

Ion balances and fluxes in deposition  
and soil solution

Nicholas Clarke  
Norwegian Forest Research Institute

---

---

---

---

---

---

---

---

In deposition monitoring, we need to know not just the concentrations of elements or ions, but their fluxes. In the same way, it is important to know the fluxes in soil solution for element/ion balance studies (e.g. nitrogen leaching, effects of harvesting).

Element fluxes are calculated using the water flux and the concentration. Both have to be determined accurately in order to make accurate element flux estimates.

---

---

---

---

---

---

---

---

Deposition

If the volume of sample and sampling area are known, the water flux can be easily calculated. Fluxes in deposition should therefore be unproblematic.....

...but this is not the case.

---

---

---

---

---

---

---

---

Results from the field intercomparison showed high deviations from the best estimate for throughfall, stemflow and bulk precipitation fluxes.

The accuracy is determined by the spatial representativity of the measurements and the accuracy of the sample volume estimates and element concentrations. These were not always good enough.

---

---

---

---

---

---

---

---

How representative is the sampling?

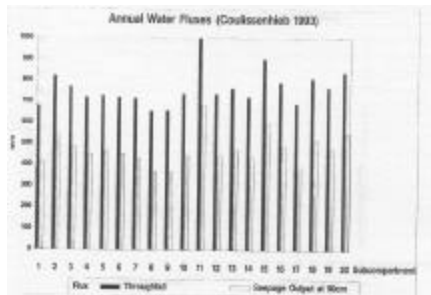


Fig. 2. Spatial variation of the water fluxes with throughfall and seepage output at 90 cm. From Manderscheid & Matzner (1995)

---

---

---

---

---

---

---

---

Soil solution

How can water fluxes in soil solution be estimated?

- Volumes obtained using lysimeters
- Anion balances
- Models

---

---

---

---

---

---

---

---

Can lysimeters be used for flux estimation?

- The most common tension lysimeters sample water from an unknown volume of soil, possibly representing several soil horizons above and below the lysimeter.
- Zero-tension lysimeters sample water entering from a known soil horizon through a known surface area. However, they disturb the hydrology by affecting macropore water pathways or severing capillary contact in the soil, so that the measured volume can not be related to water flux with confidence.

---

---

---

---

---

---

---

---

How representative is the sampling? A large number of lysimeters may be necessary to obtain an estimate representative for the plot. Often, fewer lysimeters are used.

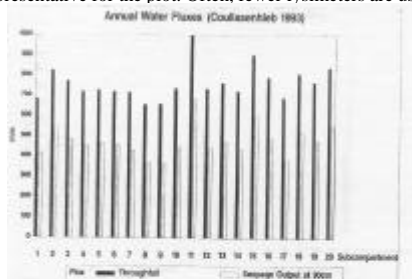


Fig. 2. Spatial variation of the water fluxes with throughfall and seepage output in 90 cm. From Manderscheid & Matzner (1995)

---

---

---

---

---

---

---

---

The number of samples required to match the true mean can be calculated, assuming a normal distribution of the sample:

$$N_x = (Z_a / (x - \mu))^2 \cdot s^2$$

$N_x$  = minimum number of samples

$Z_a$  = z-score (e.g. 1.96 for  $\alpha = 0.05$ )

$x - \mu$  = desired precision

$s$  = standard deviation of the population

A study should always be made to find out how many samplers are necessary.

---

---

---

---

---

---

---

---

*Anion balance methods*

These methods assume that certain anions behave conservatively, i.e. they do not interact with the soil to any great extent. Thus, the input flux equals the output flux. Differences in concentration can then be used to estimate water fluxes in the soil.  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  have been used for this purpose.

Anion balance models have to be calculated based on at least two years of data, because the input signal is not constant and the anions interact with the soil.

Anion balance methods do not always work well.

---

---

---

---

---

---

---

---

Soil water fluxes (mm) calculated using the Cl balance and  $\text{SO}_4$  balance methods: data from Nordmoen, Norway, 1995-1996.

	Cl	$\text{SO}_4$
Throughfall	1238	1238
5 cm	951	2327
15 cm	599	954
40 cm	696	687

Why are there problems with this method?

---

---

---

---

---

---

---

---

Incomplete data series: in northern Europe, soil water sampling is often not practical during the winter. However, in many areas there can be periods of snowmelt with water flux through the soil. Therefore, even if the water flux can be modelled, concentrations are unknown and element fluxes can not be calculated.

The spring snowmelt period is often crucial, as water fluxes are then large and sampling has often not started yet.

This is a serious difficulty if using an anion balance method, as time periods for deposition and soil solution are not the same.

---

---

---

---

---

---

---

---

Sulphate is not completely conservative:

- Adsorption/desorption
- Mineralisation of organic sulphur
- Redox reactions

Chloride is not completely conservative either.

- Interactions with organic matter

---

---

---

---

---

---

---

---

Different lysimeter types sample different types of water. Concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  may not be the same when sampled with different lysimeters.

- The most common types of tension lysimeters sample micropore water from areas both above and below the lysimeter.
- Zero-tension lysimeters sample water flowing through the soil, i.e. macropore water.

---

---

---

---

---

---

---

---

Mean annual concentrations of Cl and  $\text{SO}_4\text{-S}$  in soil water at Høylandet, Norway, in samples from cup lysimeters (tension) and plate lysimeters (zero-tension at 5 cm, tension at 15 and 40 cm).

	Depth (cm)	1998		1999	
		Cup	Plate	Cup	Plate
$\text{SO}_4\text{-S}$ (mg/l)	5	0.14	0.10	0.13	0.07
	15	0.44	0.12	0.32	0.14
	40	0.14	0.14	0.42	0.18
Cl (mg/l)	5	3.3	2.1	3.1	2.7
	15	4.6	3.3	4.2	2.9
	40	2.4	6.5	4.1	4.5

---

---

---

---

---

---

---

---

Anion balance methods may not work well because hydrological and topographical factors affect the flow of water through the ecosystem. It is not always the case that water runs vertically through the soil, especially during periods of high flow.



Overland flow at Birkenes, Norway

---

---

---

---

---

---

---

---

#### *Models*

Many models, of varying degrees of complexity, exist for estimating soil water fluxes. All require precipitation as an input.

- Climatic water balance models
- Storage models
- Richards' models

Problem: many parameters required for models have to be estimated, e.g. evapotranspiration.

---

---

---

---

---

---

---

---

#### Conclusions

Deposition: it is important to use sampler types that give good flux estimates, and also to ensure that there are enough samplers and a large enough sampling area to give a representative value.

Soil water: fluxes cannot be measured directly but must be estimated/modelled. There are several possible models available. Simplest are anion balance methods, but these must not be used uncritically. Once again, it is important to have enough samplers to obtain a representative value. Site hydrology and topography need to be considered.

---

---

---

---

---

---

---

---