the DOC that is actually moving through the soil. Tension lysimeters may be installed laterally from pits or at an angle from the surface. Zero-tension lysimeters installed under the O horizon and tension lysimeters installed at depth in the mineral soil are often used in combination and this may be the best solution in many situations.

The depth at which the lysimeters should be installed depends on the question being asked. One set of lysimeters is often installed under the O layer to capture the flux of carbon at the interface between organic and mineral soil horizons. Another set of lysimeters is often installed in or under the B horizon and may represent the flux of DOC leaving the ecosystem.

In saturated conditions, wells or piezometers are commonly used to sample soil solution, including for the analysis of DOC. Wells are slotted their entire length and give a representative sample of the entire depth of the well (i.e. the soil profile). Piezometers are slotted only at the bottom and are used to sample a specific location, depth or horizon in the soil. Typically in studies, lysimeters, wells and piezometers are used in combination in upland to wetland transects to assess soil water concentrations and fluxes of DOC (McLaughlin et al. 1994).

Sampling of soil solution for DOC analysis may occur at fixed time intervals or based on precipitation events. Samples should be filtered after collection and kept refrigerated until analysis. For lysimeters, wells, and piezometers it is necessary to wait a couple of months to let the instruments equilibrate with their surroundings before samples are collected and analyzed.

At the watershed scale, samples are typically collected at the watershed outlet as grab samples or with automated equipment. Sampling is typically either event based or on a fixed interval. DOC concentrations vary with water flux in the stream and high fluxes of water are often combined with high concentrations of DOC and it is thus important to take samples during these events.

13.3 Measurement of DOC Concentration

Before DOC analysis the samples need filtration. The most commonly used pore size is 0.45 μm, but 0.2 μm and 0.7 μm are also common. Membrane filters are most commonly used, but syringe filters may be more convenient if small amounts of water are being filtered. Different kinds of filters are used, but cellulose acetate filters are probably most common. Most important is that the filters do not release any DOC during filtration. Samples from the mineral soil collected with tension lysimeters and samples from stream water may not always need filtering, but this needs to be evaluated for each site.

Numerous analyzers exist on the market, most of which are termed TOC analyzers. Measurement of DOC entails removing inorganic carbon with acid, sparging the resultant CO_2 and oxidizing the remaining C (presumably all OC) and measuring the CO_2 generated by the oxidation process. Oxidation of DOC can be accomplished by combustion, UV persulfate oxidation, ozone, or through UV fluorescence. Good reviews of the analytical methods can be found in Bolan et al. (1996) and Doyle et al. (2004).

13.4 Calculation of Fluxes

DOC fluxes are simply calculated by multiplying DOC concentration by the water flux; however, at the plot scale, probably the most difficult measurement is the flux of water. Due to disturbed hydrology, it is usually not possible to use the amounts of water collected in the lysimeters to estimate the flux. Computer models are sometimes used to estimate water fluxes. The measurement of soil moisture and hydraulic conductivity is one method to estimate the flux of water through the rooting zone. Micrometeorological techniques can also be applied by measuring surface inputs of precipitation or throughfall, estimating surface outputs in the form of evapotranspiration (ET) through the energy balance and measuring changes in soil moisture. Transport through the rooting zone can be calculated by difference using the hydrological mass balance.

At the watershed scale, typically flow is either measured by a device such as a weir or flume that is at the outlet of the stream exiting the watershed (Kolka et al. 1999). Where such devices are unavailable, stream gauging is commonly employed. Stream gauging entails measuring flow and relating flow to stream water height or stage height. Regression relationships are developed over a range of flows relating stage height to flow (Brooks et al. 2003).

Measurement of water fluxes to lakes and wetlands typically entails the use of groundwater wells and piezometers that measure the head of water upslope of the water body which allows for the estimation of inputs in saturated soil zones if one knows soil hydraulic conductivity (e.g. Freeze and Cherry 1979, Kolka et al. 2000, Mann and Wetzel 2000).

13.5 Summary

Comparison of DOC fluxes among ecosystems, treatments (e.g. harvest) or over time can elucidate changes in ecosystem processes. The few studies assessing harvesting on stream DOC vary in the response. Harvesting generally increases soil temperatures (more decomposition, higher DOC) but also reduces redox status (higher water tables, lower DOC) (Tate and Meyer 1983). Studies that see increases relate DOC increases simply to flow increases (e.g. Hobbie and Likens

1973). A number of studies have demonstrated that the amount of wetlands, especially peatlands, controls watershed level transport of DOC in streams (e.g. Gergel et al. 1999, Kolka et al. 1999). If there are wetlands present in the watershed, that factor appears to overwhelm any vegetation management factor controlling DOC transport. A number of watersheds have been experiencing increases in DOC transport as a result of increasing temperatures from climate change (Freeman et. al. 2001); however, other studies indicate that decreases in atmospheric deposition of sulfur may be the cause of the increases (Evans et al. 2006). As a result of changes in land use, management practices, climate and atmospheric inputs, DOC will continue to be an important response variable as we strive to understand carbon storage and fluxes.

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